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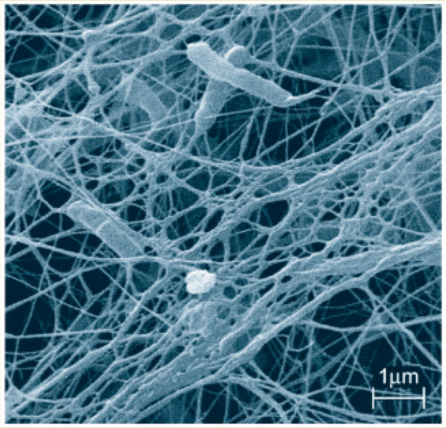

Properties and performance of natural-fibre composites

Edited by K. L. Pickering

Properties and performance of natural-fibre composites

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Edited by
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Introduction

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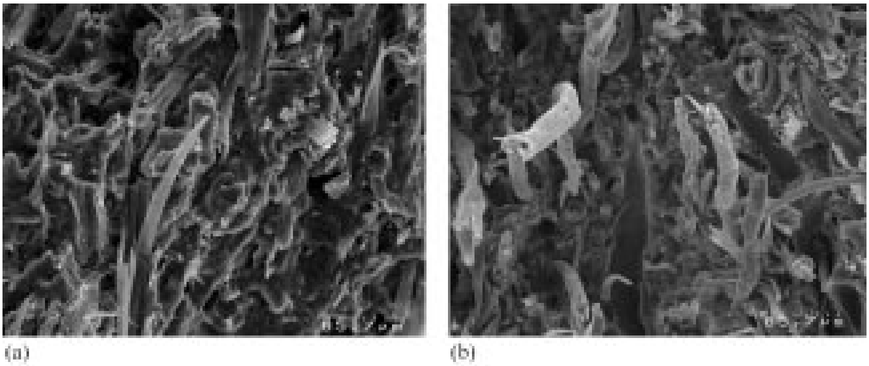
Technological development coupled with consumer expectations continues to increase demands on the Earth's resources, leading to major issues relating to material availability and environmental sustainability. Recently, a general consensus with regard to the large contribution made by humans to the current phase of global warming has been reached. This will add further emphasis to the awareness of the need to act in an environmentally responsible manner, which has already become a major influence on government policy in many countries. This awareness has also led to increased interest in materials derived from more sustainable resources that can be processed with lower energy consumption requirements, as well as recyclable materials, including those from which energy can be recovered, as found within the spectrum of natural-fibre composites. Although the use of these materials is not new (their documented use dates as early as civilisation itself), these more recent incentives have encouraged the extension of their use.

One major area of development over the past decade has been in the use of compression moulded natural-fibre reinforced thermoplastic panels that have been widely adopted in the European automotive industry for parts such as door panels, headliners, package trays, dashboards and boot liners. This has been largely influenced by the European Union End-of-life Vehicle Directive, adopted in 2000, stating that from 2006, the reuse and recovery of an end-of-life vehicle should be a minimum of 85 wt% (with 80 wt% reused or recycled), increasing to 95 wt% (with 85 wt% reused or recycled).[1] Since 2000, steady growth of the use of natural fibres in European cars has been observed, increasing in Germany, for example, from around 10 000 tonnes in 2000 to 19 000 tonnes in 2005 (excluding processed cotton or wood fibre).[2]

Another more structurally demanding area of application has been in extruded 'plastic lumber' used for decking purposes mainly within the United States, although the large sectional thicknesses of this product mean that, again, the mechanical demands are not high. Indeed, much research effort has focused on improving the mechanical performance of natural fibre thermoplastic composites which could enable extension of their application. Much of that attention has been aimed at the improvement of interfacial strength, for which a range of fibre treatments and coupling agents have been assessed. The most successful in terms of mechanical benefits along with ease of use has been obtained with maleated propylene (MAPP) as a coupling agent, giving strength and stiffness improvement of greater than 100% compared with uncoupled composites.[3] Examination of fracture surfaces for natural-fibre polypropylene composites demonstrates the general dependence of mechanical properties on the failure mechanisms of natural-fibre composites and elucidates the dramatic improvement of properties in this particular instance; in the presence of coupling agent very little fibre pull-out can be observed, with fibre fracture coinciding with the major crack front (Fig. I.1(a)) in sharp contrast to composites without MAPP coupling agent (Fig. I.1(b)). Furthermore, this suggests that interfacial strength is no longer the limitation for improving mechanical performance. It seems likely that greater benefit and thus extension of use could be obtained elsewhere; for instance, by engineering fibre orientation, increasing fibre length and the use of different matrices, all of which are current areas of research. Alternative matrices such as thermosetting polymers or biodegradable polymers are also of interest where higher performance or biodegradability, respectively, is required.

Another major area that could extend the application of natural-fibre composites is the improvement of long-term performance including improved resistance to moisture, ultraviolet radiation and creep. As previously mentioned, the natural-fibre reinforced thermoplastic composites developed for the automotive industry as well as the more traditional wood reinforced thermoset matrices used commonly for office furniture are generally for interior parts. Although obviously decking is used in exterior applications, the low mechanical performance required disguises the durability issues that would occur with more demanding situations, particularly where higher fibre weight fractions would be required.



I.1 Demonstrating the influence of interfacial strength on fracture behaviour showing a 40 wt% hemp fibre reinforced polypropylene composite (a) with and (b) without coupling agent (courtesy of Gareth Beckermann, PhD student, Waikato University).

Overall, natural-fibre composites are seen as potential materials for many engineering applications. However, there are still important issues that limit their future use, including long-term performance and the ability to be able to predict performance during service. Fracture mechanics can give great insight into the physical effects occurring within these composites which enable the production of natural-fibre composites with improved properties.

This text has been arranged in a way to best demonstrate the issues of current importance to developments in the natural-fibre composite area. It comprises three main sections. The first section (Natural-fibre composites) gives an overview of the wide variety of materials and processing techniques used as well as the historical development of these materials. This section also includes the critical area of the interface or interphase that can be engineered to alter fracture mechanics and performance. In the second section (Case studies and opportunities), work is presented across the spectrum of application areas, including the automotive, structural and packaging industries as well as assessing opportunities for integration of biomass technologies. This section also includes market issues and the future potential for natural-fibre reinforced composites. The final section (Performance of natural-fibre composites) focuses on the behaviour of these materials, including methodologies for assessing behaviour and microstructural influences, relating to available models and current understanding of fracture mechanics over the short- and long-term time periods. For myself, this book has been a very exciting project and I am very grateful for the expert opinions from the contributing authors.

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1

Natural fibres: types and properties

R M ROWELL, University of Wisconsin, USA

1.1 Introduction

It is important to start with a clear understanding of what will and will not be included in this chapter on 'natural fibers'. Natural fiber, for this chapter, is defined as fibrous plant material produced as a result of photosynthesis. These fibers are sometimes referred to as vegetable, biomass, photomass, phytomass, agromass, solarmass, or photosynthetic fibers. Another general term used is lignocellulosic fibers; however, it is a term meaning 'lignin and cellulose-containing' and some of the fibers included (cotton) have little or no lignin. Natural fibers could also include hair, feather, wool and silk fibers, and mineral fibers such as asbestos and glass but these will not be covered in this chapter.

The use of natural fibers dates back in history to about 8000 BC. Linen and hemp fabrics are known to have existed at that time and linen textiles are known to have existed in Europe about 4000 BC (Czerniak *et al.*, 1998). Reference is made to the use of textiles as reinforcements of ceramics as early as 6500 BC (Kozlowski and Machiewacz-Talarczyk, 2005). Ramie is known to have been used in mummy cloths in Egypt during the period 5000–3300 BC. Grass and straws have been used for many generations as a reinforcing fiber in mud bricks (adobe) and in ancient Egypt 3000 years ago, pharaoh mummies were wrapped in linen cloth impregnated with salts, resins, and honey to protect and reinforce them (Kozlowski and Machiewacz-Talarczyk, 2006). The use of flax for the production of linen dates back over 5000 years. Pictures on tombs and temple walls at Thebes depict flowering flax plants. Cotton fibers have been found in caves in Mexico that date back over 7000 years. There are references in early Chinese history to natural fibers for papermaking. Hemp fiber implants have been found in pottery shards in China and Taiwan over 10 000 years old. The use of hemp fiber dates back in to the Stone Age. Thomas Jefferson drafted the United States Declaration of Independence on hemp paper.

As we begin the 21st century, there is an increased awareness that non-renewable resources are becoming scarce, and dependence on renewable resources is growing. The 21st century may be the cellulosic century as we look more and more to renewable plant resources for products. It is easy to say that natural fibers are renewable and sustainable but, in fact, they are neither. Natural fibers come from plants and it is the living plants that are renewable and sustainable, not the fibers themselves. This means that we must put our emphasis on healthy forests and agricultural lands, and to manage and use our ecosystems in ways that do not put them at risk.

1.2 Fibrous plants

In terms of utilization, there are two general classifications of plants producing natural fibers: primary and secondary. Primary plants are those grown for their fiber content while secondary plants are those where the fibers come as a by-product from some other primary utilization. Jute, hemp, kenaf, sisal, and cotton are examples of primary plants while pineapple, cereal stalks, agave, oil palm, and coir are examples of secondary plants.

Table 1.1 shows an inventory of some of the major fibers now produced in the world. While wood is the major source of fiber, plant straws and stalks combined are potentially a larger source of fiber than wood. The data for this table were extracted from several sources using estimates and extrapolations for some of the numbers. For this reason, the data should be considered to be only a rough relative estimate of world fiber resources. The inventory of many agricultural resources can be found in the FAO database on its web site. By using a harvest index, it is possible to determine the quantity of residue associated with a given production of a crop.

Table 1.1 Inventory of major potential world fiber sources

Fiber source	World (dry tonnes)
Wood	1 750 000 000
Straw (wheat, rice, oat, barley, rye, flax, grass)	1 145 000 000
Stalks (corn, sorghum, cotton)	970 000 000
Sugar cane bagasse	75 000 000
Reeds	30 000 000
Bamboo	30 000 000
Cotton staple	15 000 000
Core (jute, kenaf, hemp)	8 000 000
Papyrus	5 000 000
Bast (jute, kenaf, hemp)	2 900 000
Cotton linters	1 000 000
Esparto grass	500 000
Leaf (sisal, abaca, henequen)	480 000
Sabai grass	200 000
Total	**4 033 080 000**

Table 1.2 Climatic requirements for some common natural fibers

Common name	Optimum temperature (°C)	Minimum moisture[1] (mm)	Optimum soil pH	Growing cycle (days)	Fiber yield (kg/hectare)
Flax	10–20	150	5.5–7.0	85–120	1100
Hemp	13–22	125	7.0–7.4	130–180	1225
Ramie	20–30	140	5.4–6.4	45–60	550
Jute	18–33	250	6.6–7.0	120–150	2200
Kenaf	22–30	120	6.0–6.8	150–180	1700
Roselle	25–30	150	5.2–6.4	150–180	2600
Urena	21–27	160	about 7	120–180	2200
Sunn hemp	18–33	–	–	90–120	3610
Sisal	25–30	120	about 7	continuous[2]	3360
Cotton	21–25	175	5.2–7.0	180–200	790
Abaca	25–29	200	5.2–6.4	continuous[3]	3000
Kapok	–	120	5.2–6.4	–	–

[1] Water required during the growing season, [2] 12–15 year plant life cycle, [3] 7–8 year plant life cycle.

Table 1.2 shows the climatic requirements for some of the more common fiber-producing plants. Because of the growing requirements, one way to classify natural fibers is by geographic region where they are grown; Table 1.3 shows such a classification system. Some of the plants can grow in more than one geographical area but the list separates them by the area where most production occurs.

Table 1.3 Classification of natural fibers by geographic growing area

Arid and semi-arid climate	Tropical or sub-tropical climate	Temperate
Broom	Bamboo	Hemp
Date palm	Banana	Kenaf
Jojoba	Cassava	Linseed
Olive	Caster	Rape
Sesbania	Coconut	Canary grass
Salicornia	Eucalyptus	Safflower
	Jute	Soybean
	Oil palm	Sugar beet
	Papaya	Sunflower
	Rubber tree	Switchgrass
	Sisal	Sorghum
	Palm trees	Cotton
		Softwood trees
		Hardwood trees
		Cereal grains
		Citrus plants

Source: Kozlowski and Machiewacz-Talarczyk (2006).

There are many ways to classify natural fibers. Some authors classify fibers as to industrial use, i.e. papermaking, textile, composites. Others use systems such as hard and soft fiber, long and short fibers, cellulose content, strength, color, etc.

1.3 Fiber types

The most common classification for natural fibers is by botanical type. Using this system, there are six basic types of natural fibers:

1. bast fibers such as jute, flax, hemp, ramie, and kenaf;
2. leaf fibers such as banana, sisal, agave, and pineapple;
3. seed fibers such as coir, cotton, and kapok;
4. core fibers such as kenaf, hemp, and jute;
5. grass and reed such as wheat, corn, and rice; and
6. all other types such as wood and roots.

Table 1.4 gives a more complete list of fiber types. Some plants yield more than one type of fiber. For example, jute, flax, hemp, and kenaf have both bast and core fibers. Agave, coconut, and oil palm have both fruit and stem fibers. Cereal grains have both stem and hull fibers.

1.3.1 Bast fibers

Bast fibers come from the inner bark or phloem of dicotyledonous plants and provide structural strength and rigidity to the plant stem. These fibers lay under a thin bark and exist as fiber bundles or strands and run parallel to the length of the stem. In general, bast strands vary in length but can be up to 100 cm with widths

Table 1.4 Six general types of natural fibers

Bast	Leaf	Seed					Core	Grass/ reeds	Other
		Fibers	Pod	Husk	Fruit	Hulls			
Hemp	Pineapple	Cotton					Kenaf	Wheat	Wood
Ramie	Sisal		Kapok				Jute	Oat	Roots
Flax	Agava		Loofah				Hemp	Barley	Galmpi
Kenaf	Henequen		Milk weed				Flax	Rice	
Jute	Curaua			Coir				Bamboo	
Mesta	Banana				Oil palm			Bagasse	
Urena	Abaca					Rice		Corn	
Roselle	Palm					Oat		Rape	
	Cabuja					Wheat		Rye	
	Albardine					Rye		Esparto	
	Raphia							Sabai	
	Curauá							Canary grass	

approximately 1 mm. These strands exist of smaller units called *ultimate fibers*. Some of the ultimate fibers (flax, ramie hemp, kenaf, and jute) are very long, with an aspect ratio (ratio of length to width) of 1000 (Rials and Wolcott, 1996).

Hemp

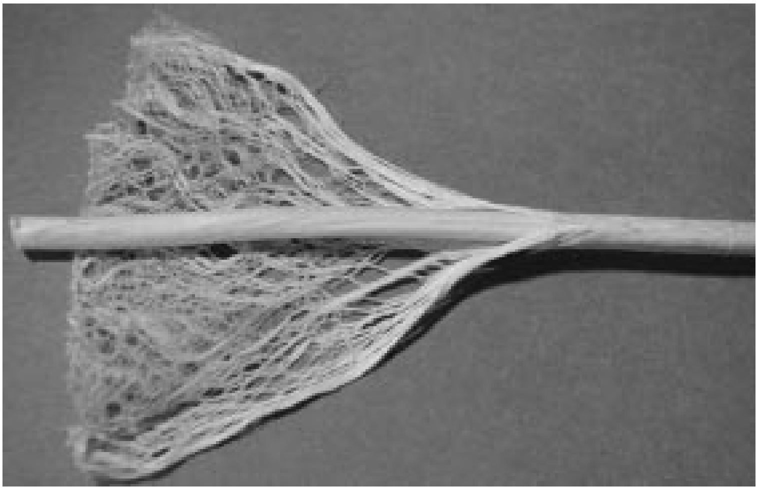
Hemp is the common name for plants belonging to the genus *Cannabis*. *Cannabis sativa* L. subsp. *sativa* var. *sativa* is the variety grown for industrial fiber in Europe, Canada, China, and elsewhere, while *C. sativa* subsp. *indica* with poor fiber quality is primarily grown for the production of recreational and medicinal drugs. It is an annual plant that grows in temperate climates. Figure 1.1 shows a young hemp plant. Hemp is considered as the oldest cultivated fiber plant in the world. The plants grow up to 4.5 m (1.2–5 m) in height in approximately 140–145 days with a stem diameter of 4–20 mm (Batra, 2007). Figure 1.2

1.1 Young hemp plant.

1.2 Hemp plants ready for harvest in a field in Poland.

shows the plant at the end of a growing season, ready to be harvested for its fiber. Fiber yields can be as high as 900–2600 kg/ha.

The growing of hemp has declined over the past two centuries but it has been a popular fiber because the plant grows fast, producing very strong bast fibers. It has a long traditional uses as a textile fiber and for canvas. The word for canvas is derived from the word cannabis. Hemp rope is famous for its strength and resistance to rot. Interestingly, hemp rope rots from the inside out, so what may look like strong rope may break without warning. There is a small market for hemp paper, mainly for cigarette paper, but the cost of hemp pulp is approximately six times that of wood pulp.



1.3 Dried hemp stalk showing outer bast fibers and inner core or stick fibers.

Figure 1.3 shows the bast and core or stick parts of the dried stalk. The bast fibers are covered by a thick layer of bark, which is removed by retting (see Section 1.4 on Fiber isolation methods) and represents about 15–25% of the total dry weight of the stalk. The average hemp bast ultimate fiber length is 25 mm (5–55 mm) with an average fiber width of 25 μm (10–51 μm) (Ilvessalo-Pfäffli, 1993). The bast fiber ends are tapered and blunt. Figure 1.4 shows isolated bast fibers before and after bleaching. Hemp has traditionally been sold by quality, dependent mainly on color and luster, and weight. Figure 1.5 shows a hemp merchant weighing hemp bast fiber for sale in Manila in the 1920s.

1.4 Hemp bast fibers before (right) and after (left) bleaching.

1.5 A hemp merchant selling hemp fiber in Manila in the 1920s.

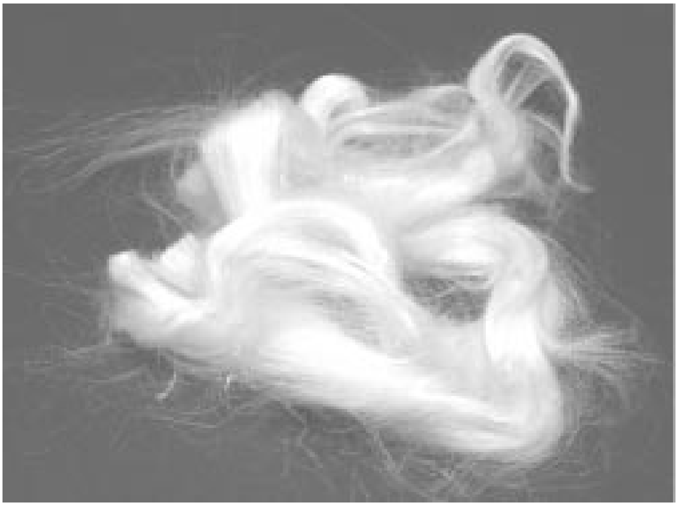
Ramie

Ramie belongs to the nettle family Urticaceae. The genus *Boehmeria* includes about 100 species. Of these, the most improtant one is *B. nivea*, which is a flowering plant native to eastern Asia. It is a perennial plant, growing to maturity in 45–55 days in hot and humid climates. It grows to 1–2.5 m tall, with heart-shaped leaves 7–15 cm long and 6–12 cm wide. Figure 1.6 shows a growing ramie plant.

Ramie fibers are located in the cortex layer of the stem underneath a thin bark layer. Because of the gummy pectinous nature of the bark, the fibers are difficult to isolate completely from the bark. Separation steps involve scraping, pounding, heating, washing, and chemical action. All of this acts to de-gum the fibers. Newer decorticating equipment developed in Japan is used to strip and scrape the stalks (Batra, 2007). Fibers can also be isolated using sodium hydroxide pulping. The fibers resemble other bast fibers such as jute and flax but are finer and are very strong in the dry state, but even stronger when wet. The bast fibers have a high degree of crystallinity, making the fibers somewhat stiff and brittle.

The bast fibers (Fig. 1.7) are sold in the form of ribbons which are also known as China glass. The ultimate fiber length averages 120 mm (60–250 mm) with a fiber width of 50 μm (11–80 μm) (Ilvessalo-Pfäffli, 1993). The fibers have rounded ends and are twisted similar to cotton.

1.6 Ramie plant.



1.7 Ramie bast fiber.

Flax

Flax belongs to the family *Linaceae* and is one of the oldest fiber crops in the world. It has been used to make linen for over 5000 years (Fig. 1.8). The genus *Linum* has about 230 species. Linen flax, *L. usitatissimum,* is an annual plant and grows 0.5–1.25 m tall with a stem diameter of 16–3.2 mm. It grows in temperate climates and the best-producing countries are China, France, and Belarus. Flax is harvested for fiber production after approximately 100 days or when the base

1.8 Flax plant and flower.

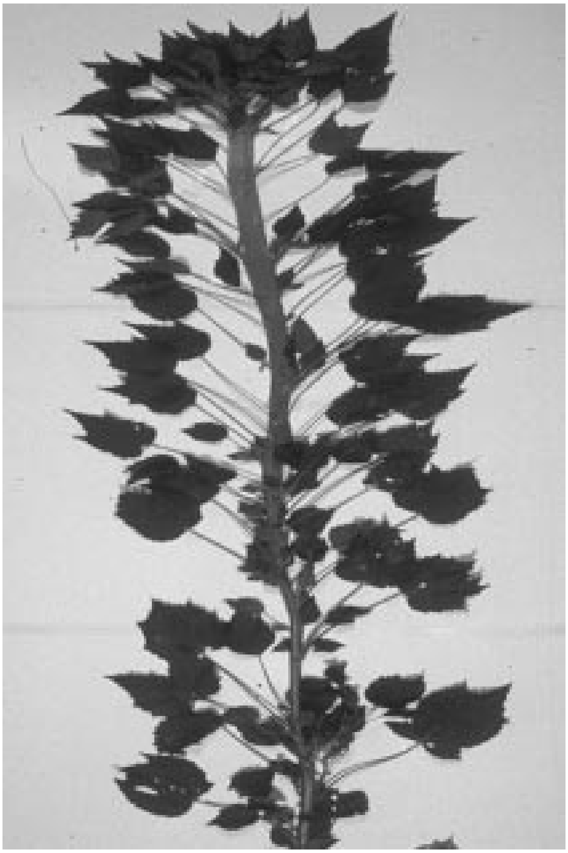
of the plant turns yellow. The plant is grown both for its fiber and for its seeds, which are used to make linseed oil.

The bast fibers (Fig. 1.9) are separated from the inner bark by retting. About 0.1–0.25 of the weight of the stalk are bast fibers. The ultimate fiber length averages 33 mm (9–70 mm) and the fibres average 19 μm (5–38 μm) in width. The fibers have tapered ends (Ilvessalo-Pfäffli, 1993).

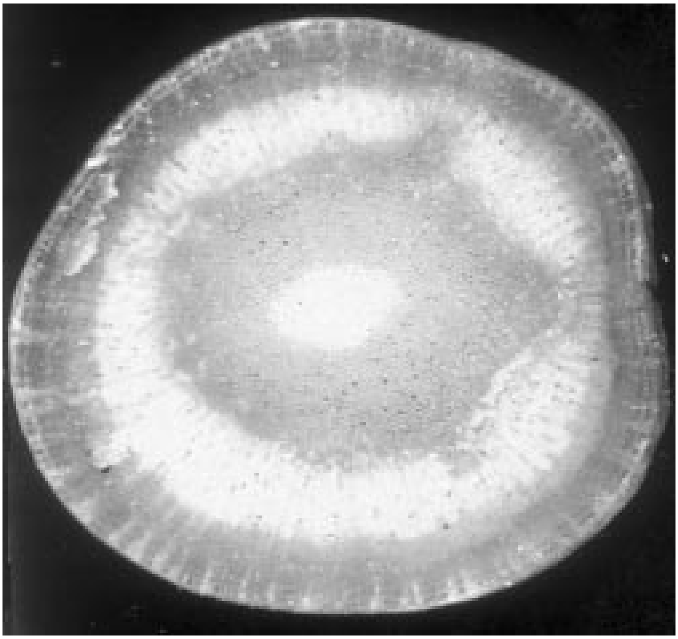
Kenaf

Kenaf is in the genus *Hibiscus* and there are about 300 species. *Hibiscus cannabinus* is native to southern Asia, India, Bangladesh, Thailand, and parts of Africa. It is an annual plant that grows in temperate climates. The plant grows 1.5–3.5 m tall with a woody base (Fig. 1.10). The growing cycle is 150–180 days. The stems are 1–2 cm in diameter, often branched. The leaves are 10–15 cm long, varying in shape. Kenaf flowers are 8–15 cm in diameter (Sellers and Reichert, 1999). The stem is composed of an outer bark, bast fibers, and a large central area of core or stick fibers (Fig. 1.11). This cross-section is similar to a cross-section of hemp stalk.

1.9 Flax bast fiber.

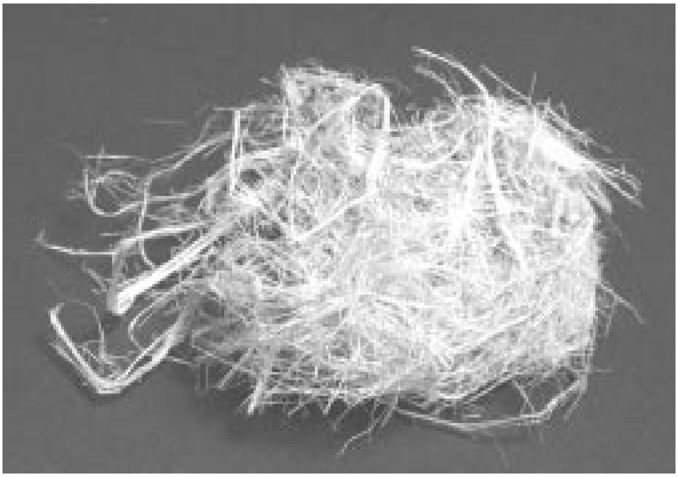


1.10 Kenaf plant.



1.11 Cross-section of a kenaf stalk.

Kenaf bast fibers (Fig. 1.12) are removed from under a thin bark layer of the stem by retting. The ultimate fibers have an average length of 5 mm (2–6 mm) and an average width of 21 μm (14–33 μm) (Ilvessalo-Pfäffli, 1993).



1.12 Kenaf bast fiber.

Jute

Jute is produced from plants in the genus *Corchorus* which has about 100 species. It is one of the cheapest natural fibers and is second only to cotton in the amount produced. *C. capsularis* (known as white jute) and *C. olitorius* (known as Tassa jute) are commercially grown in India and Bangladesh. Jute is often referred to as hessian (Fig. 1.13). The growing cycle for jute is 120–150 days with an average yield of 1700 kg/ha in warm and wet climates (Rowell and Stout, 2007). The plant grows 2.5–3.5 m in height (Pandey and Krishnan, 1990).

Jute bast fibers are 1 to 4 m long and are separated from the stalk by retting (Fig. 1.14). The core or stick fibers have been used to make paper. The ultimate

1.13 Jute plant (printed with permission of the Golden Fibre Trade Center Limited (GFTCL)).

1.14 Jute fibers.

fibers have an average length of 2 mm (2–5 mm) and an average width of 20 μm (10–25 μm). The fibers are short and narrow with think cell walls (Ilvessalo-Pfäffli, 1993).

1.3.2 Leaf fibers

Pineapple

Pineapple (*Ananas comosus*) is a tropical plant native to Brazil (Fig. 1.15). It grows to a height of 1–1.5 m and is a herbaceous perennial plant. The leaves are 30–100 cm long surrounding a thick stem. The word 'pineapple' was first recorded in 1398 in England and was named because it resembled a pine cone.

The fibers from the leaves are long fiber bundles running the length of the leaves (Fig. 1.16) (Mukherjee and Satyanarayana, 1986). The fibers are hard and stiff. The ultimate fibers are about 61.7 mm in length and 20 μm in width.

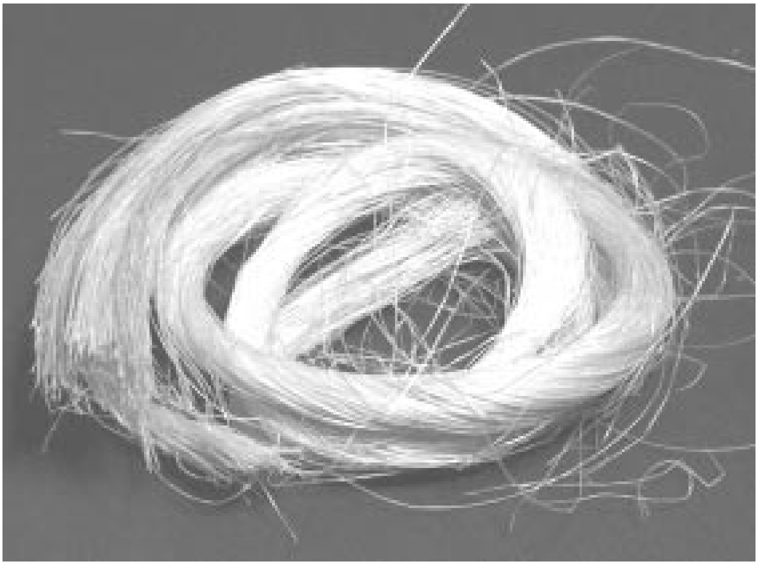
Sisal

Sisal or sisal hemp is an agave, *Agave sisalana,* which grows with sword-shaped leaves about 1.5–2 m tall (Fig. 1.17). It is indigenous to the Western hemisphere, particularly Mexico. The name comes from the Yucatan port of Sisal from which the fiber was first exported. The sisal plant has a 7–10 year lifespan and typically produces 100–250 dark to pale green leaves in the formed in a rosette on the trunk. Each leaf is approximately 1–2 m long, 10–15 cm wide, and 6 mm

1.15 Pineapple plants.

1.16 Pineapple leaf fiber.

1.17 Sisal plant.



1.18 Sisal leaf fiber.

thick, and contains an average of 1000 fibers. The fiber element, which accounts for only about 4% of the plant by weight, is extracted by a process known as decortication (see Section 1.4.2). The plant grows to a height of 2 m with a short trunk 0.15–0.23 m in diameter (Mukherjee and Satyanarayana, 1984).

The sisal leaf fibers are bundles as long as the leaf, 1–2 m long (Fig. 1.18). The ultimate fibers of sisal average 3 mm (1–8 mm) long and 20 μm (8–41 μm) wide.

Agave

Agave is the name of a succulent plant of a large botanical genus of the same name, belonging to the family Agavaceae. The most commonly grown species of agave include *Agave americana*, *A. angustifolia*, *blue agave* (*A. tequilana*) and *A. attenuata*. Figure 1.19 shows a blue agave plant being grown for the production of tequila in Mexico. The plant is similar to the sisal plant with 100–150 dark green leaves formed in a rosette on the trunk. Each leaf is approximately 1–2 m long, 10–15 cm wide, and 6 mm thick. Each rosette grows slowly to flower only once. During flowering a tall stem grows from the center of the leaf rosette.

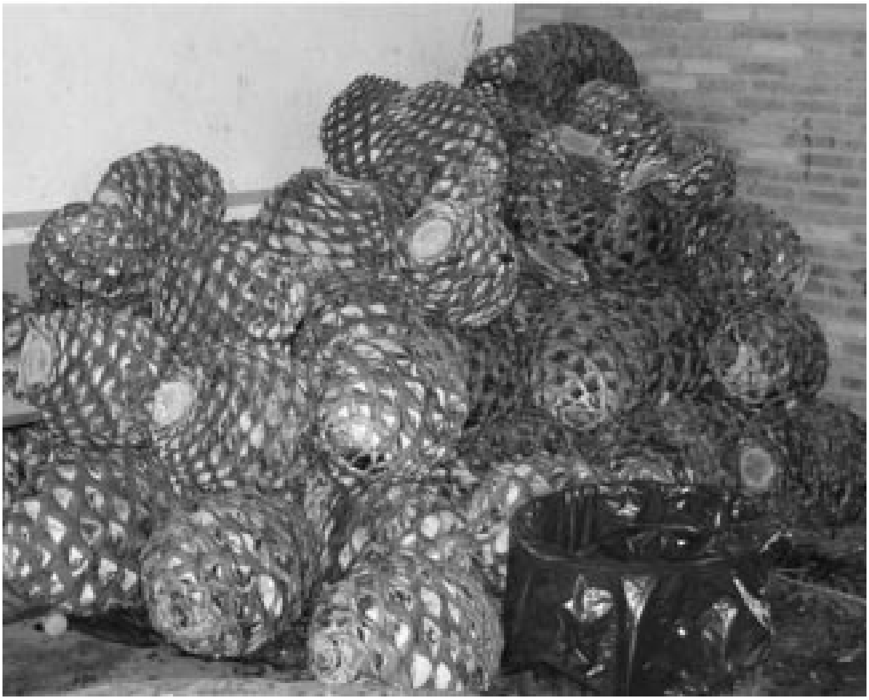
The leaf fiber bundles run the length of the leaves similar to the sisal plant (Fig. 1.20). They are 1–2 m long. The ultimate fibers are less than 5 mm long and approximately 25 μm (16–32 μm) wide.

The hearts of the blue agave are used to make tequila. The leaves are removed and the hearts are separated from the ground (Fig. 1.21). The hearts are

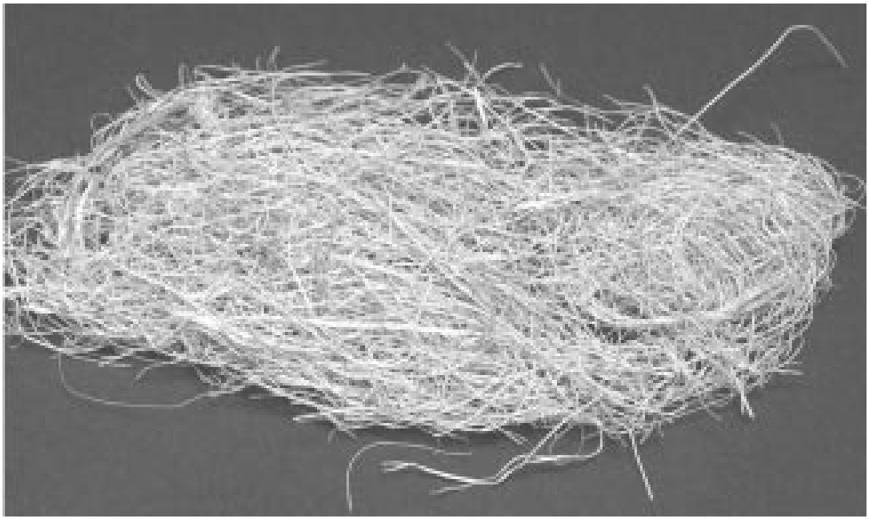
1.19 Blue agave plant.

collected, placed in a oven, cooked for a period of time and then run through a mill that breaks them into fibers and liquid. The liquid is fermented and distilled to make tequila. The heart fiber is a waste product of the tequila-making process (Fig. 1.22) and is mainly spread back on the land. It is a very coarse fiber but can be used as filters, geotextiles, and composites.

1.20 Agave leaf fiber.



1.21 Agave hearts ready for making tequila.



1.22 Agava heart fiber isolated after making tequila.

1.3.3 Seed

Fibers – cotton

The cotton plant (*Gossypium*) is a shrub native to tropical and subtropical regions around the world (Fig. 1.23). The plant grows to a height of 0.5–1.5 m. Almost all commercial cotton in the United States is the species *Gossypium hirsutum* (upland cotton) and *G. barbadense* (Egyptian cotton). Cotton production is very efficient and only about 10% or less of the weight is lost in processing to convert the raw cotton bolls (seed cases) into pure fiber. The four major producers of cotton are China, the United States, Russia, and India.

Cotton fiber (Fig. 1.24) falls into two groups: longer fibers known as lint and shorter fibers known as linters. Lint fibers are smooth and twisted while linter fibers are shorter (2–7 mm) are more cylindrical and have thicker cell walls than lint fibers. Upland cotton has a medium fiber length of 15–30 mm and fiber width of approximately 20 μm (12–38 μm). Egyptian cotton has a medium fiber length of 20–40 mm and a width of 22 μm (15–40 μm).

Pod – kapok

Kapok comes from a fast-growing tropical tree (*Ceiba pentandra*) of the order Malvales and the family Malvaceae (Fig. 1.25). It is native to Mexico, Central America, and the Caribbean. The tree grows 60–70 m tall with a large trunk, typically 3 m in diameter with buttresses. The trunk and branches are covered with large thorns. The leaves are composed of five to nine leaflets each, up to

1.23 Cotton plant ready for harvest.

1.24 Cotton seed fibers.

20 cm in length. Adult trees produce several hundred seed pods. These pods are approximately 15 cm long and contain seed surrounded by yellowish fiber. The tree is the national tree of Puerto Rico.

Kapok fiber (Fig. 1.26) is very buoyant, owing to trapped air in the fiber lumens, and resistant to water. For this reason, the fiber was used to fill lifejackets. The fiber is also very flammable. It is labor intensive to separate the fiber from the seeds and it cannot be spun to a yarn. The fibers are smooth,

1.25 Kapok tree with pods.

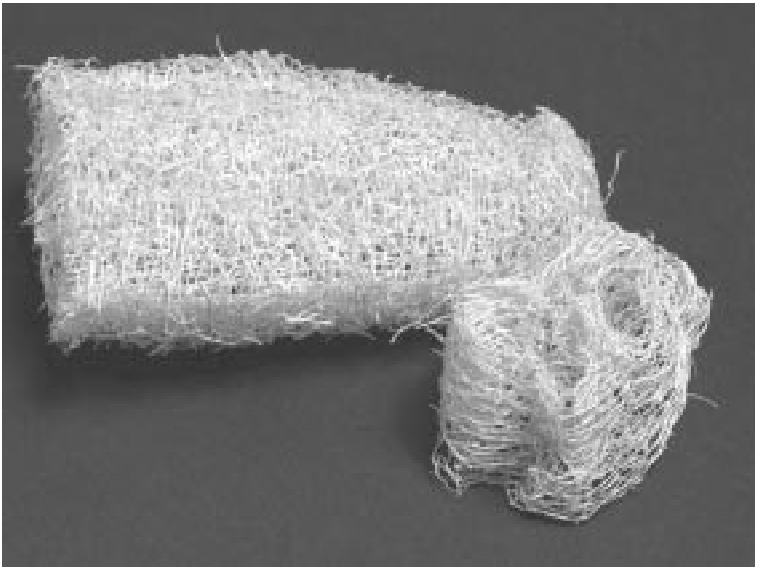
1.26 Kapok pod fibers.

transparent, cylindrical with a large lumen, thin cell walls with an average fiber length of 19 mm (8–30 mm) and average fiber width of 19 μm (10–30 μm) (Ilvessalo-Pfäffi, 1993).

Pod – loofah

Loofahs are tropical and subtropical annual vines of the genus *Luffa* (Fig. 1.27). The fruit of *Luffa acutangula* and *L. aegyptiaca* are grown and eaten as a vegetable which is also known as Chinese okra (Kirby, 1963).

1.27 Loofah vine with loofah pods.



1.28 Loofah pod fibers.

The fibrous inner structure of loofah is isolated by removing the xylem from the pod (Fig. 1.28). The fibers are very coarse and are often used as a bath or kitchen sponge. The structure can be broken up mechanically to produce very stiff and strong fibers that can be used in geotextiles and composites.

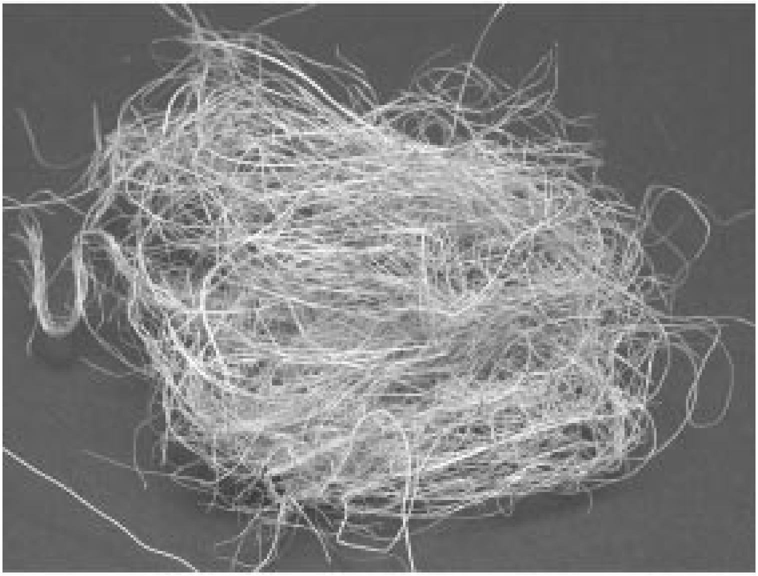
Husk – coir

Coir comes from the coconut palm tree *Tamil* and *Malayalam* (Fig. 1.29). These palms flower on a monthly basis and the fruit takes one year to ripen. Coconuts are the seed of the palm tree (Satyanarayana *et al.*, 1982). A mature coconut palm can produce 50–100 coconuts per year. The major producers of coir fiber are India and Sri Lanka and over 50% of the coir fibers produced annually is consumed in these two countries. Coir is a by-product of the copra industry. Figure 1.30 shows a very old picture of men manually husking coconuts.

Coir husk fibers are located between the husk and the outer shell of the coconut. The fiber is isolated by dehusking either by hand or with a machine. There are two types of coir fibers: white fiber and brown fiber. The white coir is produced from immature coconuts and is a finer, more flexible fiber than brown coir. It also contains less lignin than brown coir. Brown coir is obtained from mature coconuts and has a higher content of lignin (Fig. 1.31). Coir fiber is very resistant to degradation by saltwater. The ultimate fiber length of coir is about 1 mm, with a width of 10–20 μm.

1.29 Coconut palm.

1.30 Picture of men husking coconuts *c.* 1930.



1.31 Coconut husk fibers.

Fruit – oil palm

Oil palms (*Elaeis*) comprise two species of the Arecaceae or palm family. The African oil palm *Elaeis guineensis* is native to West Africa and the American oil palm *E. oleifera* is native to Central and South America. They are grown for their oil. A mature tree can grow to 20 m with leaves 3–5 m long. A young tree will produce about 30 new leaves a year while a 10-year-old tree with produce about 20 leaves a year. After flowering, the fruit takes 5–6 months to mature.

The reddish fruit grows in large bunches (Fig. 1.32). A bunch of fruit can weigh 10–40 kg. Each fruit contains a single seed called the palm kernel which is surrounded by a soft oily pulp. Oil is extracted from the pulp to produce palm oil which is edible and also used as a substitute for petroleum. Oil is also extracted from the kernel and is used mainly for soap. For every 100 kg of fruit bunches, about 22 kg of palm oil and 1.6 kg of kernel oil can be extracted. A typical oil palm can produce 7250 l/ha of oils per year. The largest producer of palm oil today is Malaysia.

There are several types of fiber that can be obtained from oil palm (Esau, 1977). Figure 1.33 shows the fiber obtained from the fruit bunches. It is a coarse fiber and rather stiff and brittle. A finer fiber can also be obtained from the leaves and trunk. The ultimate fiber length of oil palm fiber is 4 mm and a diameter of 30 μm.

1.32 Oil palm fruit bunches.

1.33 Oil palm fruit bunch fibers.

Hulls – rice

Rice (*Oryza sativa*) (Fig. 1.34) is only one of a large group of cereal grains that can be used to produce stem and hull fibers. Wheat, corn, rye, oats, and other cereal crops can also be used to produce stem and hull fibers.

1.34 Rice plants ready for harvest.

The hulls of rice and other grains are brittle (Fig. 1.35). They have been used to make particle-boards and as fillers in thermoplastics. For the most part, hulls are burned for energy but they can be used for composites.

1.3.4 Core fibers

Core or stick fibers exist on the inside of the bast fibers in the center of plants such as kenaf, jute, and hemp (see Fig. 1.11). These are very short fibers averaging less than 1 mm in length with an aspect ratio of 20. Figure 1.36 shows the core or stick isolated from the kenaf plant. In parts of the world where jute is grown, stick is used as a fuel or for small post structures. It is also used for pulping in China and Australia.

Figure 1.37 shows the cut end of a kenaf stalk, displaying the transition between bast and core fiber. The top bast fibers have a higher density and thicker cell walls than the lower core fibers.

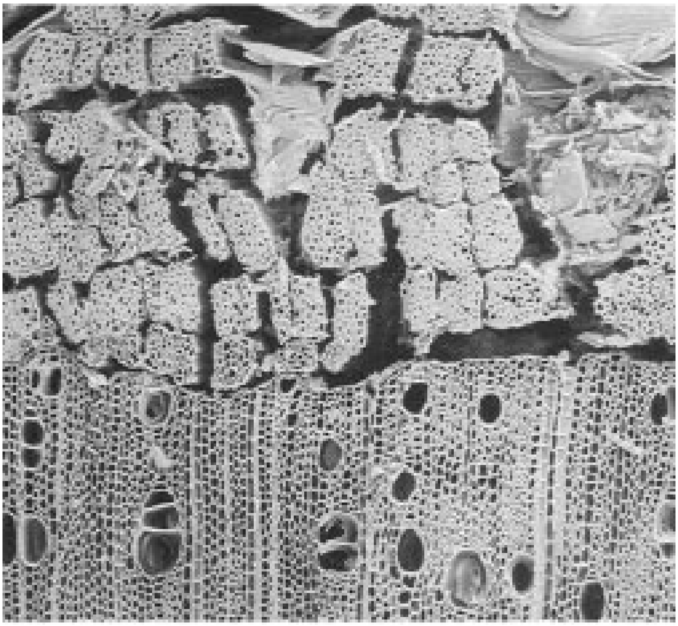
1.35 Rice stalk and hulls.

1.36 Kenaf bast fiber (left) and stick (right).

1.3.5 Grass and reed fibers

Sugar cane

Saccharum is a genus of up to 37 species of tall grasses of the Poaceae family. It is native to warm temperate to tropical regions of the world. Brazil and the tropical Pacific Islands are the largest growers of sugar cane now in the world.



1.37 Cross-section of kenaf stalk: top bast fiber, bottom core fiber (×50).

They have strong, jointed stalks that are rich in sugar. Figure 1.38 shows workers in Peru in *c.* 1900 harvesting sugar cane.

Sugar cane is usually propagated from cutting. Once planted, the cane can be harvested several times and new stalks, called rations, will grow again. Usually each successive harvest gives a smaller yield so eventually the entire field is replanted. Once the cane is harvested from the fields, the stalks (see Fig. 1.39) are washed, chopped, and shredded using revolving knives. The shredded cane is mixed with water and crushed between rollers. The juices are collected and processed into sugar, while the remaining fibrous solids, called bagasse, is collected and sometimes burned for energy to run the plant.

Wet milled bagasse usually contains about 50% moisture, 47% fiberous material, 1.5% sugar, and a small amount of ash (0.5%). The bagasse can be dried and used for papermaking or composites (Fig. 1.40). The ultimate fiber length of bagasse averages 1.7 mm (0.8–2.8 mm) and width 20 μm (10–34 μm) (Ilvessalo-Pfäffi, 1993).

Bamboo

Bamboo (*Dendrocalamus strictus*) are a group of woody perennial true grass (Poaceae) plants that grow in tropical and subtropical regions of the world (Fig. 1.41). There are 91 genera and about 1000 species of bamboos and they grow in two very different forms: one as single-stemmed plants (running or sympodial)

1.38 Harvesting sugar cane in Peru *c.* 1900.

1.39 Sugar cane stalks.

1.40 Sugar cane bagasse.

1.41 Bamboo growing.

1.42 Bamboo fiber.

and one as densely clumped plants (monopodial). They are one of the fastest growing plants in the world, growing as much as 120 cm per day, attaining a height of 15–35 m in 2–4 months. The diameter of the stem is 5–15 cm but can be much larger. Maturity is usually not reached until 3 or 4 years.

Bamboo fiber bundles are stiff and brittle (Fig. 1.42). Bamboo fibers are characterized by long narrow fibers with small rectangular thick-walled cells with blunt to pointed ends. The ultimate fiber length averages 2.7 mm (1.5–4.4 mm) with a width on average of 14 μm (7–27 μm) (Ilvessalo-Pfäffi, 1993).

Johnson grass

Johnson grass is just one example of a family of plants with stalks that can be used for their fiber content (Fig. 1.43). Johnson grass (*Sorghum halepense*) is a grass of the sorghum family. It is native to the Mediterranean region but also grows throughout Europe and the Middle East. It can be found in almost every state in the United States except the coldest ones.

Grass fibers are, in general, narrow thick-walled fibers with blunt or pointed ends. Fiber length and width vary within and among species. The ultimate fiber length of rice straw fiber is 1.4 mm (0.4–3.4 mm) with a width of 8 μm (4–16 μm) (Fig. 1.44). The ultimate fiber length of corn straw is 1.5 mm (0.5–2.9 mm) with a width of 18 μm (14–24 μm), and wheat 1.4 mm (0.4–3.2 mm) and 15 μm (8–34 μm) (Ilvessalo-Pfäffi, 1993).

1.43 Johnson grass.

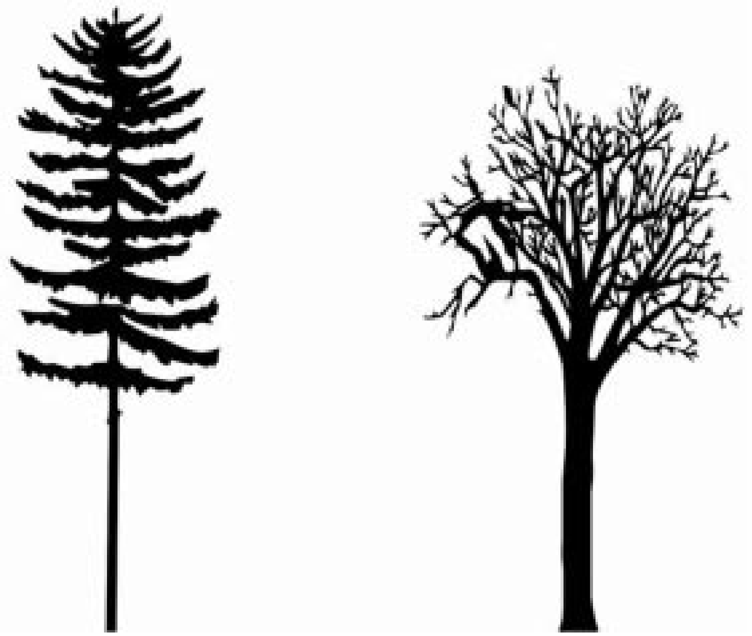
1.44 Johnson grass fiber.

1.3.6 Other fibers

Wood

Trees are divided into two broad classes, referred to as softwoods and hardwoods (Fig. 1.45). Botanically, softwoods are gymnosperms or conifers with naked seeds (not exposed in the ovary of the flower). They are non-porous and do not contain vessels. They are usually cone-bearing with needle- or scale-like evergreen leaves. Most softwoods keep their needles all year but larches and bald cypresses lose their needles during the autumn or winter. Generally, softwoods grow in a pyramid shape: small at the top and broadening as they go down. Examples of softwoods are cedar, pine, fir, spruce, hemlock, tamarack, and redwood.

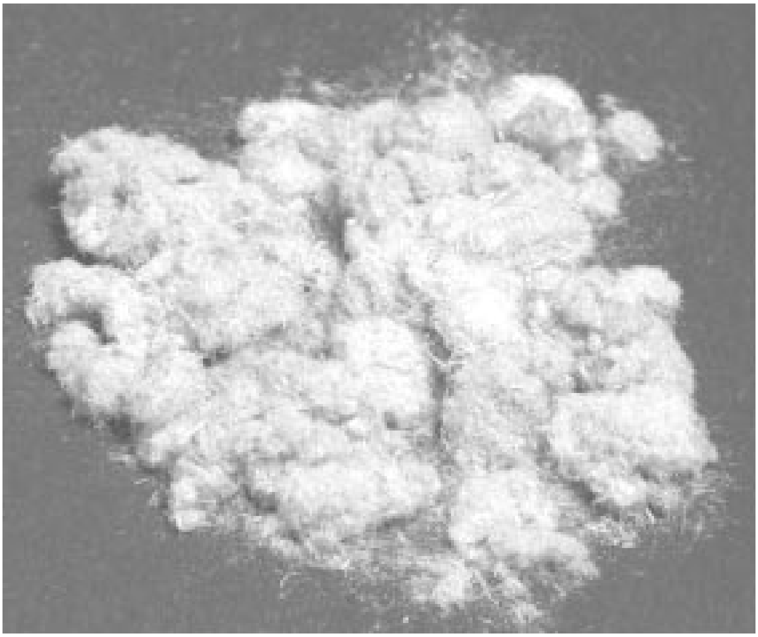
Hardwoods are angiosperms whose seeds are enclosed in the ovary of the flower. Anatomically, hardwoods are porous and contain vessel elements. A vessel element is a wood cell with open ends which transport water from one cell to the next through the vessel ends. Generally, hardwoods have broad leaves that are lost during the autumn. Hardwoods usually have a full top crown with a trunk. Examples of hardwoods are ash, beech, elm, hickory, locust, maple, oak, willow, walnut, poplar, cherry, sycamore, birch, aspen, cottonwood, basswood, butternut, and magnolia.



1.45 Typical shapes for softwoods (left) and hardwoods (right).

1.46 Southern pine fibers.

Softwood fibers are longer than hardwood fibers. Typical softwood fibers average 4.1 mm (3.5–5 mm) in length and 2.5 μm in width (Fig. 1.46). Hardwood fibers average 1.2 mm (1–1.8 mm) in length and 3 μm in width (Fig. 1.47).



1.47 Aspen fibers.

1.4 Fiber isolation methods

Fibers are isolated from the plant by three general methods: mechanical, biological, and chemical.

1.4.1 Mechanical

It is known that in ancient times, plants such as jute, flax, and hemp were allowed to rot either in the field or in a pond and were beaten on rocks to loosen the fibers from the plant. In some countries this process is still used. Figure 1.48 shows a woman in India isolating coir fibers from coconuts by pounding the coconut shell on a rock. It is more common today to see a hand-operated machine shown in Fig. 1.49 to mechanically isolate fibers from plants such as sugar cane, jute, hemp, and kenaf. The process is known as decortification. The plant is squeezed through slotted rollers that spread the plant apart and then slotted rollers with cutting edges cut and separate the fibers from the other plant tissue. The plant may have to be run through the decortification equipment several times for complete fiber isolation.

Another mechanical separation method is done on cotton using a cotton gin. A cotton gin separates the cotton fibers from the seed pods and the seeds. It uses a combination of a wire screen and small wire hooks that pull the cotton through the screen while brushes continuously remove the loose cotton lint to prevent jams. The cotton gin was invented by Eli Whitney in 1793. A modified cotton gin has also been used to separate kenaf bast from core fibers.

1.48 Beating coir fibers from coconuts.

1.49 Decortication of sugar cane in India.

1.4.2 Biological

Retting or degumming is a process of removing fibers from such plants as jute, flax, hemp, and kenaf using enzymes from microorganisms (molds and bacteria). Jute has been pond retted in India and Bangladesh for several hundreds of years by placing the entire plant in a pond and letting the natural decay process remove the bark and separate the long bast fiber from the core or stick. The process mainly removes (dissolves) pectic substances, which frees the fiber bundles to separate from the woody core. The process takes from 2 to 3 weeks (shorter times, 8–14 days, if the water is warm, i.e. 30–35 ºC) and requires large quantities of water. Since the water contains a mixture of organisms, many biological reactions are taking place other than retting. The organisms feed on pectic substances, proteins for the protoplasm of the cells, sugars, starch, fats and waxes, tannins, and the mineral content of the plants such as calcium, potassium, magnesium, iron, etc.

The quality of the bast fiber coming from this process is often reduced based on the mixture of organisms and from the dirty water. pH control is also important. In most cases the pH will drop to 4.6–4.9 and a rise in pH indicates over-retting and damage to the bast fibers. Figure 1.50 shows a commercial flax retting area in Belgium about 1920.

One of the problems in the retting procedure is that the thicker parts of the stem take longer to ret than the thinner parts, and consequently if the butt ends of the stem are fully retted, the top ends are over-retted and damaged. The use of clean water and specific microorganisms has been shown to greatly improve both the efficiency of the retting process and the quality of the bast fiber.

1.50 Retting flax in Belgium *c.* 1920.

Retting can also be done in the field after the growing season is over. The cut plant is allowed to lie in the field and dew collects on it. Naturally occurring microorganisms collect on the wet plant and the biological action removes the bark and separates the bast from the core fibers. This process takes longer than the pond retting and may take more than a month for complete fiber separation to take place.

1.4.3 Chemical

Chemical separation of fibers from plants can be done by chemical retting or pulping. Dilute alkali or dilute acids can be used to separate fiber bundles similar to microorganism retting described before. Pulping is usually done to reduce the fiber bundles to ultimate fibers for paper making (Young, 1997). Alkali, acid, and organo-solv pulping methods have been used to isolate fibers from plants.

1.5 Fiber properties

There are many reports in the scientific literature on the mechanical properties of natural fibers. It is very difficult to present one table that lists all the properties as the data differ among each citation because of using different fibers, differing moisture conditions, and different testing methods. Many factors

Table 1.5 Mechanical properties of some natural fibers

Fiber	Density (g/m^3)	Length (mm)	Diameter (μm)	Elongation at break (%)	Tensile strength* (MPa)
Cotton	1.21	15–56	12–35	2–10	287–597
Coir		0.3–3.0	7–30	15–25	
Flax	1.38	10–65	5–38	1.2–3	343–1035
Jute	1.23	0.8–6	5–25	1.5–3.1	187–773
Sisal	1.20	0.8–8	7–47	1.9–3	507–855
Hemp	1.35	5–55	10–51	1.6–4.5	580–1110
Henequen	1.4		8–33	3–4.7	430–580
Ramie	1.44	40–250	18–80	2–4	400–938
Kenaf (bast)	1.2	1.4–11	12–36	2.7–6.9	295–930
Kenaf (core)	0.31	0.4–1.1	18–37		
Pineapple	1.5	3–8	8–41	1–3	170–1627
Bagasse	1.2	0.8–2.8	10–34	0.9	20–290
Southern yellow pine	0.51	2.7–4.6	32–43		
Douglas fir	0.48	2.7–4.6	32–43		
Aspen	0.39	0.7–1.6	20–30		

* Biagiotti *et al.* (2004).

influence mechanical properties of natural fibers. In many cases, the experimental conditions are not given in the literature citation. In some cases, it is not clear which type of fiber is being tested, i.e. fiber bundles or ultimate fibers. The greatest differences encountered in extracting data from the literature are the data given by each author on lengths and diameters of ultimate fibers. Table 1.5 is an attempt to put all the different data into one table.

The density data represent the apparent density, which is the density of the whole fiber not the fiber cell wall. In general, all of the natural fibers have a cell wall density of approximately 1.5 g/m^3. Table 1.5 shows that there is a very wide range of physical properties depending on the fiber type. In general, bast fibers are the strongest.

Table 1.6 shows the tensile and flexural properties of some natural fibers (Kozlowski and Machiewacz-Talarczyk, 2006). Curauá and ramie fibers stand out with the highest tensile and flexural strength. Figure 1.51 shows the stress–strain curves for several natural fibers. Ramie is the most flexible fiber and coir the least flexible.

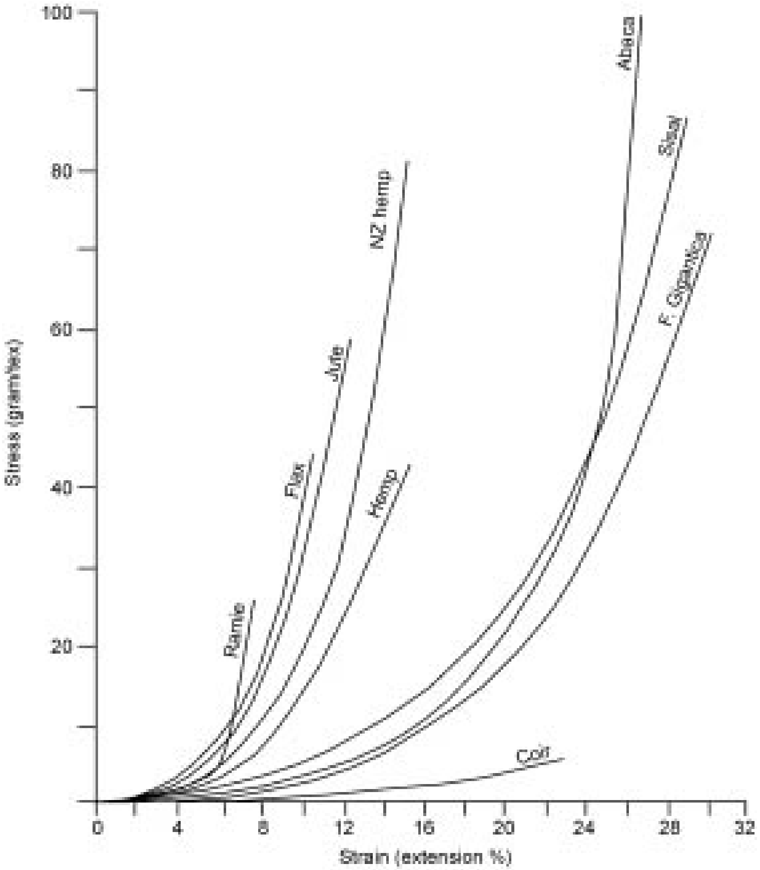
1.6 Moisture properties

Table 1.7 is a compilation of data on equilibrium moisture content (EMC) of different natural fibers at 65% relative humidity (RH) and 21 °C. As with the mechanical data, there is some variation in the data given in the literature, so the

Table 1.6 Tensile and flexural properties of some natural fibers

Fiber	Tensile – MOR* (MPa)	Tensile – MOE* (GPa)	Flexural – MOR* (MPa)	Flexural – MOE* (GPa)
Wood	30.5	8.2	55.3	7.5
Bagasse	27.0	5.4	47.8	5.1
Coir	25.9	3.6	46.9	3.6
Curauá	48.1	7.1	77.6	6.1
Flax	36.1	6.1	58.4	5.8
Hemp	33.5	6.1	61.5	6.2
Jute	34.6	7.2	57.8	6.9
Ramie	43.2	5.4	70.2	5.1
Sisal	34.3	7.1	60.0	6.6

* MOR: modulus of rupture; MOE = modulus of electricity.

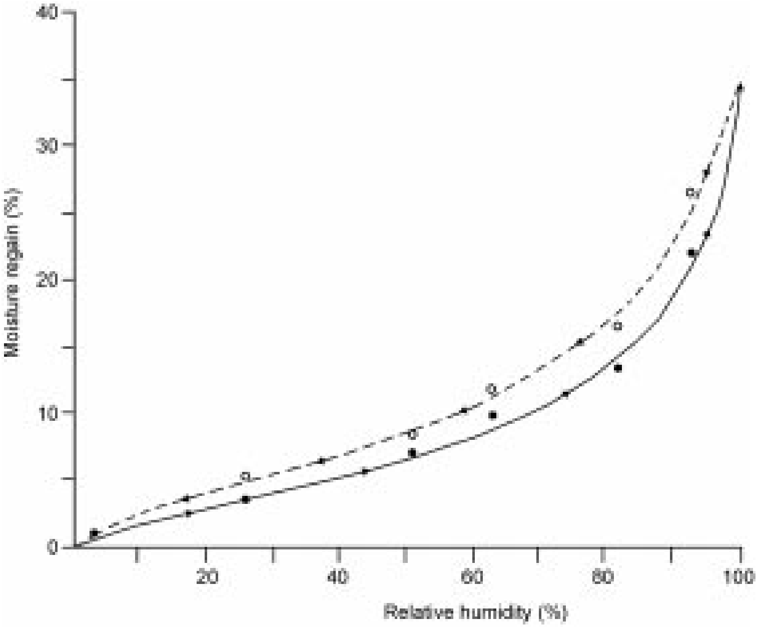


1.51 Stress–strain curve for several natural fibers (reproduced with permission from the Jute Technological Research Laboratories, Calcutta).

Table 1.7 Equilibrium moisture content of different natural fibers

Fiber	EMC (%)
Sisal	11
Hemp	9.0
Coir	10
Aloe	12.0
Banana	15
Pineapple	13
Wood	12
Abaca	9.5
Cotton	8
Jute	12
Kapok	10
Ramie	9
Flax	7

data in Table 1.7 are average values. Figure 1.52 shows the curve for sorption isotherm at different RH for jute fibers in both a drying and moisture regain modes.



1.52 Moisture regain versus relative humidity curves for jute (● = gain in moisture, ○ = moisture loss) (reproduced with permission from the Jute Technological Research Laboratories, Calcutta).

1.7 Fiber chemistry

Table 1.8 gives some general data on the chemical composition of some natural fibers. As with Tables 1.5 and 1.7, different data are given by different authors. The variation in chemical composition can be clearly seen in the master chemical table given in the Appendix at the end of this chapter. Straw fibers contain a lot of silica as do several species of tropical woods.

Table 1.8 Chemical composition of some natural fibers

Type of fiber	Cellulose	Lignin	Pentosan	Ash	Silica
Stalk fiber: straw					
Rice	28–48	12–16	23–28	15–20	9–14
Wheat	29–51	16–21	26–32	4.5–9	3–7
Barley	31–45	14–15	24–29	5–7	3–6
Oat	31–48	16–19	27–38	6–8	4–6.5
Rye	33–50	16–19	27–30	2–5	0.5–4
Cane fiber					
Sugar	32–48	19–24	27–32	1.5–5	0.7–3.5
Bamboo	26–43	21–31	15–26	1.7–5	0.7
Grass fiber					
Esparto	33–38	17–19	27–32	6–8	–
Sabai	–	22.0	24	6	–
Reed fiber					
Phragmites communis	44–46	22–24	20	3	2
Bast fiber					
Seed flax	43–47	21–23	24–26	5	–
Kenaf	44–57	15–19	22–23	2–5	–
Jute	45–63	21–26	18–21	0.5–2	–
Hemp	57–77	9–13	14–17	0.8	–
Ramie	87–91	–	5–8	–	–
Core fiber					
Kenaf	37–49	15–21	18–24	2–4	–
Jute	41–48	21–24	18–22	0.8	–
Leaf fiber					
Abaca	56–63	7–9	15–17	3	–
Sisal	47–62	7–9	21–24	0.6–1	–
Seed hull fiber					
Cotton linter	90–95	0.7–1.6	1–3	0.8–2	–
Wood fiber					
Coniferous	40–45	26–34	7–14	<1	–
Deciduous	38–49	23–30	19–26	<1	–

It can be seen that there is a wide variety of chemical compositions in the various fibers. Fibers high in cellulose include cotton and ramie. A more complete listing of chemical properties is given in the Appendix at the end of this chapter.

1.8 Changes in properties during the growing season

It is well known that different parts of a plant or tree have different chemical and physical properties. The chemical composition and fiber properties of plants taken from the roots, stem, trunk, and leaves differ. What is not so well known is that the chemical composition and fiber properties of plant tissue are also different at different stages of the growing season (Rowell *et al.*, 1997).

Plants and trees have, in general, five stages in their life cycle: germination, growth, flowering, seed formation, and death. Annual plants go through these stages in one growing season. Biennials have a two-year cycle where the second year's plant grows from the root system of the first year's plant. Perennial plants have the same cycle as annual plants except growth, flowering, and seed formation occur many times before the plant dies.

Various industries harvest plants for products at different times during the plant life cycle. For example, the food industry harvests young sprouts such as beans just after germination. Crops such as lettuce and asparagus are harvested during the early growing part of their cycle. The cut-flower industry harvests the plant flowers at the bud stage or shortly thereafter. Seeds used for food or oil production are harvested after the flowering stage but before the seeds drop from the seed pod. Many crops, however, are allowed to complete their life cycle before harvesting. For example, annual grain crops are allowed to field ripen and dry before harvesting.

In general, annual plants used for fiber are harvested at the end of the growing season, allowed to dry in the field, and then processed into fiber. Fiber from trees is derived from logs of various ages, and fiberized by one of several methods.

There may be an advantage in harvesting fiber from plants at some time earlier than from a mature plant. For example, fiber from an immature plant may be low in lignin, which could be used for paper since there would be little chemical pulping required to remove the lignin. While the yield may be lower, there may be an advantage in chemical and energy use to harvest early. In the case of annual plants, it may be possible to harvest two crops in one season to give the same yield of fiber but with much less lignin. Fiber from juvenile plants such as jute and kenaf is reported to be 'silk-like', i.e. fine texture, very flexible, and thin. Again, the yield may be lower, based on the traditional end of the season yield, but an early-harvested fiber that could be used for textiles may command a higher price.

The earliest literature on changes in chemical composition as a function of the growing season was reported with wheat in the 1930s (Phillips *et al.*, 1931). The cellulose content was found to be highest in the early part of the growing season and lignin and ash content was found to vary with the amount of fertilizer used. In a study using several varieties of flax, Overbeke and Mazingue (1949) found that both cellulose and lignin content increased with plant age, but pectins, hemicellulose and ash content followed no systematic progression with age.

A great deal of research was done on cotton during the 1950s. Usmanov (1957) and Usmanov *et al.* (1958) found that the degree of polymerization (DP) of cellulose increased up to the 15th day after bloom, then slowed and stopped on approximately the 40th day. The DPs 3 days prior to the opening of the boll, and 0, 1, 5, 7, 10, 12, 15, and 17 days after the opening of the boll were 2920, 3758, 4286, 4564, 4406, 4282, 4082, 3622, and 3326, respectively. Strength and DP of the cellulose were at a maximum at 5–6 days after the boll opened and it was recommended that the cotton should be picked 12–15 days after the opening of the boll. Using the electron microscope, Usmanov and Nikonovich (1960) went on to show that the most rapid accumulation of crystalline microfibrils took place between 17 and 20 days of growth and reached a maximum at 40 days. After that, the main growth was across fibers that led to the formation of the primary wall.

Ono (1957) and Ono and Sato (1957) studied the relationship between cellulose, nitrogen, phosphorus, ash, wax, and pectin as they related to maturity. They reported that immature lint contained a large amount of non-cellulosic substances and, hence, lost a large amount of weight during purification. Immature fiber was harder to bleach and dye than mature fiber. The reducing sugar content was higher in immature lint and decreased as the plant aged.

The University of Manchester, the Shirley Institute, and the British Textile Technology Group in the United Kingdom have spent years working on jute. Although some of the research has been published, the results relating to the changes in properties of jute fiber as a function of the growing season were obtained for the International Jute Organization in Bangladesh and never published (V. Ozsanlav, personal communication, 1992). Personal communications concerning these results indicate that juvenile jute fiber looks and feels like silk but this has never been documented in print.

Chatterjee (1959), working at the Technological Jute Research Laboratories in Calcutta, India, first reported the changes in chemical composition at different stages of jute plant growth. Table 1.9 shows a summary of his results. These results show that there is little difference in cellulose, holocellulose, and lignin content but that xylan, ash and iron content decrease as the plant matures. The aggregate fiber length increases as the growing season progresses.

Later, Mukherjee *et al.* (1986), working at the Indian Jute Industries' Research Association in Calcutta, studied characteristics of jute fiber at different stages of growth. They found that at the early stages of growth, there was an incomplete formation of the middle lamella in the cell wall and the parallel bundles of fibrils were oriented at an angle with respect to the fiber axis, which gradually decreased with growth. After about 35 days of growth, the fibrils run

Table 1.9 Changes in chemical composition of jute (%) at different stages of plant growth (reported on 100 g of dry material)

Component	Stage of plant growth				
	Pre-Bud	Bud	Flower	Small pod	Large pod
α-Cellulose	58.3	57.6	59.4	58.7	59.1
Holocellulose	86.8	87.8	87.3	87.1	86.8
Xylan	15.5	14.8	14.4	13.7	13.9
Lignin	12.7	12.1	12.4	12.0	12.0
Ash	0.57	0.53	0.47	0.67	0.47
Iron	0.020	0.018	0.009	0.011	0.008
Reed length	200 cm	275 cm	280 cm	290 cm	320 cm

parallel to the fiber axis. In that mature plant, a few helically oriented fibrils in the *Z*-direction were observed just below the primary cell wall layer.

The earliest work on chemical changes in bamboo during its growing season was done by Migita in 1947. He reported that the α-cellulose content of madake was almost constant from a week to three years but that lignin increased steadily from 8.4% to 24.0% during the same period. Taniguchi (1956) showed that there were ultrastructural changes in bamboo during its growth particularly as it related to its fine structure. Normura and Yamada (1974b) studied the changes in crystallinity using X-ray analysis in bamboo internodes during the growing stages and found that the amorphous pattern observed in juvenile nodes gradually changed to orientation of the fiber in a mature node. Crystallinity increased slightly during the formation of the first 10 internodes but then decreased over the next 30 nodes and finally leveled off after 35 nodes. They also showed that the internode length increased up to 6 weeks of growth and then decreased back to a value reported at 5 weeks in a mature plant.

Normura and Yamada (1974a) followed the variation of amino acids in bamboo using X-ray analysis and reported that tyrosine was at the highest concentration (about 30% based on dry weight of the plant) in the fourth week of growth or about the 17th internode. Higuchi and Shimada (1969) had found earlier that tyrosine was present in the highest amount of any stage of growth as compared with all other amino acids present. Higuchi *et al.* (1953, 1966, 1967) studied the formation of lignin in bamboo and reported that lignification increased with plant age.

Fujii *et al.* (1993) have done the most complete chemical analysis of bamboo as a function of its growth. Their results are shown in Table 1.10. Cold water, alcohol/benzene, and 1% NaOH extractives, ash content and protein decreased as the plant aged, while cellulose, holocellulose, pentosan, lignin, and crystallinity increased with plant age.

The first wood substance laid down by a tree is known as juvenile wood. It differs both in physical and chemical properties as compared with mature wood.

Table 1.10 Changes in chemical composition of bamboo (%) at different stages of plant growth

Component	Stage of plant growth (by node position)					
	1–11	12–16	17–20	21–24	25–27	28–40
Moisture dry weight	79.4	80.0	84.6	88.5	90.3	90.3
Extractives	15.3	16.7	25.2	38.9	46.9	48.7
Lignin	8.8	8.2	5.4	2.6	0.6	0.3
Holocellulose	47.3	48.8	37.6	32.6	23.0	13.9
α-Cellulose	80.6	81.1	71.0	65.2	53.1	39.8
Pentosan	24.5	34.3	28.0	21.9	11.4	5.1
Protein	5.0	5.8	7.6	11.7	19.6	30.6
Ash	2.0	2.1	3.1	5.0	7.5	10.8
Crystallinity index	44.1	43.2	40.7	32.2	23.2	8.5

Usually, the percentage of juvenile wood is low in a large, mature tree but may be high in small, young trees. For example, a 10-year-old Sitka spruce tree may contain up to 90% juvenile wood whereas a 100-year-old Sitka spruce tree may contain only 1% juvenile wood at its center. Juvenile wood usually grows in wider annual rings, has a higher amount of earlywood (wood substance laid down in the spring and early summer) than latewood (wood substance laid down in the late summer and early fall), lower basic density, and higher moisture content than mature wood (Panshin and de Zeeuw, 1980). Mature wood shrinks very little in the longitudinal (growing) direction whereas juvenile wood can shrink a great deal in the growing direction. At the ultrastructural level, juvenile wood fibers have a larger microfibril angle in the S_2 layer than mature wood, which is why juvenile wood shrinks more in the longitudinal direction (0.6%) than mature wood (less than 0.1%) (Rowell, 1984).

The fiber length of juvenile wood is much shorter (3.0 mm) than mature wood (4.2 mm) while the lumen size is larger (42.3 μm) in juvenile wood than in mature wood (32.8 μm). Cell wall thickness is about 3.9 μm for juvenile wood compared with about 8 μm for mature wood. Cell diameters are about the same for both (juvenile, 50 μm; mature, 49 μm). The breaking strength of mature wood is about 30% higher and the compression strength parallel to the grain is about 20% higher then juvenile wood.

In general, juvenile wood from both hardwoods and softwoods have less cellulose (lower pulp yields) more lignin and hemicellulose content than mature wood (Taniguchi, 1956; Panshin and de Zeeuw, 1980). There is little difference between the types and amounts of hemicelluloses in both hardwoods and softwoods in juvenile and mature wood.

The extractives can be very different in juvenile wood from those in mature wood. Extractives from juvenile wood are often more toxic and in higher concentration. This may account for the decreased digestibility of new growth in birch trees (Palo *et al.*, 1985). The concentration of phenolic acids in the extractives are higher in juvenile wood just after leafing has started compared with mature wood.

Theander (1991) recently completed a study of the changes in chemical composition of several Swedish grasses as a function of growing time. He found that cellulose and lignin increased as the plant matured, while protein decreased in reed canary grass (*Phalaris arundinacea*). Hemicellulose content and pectin remained constant during the entire plant life.

Otoguro *et al.* (1991) reported on the amino acid content as a function of plant growth and also found that cellulose and hemicelulose content decreased with plant age. Chand and Hashmi (1993) found that the density of plant fibers decreased from 1.18 to 1.16 g/cm^3 as the plant aged from 2 to 5 years but then increased to 1.27 g/cm^3 when the plant reached age 9. Hemicellulose content was found to be the highest when the plant was 5 years old. Tensile strength increased from 285 to 393 MPa with an increase in plant age from 2 to 9 years. This change in strength was explained in terms of plant fiber structure.

Clark and Wolff (1969) carried out the first studies on the changes in chemical composition of kenaf as a function of the growing season. They also studied chemical differences along the stem and between leaves and stem. The values shown in Table 1.11 were taken from the bottom (all but the top 0.66 m of the plant) and shows that the pentosans, lignin, and α-cellulose content increase with age while the protein and hot water extractives content decrease with age. Data taken from the top part of the plant show similar trends but the top part has less cellulose, pentosans, and lignin but higher hot water extractives and protein than the bottom part of the plant.

Clark *et al.* (1967) studied the changes in kenaf fiber properties during the growing season and found that the bast single fibers are longer than core fibers and both decrease in length with age. Core single fibers are twice as wide and have twice the cell wall thickness as bast single fibers and both dimensions decrease with age. Finally, the lumen width is wider in pith fibers than in bast single fibers and both decrease with age.

Table 1.11 Changes in chemical composition of kenaf at different stages of plant growth

Component	90 dap	120 dap	138 dap	147 dap	158 dap	244 dap
Hot water extractives	37.4	39.0	35.2	31.6	30.6	12.8
Lignin	4.5	3.9	6.4	7.2	7.4	11.4
α-cellulose	10.6	14.5	18.5	18.1	20.6	29.8
Pentosan	5.0	12.5	16.1	17.0	16.7	20.1
Protein	25.0	17.9	16.1	13.3	14.9	11.1

dap: days after planting.
Data from the top 0.66 m of the plant, % by weight.

Table 1.12 Chemical composition of kenaf fiber (% oven dry basis)

			Polysaccharide content (% anhydro sugars on oven dry basis)					
Growth (dap)	Extractives	Lignin	Arabinan	Rhamnan	Galactan	Glucan	Xylan	Mannan
35	14.87	4.32	3.95	2.72	0.78	28.86	6.54	1.76
42	8.80	6.00	3.18	1.82	0.62	33.20	7.31	1.63
57	5.13	8.32	2.21	1.46	0.55	35.45	8.08	1.59
63	4.34	7.74	2.43	1.48	0.62	37.08	8.61	1.53
70	4.63	8.70	2.02	1.25	0.46	40.53	9.37	1.47
77	4.99	9.23	2.05	1.36	0.39	40.52	9.16	1.34
84	5.07	8.33	2.27	1.63	0.49	39.88	9.39	1.53
91	5.68	9.38	1.91	1.35	0.42	42.82	9.98	1.31
98	2.42	8.81	2.13	1.43	0.48	41.60	9.69	1.35
133	8.03	8.94	1.67	1.15	0.48	41.98	9.72	1.31
155	7.83	9.99	1.27	0.87	0.38	46.39	11.20	1.19
161	11.51	10.22	2.54	1.52	0.56	39.22	9.75	1.33
168	12.31	9.74	2.18	1.37	0.47	41.41	10.36	1.39
175	8.23	9.69	1.40	0.87	0.36	49.33	12.29	1.02

dap: days after planting.

Han *et al.* (1995) determined extractives, lignin, and sugar contents of kenaf at different growing times (Table 1.12). Klason lignin analysis was done after the extraction. The klason lignin values increased from *ca.* 4% at the beginning to 10% at the end of growing season. (Bagby (1971) reported about 10% using Florida kenaf.) Kjeldahl determination of protein was performed (Han *et al.*, 1995) on several batches of combined klason lignin samples and the amount of protein in the klason lignin was measured. The protein content of kenaf is between 4 and 14% of the klason lignin, depending upon the age of the plant. Only 38% of the protein was found in the klason lignin and the rest was found in the hydrolysate. In general, protein content decreased with plant age.

Solvent extractive content varied as a function of growth: in general, it was high at the beginning, decreased during the first part of the growing time and then increased again. L-Arabinose, L-rhamnose, L-galactose, and D-mannose content decreased as a function of growth, while D-glucose and D-xylose content increased over this same period of time.

1.9 Conclusions

There are hundreds if not thousands of different fibers in the world and this chapter has covered only a very few of them. In fact, only a few of these fibers have even been studied. Most research has been carried out to study the potential use of natural fibers for papermaking. However, many other applications such as filters, sorbents, geotextiles, and composites can be made from these fibers. We have only touched the surface of the world of natural fibers. The future holds the discovery and characterization of many new plants and their fibers and many different potential applications. We can also look forward to research in genetics to alter both chemical and physical properties of natural fibers to tailor their use to specific end product applications.

1.10 Acknowledgment

The author thanks Steve Schmieding of the Forest Products Laboratory for taking the pictures of the fibers for this chapter.

1.11 Appendix: Chemical properties of natural plant fibers

Table 1.13 is a compilation of the chemical composition of some natural plant fibers taken from many references in the scientific literature. Analytical procedures were different and the data include different anatomical parts of the plants such as bast fibers and core fibers.

Table 1.13 Master list of chemical composition of various natural fibers

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Agavaceae					
Agave sisalana	Sisal	India	43–56	8–9	21–24
Agave sisalana	Sisal	–	63.9	8.6	17.9
Agave sisalana	Sisal	–	–	11.0	–
Musa textilis	Abaca	–	–	5.7	–
Musa textilis	Manila hemp	–	61.0	9.0	17.0
Phormium tenax	Phormium	–	–	–	–
Yucca schidigera (leaves)	–	California, US	22.3	–	–
Ananas erectifloius	Curauá	Brazil	73.6	7.5	9.9
Bromeliaceae					
Ananas comosus	Pineapple	Hawaii, US	69.5	4.4	17.8
Ananas comosus	Pineapple	–	–	12.0	–
Cyperaceae					
Bulboslylis capilleris	–	Maryland, US	7.8	–	–
Cyperus esculentus	Nut sedge	Maryland, US	23.1	–	–
Cyperus filiculmis	–	Maryland, US	24.9	–	–
Cyperus papyrus	Papyrus	–	39.6	19.7	–
Cyperus papyrus	Papyrus	India	40.1	16.1	–
Scirpus rubricosus	–	Maryland, US	30.4	–	–
Scirpus americanus	–	California, US	22.3	–	–
Scirpus americanus	–	California, US	23.5	–	–
Scirpus paludosus	–	California, US	23.8	–	–
Scirpus sp.	–	New England, US	27.0	–	–
Gramineae					
Agropyron elongatum	Wheatgrass	New England, US	21.4	–	–
Agropyron intermedium	Wheatgrass	New England, US	26.2	–	–
Agrostis sp.	Bent grass	Maryland, US	14.4	–	–
Andropogon barbinodis	Beard grass	Texas, US	27.7	–	–
Andropogon gerardi	–	Kansas, US	33.4	–	–
Andropogon hallii	–	Kansas, US	33.5	–	–
Andropogon intermedius	–	Kansas, US	31.5	–	–
Andropogon virginicus	–	Texas, US	33.1	–	–
Aristida wrighii	–	Texas, US	25.9	–	–
Arundinaria alpina	Bamboo	Ethiopia	30.4	–	–
Arundinaria longifolia	Bamboo	Arizona, US	39.3	–	–
Arundinaria tecta	Bamboo	Maryland, US	26.4	–	–
Arundo donax	Addar grass	Maryland, US	29.3	–	–
Avena barbata	Oat	Arizona, US	27.1	–	–
Avena sativa	Oat	America	35.9	16.1	26.2
Avena sativa	Oat	–	39.4	17.5	27.1
Avena sativa	Oat	The Netherlands	31–37	16–19	27–38
Avena sativa	Oat	India	37.1	15.5	24.9
Bambusa vulgaris	Bamboo	Brazil	36.3	–	–
Botanical names not given	Bamboo	–	32–44	19–24	27–32
Botanical names not given	Bamboo	Dowga	26–43	21–31	15–26
Botanical names not given	Bamboo	Medar	–	24.6	17.2

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Botanical names not given	Bamboo	Chiva	–	26.6	17.7
Botanical names not given	Bamboo	–	–	27.5	17.5
Bothriochloa intermidia	Bluestem	Oklahoma, US	8.5	–	–
Bouteloua curtipendula	Gramagrass	Texas, US	23.0	–	–
Bromus rigidus	Bromgrass	Maryland, US	24.8	–	–
Cenchrus myosuroides	–	Arizona, US	30.4	–	–
Cymbopogon validus	Oilgrass	S. Africa	29.3	–	–
Cynodon dactylon	Bermuda grass	Georgia, US	24.5	–	–
Dactylis glomerata	Orchard grass	Maryland, US	31.5	–	–
Digitaria sanguinalis	Crabgrass	Maryland, US	16.7	–	–
Echinochloa crusgalli	Barnyard grass	Maryland, US	27.5	–	–
Echinochloa pyramidalis	–	S. Africa	30.6	–	–
Eleusine indica	Wiregrass	North Carolina, US	8.0	–	–
Elymus canadensis	Wild rye	North Dakota, US	27.0	–	–
Elymus giganteus	Wild rye	New England, US	32.1	–	–
Elymus sp.	Wild rye	California, US	30.8	–	–
Eragrostis chloromelas	Love grass	Arizona, US	94.6	–	–
Eragrostis curvula	Love grass	Oklahoma, US	28.2	–	–
Eragrostis curvula	Love grass	Oklahoma, US	25.4	–	–
Erianthus ravennae, stalks	Ravenna grass	Illinois, US	35.1	–	–
Guadua amplexifolia, base	–	Mexico	40.6	–	–
Guadua amplexifolia, middle	–	Mexico	42.8	–	–
Guadua amplexifolia, top	–	Mexico	43.0	–	–
Guadua angustifolia	–	Ecuador	29.8	–	–
Gynerium sagittatum	Wild cane	Honduras	38.5	–	–
Holcus lanatus	Velvet grass	Maryland, US	29.1	–	–
Hordeum vulgare	Barley	Europe	36.4	16.6	26.7
Hordeum vulgare	Barley	America	31–34	16–19	24–29
Hordeum vulgare	Barley	–	33.8	14.5	14.7
Hyparrhenia hirta	–	S. Africa	34.1	–	–
Ischaemum arcuatum	–	S. Africa	30.8	–	–
Lolium multiflorum	Ryegrass	Spain	34.5	–	–
Lygeum spartum	–	Maryland, US	24.4	–	–
Melica mulica	Melic grass	Maryland, US	35.5	–	–
Miscanthus sinensis	–	Maryland, US	26.6	–	–
Muhlenbergia rigens	–	California, US	22.8	–	–
Oryza sativa	Rice	Egypt	36.2	11.9	24.5
Oryza sativa	Rice	Sri Lanka	28.1	12.5	26.5
Oryza sativa	Rice	–	–	12.0	21.0
Oryza sativa	Rice	India	28–36	12–16	23–28
Oryza sativa	Rice	–	–	25.5	21.0
Oxytenanthera abyssinica	–	Ethiopia	39.8	–	–
Panicum antidotale	Panic grass	Texas, US	24.4	–	–
Panicum deustum	Panic grass	S. Africa	24.3	–	–
Panicum subjunceum	Panic grass	Uruguay	27.4	–	–
Panicum virgatum	Panic grass	Kansas, US	32.4	–	–
Paspalum arechavaletae	–	Uruguay	31.1	–	–
Paspalum exaltatum	–	Uruguay	31.2	–	–
Paspalum haumanii	–	Uruguay	29.4	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Paspalum quadrifarium	–	Uruguay	30.5	–	–
Pennisetum macrourum	–	Georgia, US	30.2	–	–
Pennisetum spicatum	–	Missouri, US	26.0	–	–
Pennisetum typhoides	–	S. Africa	31.4	–	–
Pennisetum typhoides	–	Illinois, US	31.7	–	–
Phleum pratense	–	Maryland, US	18.1	–	–
Phragmites communis	Reeds	China	–	14.7	18.2
Phragmites communis	Reeds	Romania	–	22.9	26.6
Phragmites communis	Reeds	Russia	–	–	38.8
Phragmites communis	Reeds	Germany	–	35.8	16.8
Phragmites communis	Reeds	Italy	–	15.7	23.7
Phragmites communis	Reeds	–	45.0	22.0	20.0
Phragmites communis	Reeds	New England, US	25.1	–	–
Phyllostachys angusta	Bamboo	Georgia, US	35.6	–	–
Phyllostachys aureosuslcata	Bamboo	Georgia, US	36.3	–	–
Phyllostachys bamusoides	Bamboo	Georgia, US	36.3	–	–
Phyllostachys bamusoides cv. *castillon*	Bamboo	Georgia, US	35.6	–	–
Phyllostachys bamusoides cv. *slender crookstem*	Bamboo	Georgia, US	35.7	–	–
Phyllostachys bamusoides cv. *white crookstem*	Bamboo	Georgia, US	34.2	–	–
Phyllostachys bambusoides (base)	Bamboo	Georgia, US	35.5	–	–
Phyllostachys bambusoides (middle)	Bamboo	Georgia, US	36.6	–	–
Phyllostachys bissetii	Bamboo	Georgia, US	35.0	–	–
Phyllostachys congesta	Bamboo	Georgia, US	35.6	–	–
Phyllostachys decora	Bamboo	Georgia, US	35.0	–	–
Phyllostachys dulcis	Bamboo	Georgia, US	32.9	–	–
Phyllostachys flexuosa	Bamboo	Georgia, US	35.5	–	–
Phyllostuahys lithophila	Bamboo	Taiwan	39.0	–	–
Phyllostachys makinoi	Bamboo	Taiwan	38.7	–	–
Phyllostachys meyeri	Bamboo	Georgia, US	36.9	–	–
Phyllostachys nidularia cv. *smooth sheath*	Bamboo	Georgia, US	33.0	–	–
Phyllostachys nigra	Bamboo	Georgia, US	36.4	–	–
Phyllostachys nigra cv. *bory*	Bamboo	Georgia, US	36.7	–	–
Phyllostachys nuda	Bamboo	Georgia, US	36.1	–	–
Phyllostachys pubescens	Bamboo	Georgia, US	34.1	–	–
Phyllostachys purpurata	Bamboo	Georgia, US	35.7	–	–
Phyllostachys rubromarginata	Bamboo	Georgia, US	35.6	–	–
Phyllostachys viridiglaucescens	Bamboo	Georgia, US	34.9	–	–
Phyllostachys viridis	Bamboo	Georgia, US	34.1	–	–
Phyllosachys vivax	Bamboo	Israel	36.0	–	–
Saccharum biflorum		S. Africa	32.3	–	–
Saccharum officinanum	Sugar cane or bagasse	Florida, US	29.9	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Saccharum officinanum	Sugar cane or bagasse	Hawaii, US	31.6	17.8	27.6
Saccharum officinanum	Sugar cane or bagasse	Louisiana, US	32.4	20.8	30.3
Saccharum officinanum	Sugar cane or bagasse	Florida, US	–	18.9	30.0
Saccharum officinanum	Sugar cane or bagasse	Hawaii, US	–	18.1	27.9
Saccharum officinanum	Sugar cane or bagasse	Hawaii, US	–	21.3	27.7
Saccharum officinanum	Sugar cane or bagasse	Puerto Rico	–	19.3	31.3
Saccharum officinanum	Sugar cane or bagasse	Mexico	–	18.1	29.6
Saccharum officinanum	Sugar cane or bagasse	Philippines	–	22.4	29.9
Saccharum officinanum	Sugar cane or bagasse	India	–	22.3	31.8
Saccharum officinanum	Sugar cane or bagasse		–	23.0	27.5
Saccharum sp.	Sugar cane or bagasse	Florida, US	31.0		
Secale cereale	Rye	America	33–35	16–19	27–30
Secale cereale	Rye	Europe	37.6	19.0	30.5
Secale cereale	Rye		39.3	17.8	27.9
Secale cereale	Rye	Europe	37.2	17.6	25.7
Setaria italica	Foxtail millet	New England, US	25.3	–	–
Setaria sphacelata	–	S. Africa	30.9	–	–
Setaria verticillata	–	Maryland, US	17.5	–	–
Semiarundinaria munielae	Bamboo	The Netherlands	35.6	–	–
Sorghum almum	Sorghum	–	29.1	15.8	23.0
Sorghum caffrorum	Sorghum	–	28.8	14.7	27.0
Sorghum caudatum	Sorghum	–	29.7	16.0	27.4
Sorghum drummondii	Sorghum	–	27.5	–	–
Sorghum nervosum	Sorghum	–	27.9	13.6	26.8
Sorghum subglabrecens	Sorghum	–	29.9	15.0	24.7
Sorghum technicum	Sorghum	–	28.0	–	–
Sorghum	Sorghum	–	30.1	14.6	27.4
Sorghum	Sorghum	–	27.0	–	–
Sorghum durra	Sorghum	–	29.9	15.0	28.0
Sorghum helpense	Sorghum	–	29.3	12.1	26.5
Sorghum sudanese	Sorghum	The Netherlands	28.0	13.8	–
Sorghum almum	–	Illinois, US	36.3	–	–
Sorghum vulgare (grain)	–	Texas, US	29.4	–	–
Sorghum vulgare (broom corn)	–	Texas, US	32.5	–	–
Sorghum halepense (forage)	–	Maryland, US	33.2	–	–
Sorghastrum nutans	Wood grass	New England, US	31.4	–	–
Spartina cynosuroides	Marsh grass	Virginia, US	25.0	–	–
Spartina pectinata	Marsh grass	New England, US	27.3	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Sporobolus cryptandrus	Rush grass	Oklahoma, US	28.9	–	–
Sporobolus fimbriatus	Rush grass	S. Africa	26.3	–	–
Stipa coronata	Esparto	California, US	26.4	–	–
Stipa speciosa	Esparto	California, US	27.8	–	–
Stipa splendens	Esparto	New England, US	27.2	–	–
Stipa tenacissima	Esparto	Spain	47.8	–	–
Stipa viridula	Esparto	North Dakota, US	29.4	–	–
Stipa sp.	Esparto		33–38	17–19	27–32
Stipa sp.	Esparto	–	48.0	14–16	22–28
Trispeacum dactyloides	–	Maryland, US	25.5	–	–
Triticum sp.	Wheat	America	34.7	16.3	26.8
Triticum sp.	Wheat		39.9	16.7	28.2
Triticum sp.	Wheat	The Netherlands	29–35	16–21	16–21
Triticum sp.	Wheat	India	33.3	15.6	24.6
Triticum sp.	Wheat		–	21.5	23.5
Zea mays	Corn	Illinois, US	34.2	–	–
Zea mays, stalk	Corn	Baroni	–	16.7	27.1
Zea mays	Corn	–	–	34.0	–
Zea mays, stalk	Corn	–	34.0	5.0	20.0
Zea mays, corncobs	Corn	–	32.0	14.0	41.0
Zea mays	Corn	Europe	–	14.0	–
Juncaceae					
Juncus acutus	–	California, US	25.4	–	–
Juncus xiphioides	–	California, US	30.0	–	–
Liliaceae					
Asparagus officinalis	–	Maryland, US	25.2	–	–
Musaceae					
Musa sp.	Banana	India	61.5	9.7	14.9
Musa sp.	Banana	India	–	14.0	18.0
Musa sp.	Banana	India	61.5	9.7	14.9
Palmae					
Cocos nucifera	Coconut coir	–	29.8	34.8	19.3
Cocos nucifera	Coconut coir	India	–	45.0	–
Cocos nucifera, pith	Coconut coir	Philippines	–	25.2	7.5
Cocos nucifera, husk dust	Coconut coir		–	29.3	16.9
Cocos nucifera	Coconut coir		–	39.2	11.0
Cocos nucifera, trunk	Coconut coir		–	30.9	9.6
Cocos nucifera, petiole	Coconut coir		–	25.1	22.9
Cocos nucifera, leaves	Coconut coir		–	16.2	18.6
Cocos nucifera	Coconut coir		–	27.7	11.6
Sabal texana	Mexican palm	Texas, US	14.9		
Papavearceae					
Papaver sp.	Poppy straw	America	42.2	20.0	27.6

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Restionaceae					
Wildenowia striata	–	S. Africa	23.1	–	–
Typhaceae					
Typha angustifolia	–	California, US	28.1	–	–
Amaranthaceae					
Amaranthus graecizans	Tumbleweed	Maryland, US	25.3	–	–
Amaranthus hybridus	Pigweed	New England, US	24.9	–	–
Amaranthus palmeri	–	Maryland, US	24.3	–	–
Amaranthus retroflexus	Redweed	North Carolina, US	26.8	–	–
Apcynaceae					
Apocynum cannabinum	Indian hemp	Maryland, US	29.5	–	–
Asclepiadaceae					
Asclepias syriaca	–	New England, US	31.2	–	–
Asclepias tuberosa	Butterfly weed	New Jersey, US	27.2	–	–
Asclepias incarnata	–	Maryland, US	29.9	–	–
Caprifoliaceae					
Sambucus canadensis	American elder	New England, US	27.9	–	–
Sambucus canadensis	American elder	Maryland, US	28.3	–	–
Bombacaceae					
Ceiba petandra	Kapok	–	–	13.0	–
Boraginaceae					
Echium vulare	Blueweed	Connecticut, US	20.0	–	–
Lithostpermum arvense	–	Maryland, US	21.5	–	–
Campanulaceae					
Lobelia cardinalis	Cardinal flower	Virginia, US	28.3	–	–
Specularia perfoliata	–	Maryland, US	22.6	–	–
Capparidaceae					
Cleome spinosa	–	Maryland, US	29.9	–	–
Cleome serrulata	Stinking clover	New England, US	33.2	–	–
Caryophyllaceae					
Agroustemma githago	Corn cockle	Maryland, US	28.3	–	–
Arenaria serpyllifolia	Thyme-leaves	Maryland, US	17.6	–	–
Dianthus ameria	–	Maryland, US	23.8	–	–
Saponaria officinalis	Bouncing bet	Connecticut, US	35.3	–	–
Silene antirrhina	Sleepy catchfly	Maryland, US	23.1	–	–
Silene noctiflola	Sticky cockle	Connecticut, US	24.3	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Chenopodiaceae					
Atriplex mulleri	Saltbush	Georgia, US	27.2	–	–
Euphorbia maginata	–	New England, US	32.5	–	–
Ricinus communis	–	New England, US	34.0	–	–
Guttiferae					
Ascyrum hypericodes	–	Virginia, US	26.7	–	–
Hypericum perforatum	–	Kansas, US	27.1	–	–
Hypericum punctatum	–	Maryland, US	27.2	–	–
Hydrophyllaceae					
Phacelia californica	–	California, US	23.7	–	–
Labiatae					
Monarda citriodora	–	Texas, US	32.0	–	–
Monarda fistutulosa	–	Maryland, US	26.8	–	–
Nepeta cataria	–	Delaware, US	25.7	–	–
Salvia azure	–	Kansas, US	28.0	–	–
Trichostema dichotomumt	–	Maryland, US	28.5	–	–
Leguminosae					
Aeschynomene scabra	–	Mexico	33.5	–	–
Alysicarpus rugosus	–	Georgia, US	27.1	–	–
Alysicarpus vaginalis	–	Georgia, US	25.3	–	–
Arachis hypogaea, hulls	Peanut	–	36.0	33.0	19.0
Astragalus cicer	–	Kansas, US	28.2	–	–
Astragalus sp.	–	Kansas, US	24.9	–	–
Astragalus sp.	–	New England, US	32.4	–	–
Baptisia leucophaea	–	Kansas, US	28.9	–	–
Baptisia minor	–	Kansas, US	31.7	–	–
Baptisia tinctoria	–	Maryland, US	29.6	–	–
Cassia fasciculata	–	Iowa, US	20.5	–	–
Cassia marilandica	–	Kansas, US	31.3	–	–
Cassia tora	–	North Carolina, US	28.0	–	–
Crotalaria eriocarpa	–	Mexico	36.1	–	–
Crotalaria intermedia	–	Georgia, US	38.1	–	–
Crotalaria incana	Sunnhemp	Florida, US	34.8	–	–
Crotalaria juncea	Sunnhemp	Illinois, US	37.9	–	–
Crotalaria juncea (Brazilian)	Sunnhemp	Illinois, US	39.2	–	–
Crotalaria juncea (ridged stem)	Sunnhemp	Texas, US	36.3	–	–
Crotalaria juncea (smooth stem)	Sunnhemp	Texas, US	35.6	–	–
Crotalaria juncea	Sunnhemp	Florida, US	78.3	–	–
Crotalaria juncea	Sunnhemp	Georgia, US	38.7	–	3.6
Crotalaria juncea	Sunnhemp	Illinois, US	36.3	4.0	–
Crotalaria juncea	Sunnhemp	Indiana, US	36.9	–	–
Crotalaria juncea	Sunnhemp	Louisiana, US	36.3	–	–
Crotalaria juncea	Sunnhemp	Michigan, US	41.5	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Crotalaria juncea	Sunnhemp	Missouri, US	38.9	–	–
Crotalaria juncea	Sunnhemp	Texas, US	37.6	–	–
Crotalaria juncea	Sunnhemp	–	35.6	–	–
Crotalaria mucronata	–	Florida, US	38.0	–	–
Crotalaria spectabilis	–	Florida, US	29.0	–	–
Crotalaria sp.	–	Georgia, US	34.1	–	–
Crotalarta striata	–	Florida, US	34.2	–	–
Cyamopsis tetragonoloba	–	New England, US	34.8	–	–
Dalea alopecuroides	Foxtail dalea	Iowa, US	32.5	–	–
Dalea enneandra	–	Kansas, US	35.9	–	–
Dalea deffusa	–	Mexico	35.2	–	–
Dalea leporina	–	Mexico	34.9	–	–
Dalea mutabies	–	Mexico	33.3	–	–
Dalea vernicia	–	Mexico	30.7	–	–
Desmanthus sp.	–	Kansas, US	31.0	–	–
Desmanthus illinoensis	–	New England, US	31.7	–	–
Desmanthus interior	–	Mexico	31.8	–	–
Desmodium distortum	–	Georgia, US	31.9	–	–
Desmodium gyrans	–	Kansas, US	29.7	–	–
Desmodium illinoensis	–	Kansas, US	31.1	–	–
Desmodium nicaraguense	–	Mexico	40.2	–	–
Desmodium virgatum	–	Georgia, US	30.1	–	–
Glycine max	Soy bean	Illinois, US	34.8	–	–
Glycyrrhiza lepidota	Wild licorice	New England, US	28.3	–	–
Indigofera hiruta	–	Florida, US	36.3	–	–
Indigofera sp.	Indigo	Georgia, US	24.3	–	–
Lespedeza capitata	–	New England, US	31.5	–	–
Lespedeza hedysarioides	–	Kansas, US	27.3	–	–
Lespedeza inschanica	–	Kansas, US	26.9	–	–
Lespedeza sp.	Bush-clover	Georgia, US	34.6	–	–
Lotus scoparius	–	California, US	22.8	–	–
Lupinus formosus	–	California, US	32.6	–	–
Lupinus latifolius	–	California, US	25.9	–	–
Lupinus micranthus	–	California, US	18.3	–	–
Melilotus albus	–	Illinois, US	26.4	–	–
Melilotus officinalis	Yellow melilot	Maryland, US	27.0	–	–
Petalostemon mutiflorum	Prairie clover	Kansas, US	23.3	–	–
Petalostemon purpureum	Prairie clover	Kansas, US	23.3	–	–
Sesbania arabica	–	Oklahoma, US	35.3	–	–
Sesbania cannabina	–	Oklahoma, US	33.9	–	–
Sesbania cinerescens	–	Georgia, US	30.3	–	–
Sesbania drummondii	–	Texas, US	31.6	–	–
Sesbania exaltata	Colorado River hemp	Texas, US	34.5	–	–
Sesbania sonorae	–	Arizona, US	36.3	–	–
Sesbania vesicaria	–	Texas, US	33.1	–	–
Sesbania sp.	–	Texas, US	40.2	–	–
Tephrosia virginiana	–	Maryland, US	30.0	–	–
Tephrosia sp.	Horay pea	Georgia, US	28.6	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Swainsona salsula	–	Colorado, US	27.3	–	–
Linaceae					
Linum usitatissimum	Flax	–	45–68	10–15	6–17
Linum usitatissimum	Flax	–	–	2.2	–
Linum usitatissimum	Flax	Illinois, US	27.2	–	–
Lythraceae					
Heimia salicifolia	–	Uruguay	28.9	–	–
Malvaceae					
Abutilon americanum	–	Mexico	28.8	–	–
Abutilon crispum	–	Mexico	31.3	–	–
Abutilon theophrasti	–	Maryland, US	27.6	–	–
Abutilon trisulcatum	–	Mexico	32.1	–	–
Altaea rosea	–	Maryland, US	30.5	–	–
Althaea cannabina	Hollyhock	Spain	27.5	–	–
Althaea setosa	–	Israel	28.8	–	–
Anoda pentaschista	–	Mexico	30.7	–	–
Gossypium spp.	Cotton, staple	–	85–90	3–3.3	21–23
Gossypium spp.	Cotton, linters	Indonesia	80–85	3–3.5	–
Hibiscus cannabinus	Kenaf, hurds	Illinois, US	34.7	15–18	–
Hibiscus cannabinus	Kenaf	Florida, US	34.0	10.5	21–23
Hibiscus cannabinus	Kenaf	–	31–39	12.1	18.3
Hibiscus cannabinus	Kenaf, stem	Maryland, US	36.5	13.2	22.7
Hibiscus cannabinus	Kenaf, stem	Georgia, US	40.2	7.7	19.7
Hibiscus cannabinus	Kenaf, whole	–	37.4	8.0	16.1
Hibiscus cannabinus	Kenaf, bast	–	42.2	17.4	16.0
Hibiscus cannabinus	Kenaf, core	–	33.7	13.4	19.0
Hibiscus cannabinus	Kenaf, bottom	–	35.3	–	20.1
Hibiscus cannabinus	Kenaf, top	–	29.8	–	–
Hibiscus cisplantinus	Kenaf	North Carolina, US	30.5	–	–
Hibiscus eelveldeanus	Kenaf	Florida, US	36.3	–	–
Hibiscus esculentus	Okra	New England, US	23.3	–	–
Hibiscus esculentus (pods only)	Okra	South Carolina, US	34.7	–	–
Hibiscus grandiflorus		Florida, US	31.6	–	–
Hibiscus militaris	Halberd-leaved Rose mallow	Mexico	28.9	–	–
Hibiscus lasiocarpus	–	Mexico	33.2	–	–
Hibiscus rosa-sinensis	Chinese rose	Florida, US	29.4	–	–
Hibiscus sabdariffa	Roselle	California, US	32.3	–	–
Hibiscus syriacus	Rose-of-Sharon	Maryland, US	22.9	–	–
Hibiscus trionum	Flower of-an-hour	Maryland, US	23.1	–	–
Hibiscus sp.	Rose mallow	Uruguay	32.2	–	–
Horsfordia newberryi	–	Mexico	34.0	–	–
Kosteletzkya althacifolia	–	Florida, US	31.4	–	–
Kosteletzkya sagittata	–	Mexico	28.5	–	–
Lavatera arborea	Tree mallow	California, US	28.9	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Lavatera punctata	–	Israel	25.0	–	–
Lavatera rotundata	–	Spain	25.5	–	–
Malachra alceaefolia	–	Mexico	30.4	–	–
Malva rotundifolia	–	Maryland, US	27.2	–	–
Malva sylvestris	–	Israel	18.4	–	–
Malva tournefortiana	–	Spain	27.5	–	–
Malvastrum sp.	–	S. Africa	33.0	–	–
Pavonia xanthogloca	–	Urguay	29.0	–	–
Sida acuta	–	Mexico	28.6	–	–
Sida carpinifolia	–	Georgia, US	24.5	–	–
Sida inflexa	–	North Carolina, US	23.3	–	–
Sida rhombifolia	–	Mexico	32.6	–	–
Sida sp.	–	Florida, US	34.1	–	–
Sphaeralcea angustifolia	–	Mexico	30.3	–	–
Sphaeralcea bonariensis	–	Uruguay	29.9	–	–
Sphaeralcea coccinea	Prairie mallow	New Mexico, US	16.4	–	–
Sphaeralcea emoryi	–	–	26.3	–	–
Sphaeralcea sp.	Flase mallow	California, US	30.2	–	–
Urena lobata	–	Florida, US	34.4	–	–
Wissadula amplissima	–	Mexico	33.3	–	–
Wissadula cineta	–	Mexico	34.5	–	–
Moraceae					
Cannabis sativa	Hemp	–	–	3.7	–
Cannabis sativa	Hemp	Illinois, US	37.6	–	–
Onagraceae					
Gaura parviflora	–	New England, US	26.9	–	–
Oenothera affinis	–	Uruguay	38.7	–	–
Oenothera biennis	Evening primrose	Connecticut, US	31.4	–	–
Oenothera humifusa	–	Maryland, US	23.5	–	–
Oenothera laciniata	–	Maryland, US	23.2	–	–
Phytolaccaceae					
Phytolacca americana	Virginian pokeweed	Maryland, US	28.4	–	–
Polemonuaceae					
Phlox paniculata	–	Maryland, US	35.4	–	–
Polygonaceae					
Eriogonum annuum	–	Kansas, US	25.6	–	–
Eriogonum fasciculatum	California buckwheat	California, US	30.4	–	–
Polygonoceae					
Polygonum persicaria	–	Connecticut, US	29.0	–	–
Polygonum orientale	Prince's feather	New England, US	30.4	–	–
Rumex crispus	–	Maryland, US	30.9	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Ranunculaceae					
Thalictrum polycarpum	–	California, US	30.6	–	–
Rosaceae					
Potentilla fruiticosa	Golden hardhack	Connecticut, US	27.1	–	–
Petentilla norvegica	–	Maryland, US	23.9	–	–
Rubiaceae					
Diodia teres	–	Virginia, US	22.8	–	–
Scrophulariceae					
Gerardia flava	–	New Jersey, US	27.0	–	–
Linaria canadensis	Old-field toadflax	Maryland, US	24.9	–	–
Mimulus guttatus	Common monkey flower	California, US	20.1	–	–
Mimulus ringens	Allegheny monkey flower	Connecticut, US	16.2	–	–
Penstemon digitalis	–	Maryland, US	23.6	–	–
Penstemon palmeri	–	California, US	21.1	–	–
Scrophularia californica	–	California, US	26.4	–	–
Scrophularia marilandica	Carpenter's-square	Maryland, US	30.6	–	–
Veronica peregrinia	–	Maryland, US	17.7	–	–
Verbascum blattaria	Moth mullein	Maryland, US	26.5	–	–
Vervascum sinuatum	–	Maryland, US	29.8	–	–
Solanaceae					
Datura stramonium	Stramonium	New England, US	33.1	–	–
Thymelaeaceae					
Gnidia oppositifolia	–	S. Africa	34.9	–	–
Tiliaceae					
Corhorus capsularis	Jute	Florida, US	39.1	–	–
Corhorus capsularis	Jute	–	–	21–26	18–21
Corhorus capsularis	Jute	–	–	26.8	
Corhorus capsularis	Jute	–	–	8.1	21.6
Corrhorus capsularis	Jute	India	60.7	12.5	–
Corchorus olitorius	Jute	India	61.0	13.2	15.6
Corhorus capsularis	Jute	India	58.9	13.5	15.9
Corhorus capsularis	Jute	India	–	21.3	17.0
Umbelliferae					
Cicuta maculata	Water hemlock	Maryland, US	31.6	–	–
Daucus carata	Wild carrot	Maryland, US	28.0	–	–
Heracleum lanatum	–	Maryland, US	30.4	–	–
Pastinaca sativa	Parsnip	Maryland, US	29.8	–	–
Pituranthos tortuosa	–	Israel	28.0	–	–

Table 1.13 continued

Botanical name	Common name	Place grown	α-Cellulose	Lignin	Pentosans
Urticaceae					
Boehmeria cylindrica	Bog hemp	North Carolina, US	28.8	–	–
Boehmeria nivea	Ramie	Louisiana, US	37.7	–	–
Boehmeria nivea	Ramie	India	86.9	0.5	–
Boehmeria nivea	Ramie	–	–	0.7	3.9
Laportea canadensis	–	North Carolina, US	28.6	–	–
Verbenceae					
Verbena hastata	–	Connecticut, US	25.5	–	–
Verbena urticifolia	White Vervain	Maryland, US	29.4	–	–
Other fibers					
Botanical name not given	Seed flax tow	India	34.0	23.0	25.0
Botanical name not given	Sabai	–	–	22.0	23.9
Botanical name not given	Sabai	–	–	17–22	18–24
Botanical name not given	Mesta	India	60.0	10.1	14.8
Botanical name not given	Roselle	India	59.7	9.9	15.0
Botanical name not given	Dhaincha	India	63.6	16.3	9.8
Botanical name not given	Bhindi	–	53.5	10.4	21.0
Botanical name not given	Palmyrah	–	–	42–43	–
Botanical name not given	Talipot	India	–	28–29	–
Botanical name not given	Bhabar	India	–	22.2	24.0
Botanical name not given	Groundnut husk	India	–	30.6	11.1
Botanical name not given	Munj	Pakistan	–	20.5	23.7
Botanical name not given	Bindi	–	–	9.4	–

Botanical name	Common name	Holo Cellulose	α-Cellulose	Pentosans	Lignin
Hardwoods					
Acer macrophyllum	Bigleaf maple	–	46.0	22.0	25.0
Acer negundo	Boxelder	–	45.0	20.0	30.0
Acer rubrum	Red maple	77.0	47.0	18.0	21.0
Acer saccharinum	Silver maple	–	42.0	19.0	21.0
Acer saccharum	Sugar maple	–	45.0	17.0	22.0
Alnus rubra	Red alder	74.0	44.0	20.0	24.0
Arbutus menziesii	Pacific madrone	–	44.0	23.0	21.0
Betula alleghaniensis	Yellow birch	73.0	47.0	23.0	21.0
Betula nigra	River birch	–	41.0	23.0	21.0
Betula papyrifera	Paper birch	78.0	45.0	23.0	18.0
Carya cordiformus	Bitternut hickory	–	44.0	19.0	25.0
Carya glaubra	Sweet pignut hickory	71.0	49.0	17.0	24.0
Carya ovata	Shagbark hickory	71.0	48.0	18.0	21.0
Carya pallida	Sand hickory	69.0	50.0	17.0	23.0
Carya tomentosa	Mockernut hickory	71.0	48.0	18.0	21.0
Celtis laeoigata	Sugarberry	–	40.0	22.0	21.0
Eucalyptus gigantea	–	72.0	49.0	14.0	22.0
Fagus grandifolia	American beech	77.0	49.0	20.0	22.0

Table 1.13 continued

Botanical name	Common name	Holo Cellulose	α-Cellulose	Pentosans	Lignin
Fraxinus americana	White ash	–	41.0	15.0	26.0
Fraxinus pennsyloanica	Green ash	–	40.0	18.0	26.0
Gleditsia triacanthos	Honey locust	–	52.0	22.0	21.0
Laguncularia racemosa	White mangrove	–	40.0	19.0	23.0
Liquidambar styraciflua	Sweetgum	–	46.0	20.0	21.0
Liriodendron tulipifera	Yellow-poplar	–	45.0	19.0	20.0
Lithocarpus densiflorus	Tanoak	71.0	46.0	20.0	19.0
Milalenca quinqueneroi	Cajeput	–	43.0	19.0	27.0
Nyssa aquatica	Water tupelo	59.0	–	16.0	24.0
Nyssa syloatica	Black tupelo	72.0	45.0	17.0	27.0
Populus alba	White poplar	67.0	–	23.0	16.0
Populus deletoides	Eastern cottonwood	–	47.0	18.0	23.0
Populus tremoides	Quaking aspen	78.0	49.0	19.0	19.0
Populus trichocarpa	Black cottonwood	–	49.0	19.0	21.0
Prunus serotina	Black cherry	85.0	45.0	20.0	21.0
Quercus alba	White oak	67.0	47.0	20.0	27.0
Quercus coccinea	Scarlet oak	63.0	46.0	18.0	28.0
Quercus douglasii	Blue oak	59.0	40.0	22.1	27.0
Quercusfalcata	Southern red oak	69.0	42.0	20.0	25.0
Quercus kelloggii	California black oak	60.0	37.0	23.0	26.0
Quercus lobata	Valley oak	70.0	43.0	19.0	19.0
Quercus lyrata	Overcup oak	–	40.0	18.0	28.0
Quercus marylandica	Blackjack oak	–	44.0	20.0	26.0
Quercus prinus	Chestnut oak	76.0	47.0	19.0	24.0
Quercus rubra	Northern red oak	69.0	46.0	22.0	24.0
Quercus stellata	Post oak	–	41.0	18.0	24.0
Quercus velutina	Black oak	71.0	48.0	20.0	24.0
Salix nigra	Black willow	–	46.0	19.0	21.0
Tilia heterophylla	Basswood	77.0	48.0	17.0	20.0
Ulmus americana	American elm	73.0	50.0	17.0	22.0
Ulmus crassifolia	Cedar elm	–	50.0	19.0	27.0
Softwoods					
Abies amabilis	Forbes/Pacific silver fir	–	44.0	10.0	29.0
Abies balsamea	Balsam fir	–	42.0	11.0	29.0
Abies concolor	White fir	66.0	49.0	6.0	28.0
Abies lasiocarpa	Subalpine fir	67.0	46.0	9.0	29.0
Abies procera	Noble fir	61.0	43.0	9.0	29.0
Chamaecyparis thyoides	Atlantic white cedar	–	41.0	9.0	33.0
Juniperus deppeana	Alligator juniper	57.0	40.0	5.0	34.0
Larix larcina	Tamarack	64.0	44.0	8.0	26.0
Larix occidentalis	Western larch	65.0	48.0	9.0	27.0
Libocedrus decurrens	Incense cedar	56.0	37.0	12.0	34.0
Picea enlgellmanni	Eangelman spruce	69.0	45.0	10.0	28.0
Picea glauca	White spruce	–	43.0	13.0	29.0

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2

Matrices for natural-fibre reinforced composites

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2.1 Introduction

Composite materials are the most advanced and adaptable engineering materials. A composite is a heterogeneous material created by the synthetic assembly of two or more components constituting reinforcing matrix and a compatible matrix, in order to obtain specific characteristics and properties.[1] The matrix may be metallic, ceramic or polymeric in origin. The matrix gives a composite its shape, surface appearance, environmental tolerance and overall durability while the fibrous reinforcement carries most of the structural loads, thus giving macroscopic stiffness and strength. It is the behaviour and the characteristics of the interface that generally control the properties of a composite. Development of advanced composite materials having superior mechanical properties opened new horizons in the engineering field. Advantages such as corrosion resistance, electrical insulation, reduction in tooling and assembly costs, low thermal expansion, higher stiffness and strength, fatigue resistance, such as greater stiffness at lower weight than metals, etc., have made polymer composites widely acceptable in structural applications. However, the disadvantages of composite materials cannot be ignored: their complex nature, designers' lack of experience, little knowledge of material databases and difficulty in manufacturing are barriers to large-scale use of composites.

Composites can be classified based on the form of their structural components: fibrous (composed of fibres in a matrix), laminar (composed of layers of materials) and particulate (composed of particles in a matrix). The particulate class can further be subdivided into flake (flat flakes in a matrix) and skeletal (composed of a continuous skeletal matrix filled by a second material). In general, the reinforcing agent can be fibrous, powdered, spherical, crystalline or whiskered and either an organic, inorganic, metallic or ceramic material.

2.2 Natural-fibre reinforced polymer composites

Concern about the preservation of natural sources and recycling has led to renewed interest in biomaterials with the focus on renewable raw materials. As a result, new types of composites based on plant fibres have been developed in recent years. Natural-fibre reinforced composites offer a good mechanical performance and eco-friendliness. The application of natural-fibre-based composites is increasing rapidly. This is especially related to certain problems concerning the use of synthetic fibre reinforced composites. As far as synthetic polymer composites are concerned, waste disposal and recycling are major issues worldwide. Landfill disposal is being increasingly excluded around the world due to growing environmental sensitivity. Therefore, in recent years environmentally compatible alternatives have been examined by researchers. This research covers factors such as efficient cost-effective and environmentally friendly recovery of raw materials, CO_2-neutral thermal utilisation or biodegradation in certain circumstances. That is why composites based on renewable resources consisting of either natural fibres or so-called biopolymers, or both, are economically and ecologically acceptable.

Natural fibres such as flax, hemp, banana, sisal, oil palm and jute have a number of techno-economical and ecological advantages over synthetic fibres such as glass fibres. The combination of interesting mechanical and physical properties together with their environmentally friendly character has aroused interest in a number of industrial sectors, notably the automotive industry. The advantages and disadvantages of using natural fibres in composites are given in Table 2.1. Lignocellulosic fibres have an advantage over synthetic ones since they buckle rather than break during processing and fabrication. In addition, cellulose possesses a flattened oval cross-section that enhances stress transfer by presenting an effectively higher aspect ratio.

Table 2.1 Advantages and disadvantages of using natural fibres in composites

Advantages	Disadvantages
Low specific weight, compared with glass reinforced composites	Enormous variability
Renewable resource with production requiring low CO_2 emissions	Poor moisture resistance
The processing atmosphere is worker-friendly with better working conditions	Poor fire resistance
High electrical resistance	Lower durability
Good thermal and acoustic insulating properties	Lack of fibre–matrix adhesion
Biodegradability	

2.3 Different matrices

2.3.1 Thermoplastic matrices

Polymers that soften or melt upon heating, called thermoplastic polymers, consist of linear or branched chain molecules having strong intramolecular bonds but weak intermolecular bonds. Melting and solidification of these polymers are reversible and they can be reshaped by application of heat and pressure. They are either semicrystalline or amorphous in structure. Examples include polyethylene (PE), polystyrene (PS), nylons, polycarbonate (PC), polyacetals, polyamide-imide, polyether-ether ketone (PEEK), polysulphone polyphenylene sulphide and polyether imide.

2.3.2 Thermosetting matrices

Thermosetting plastics have crosslinked or network structures with covalent bonds between all molecules. They do not soften but decompose on heating. Once they have been solidified by crosslinking, they cannot be reshaped. Common examples of thermosetting polymers include epoxies, polyesters and phenol formaldehyde.

2.3.3 Rubber matrices

The principal classes of rubber composites that have been used for the preparation of composites are: natural rubber (NR), styrene butadiene rubber (SBR), butyl rubber (IIR), butadiene rubber (BR), nitrile rubber (NBR), chloroprene rubber (CR), ethylene propylene diene rubber (EPDM), polyurethane rubber and silicon rubbers. The most widely used rubber matrix is natural rubber.

2.3.4 Biodegradable matrices

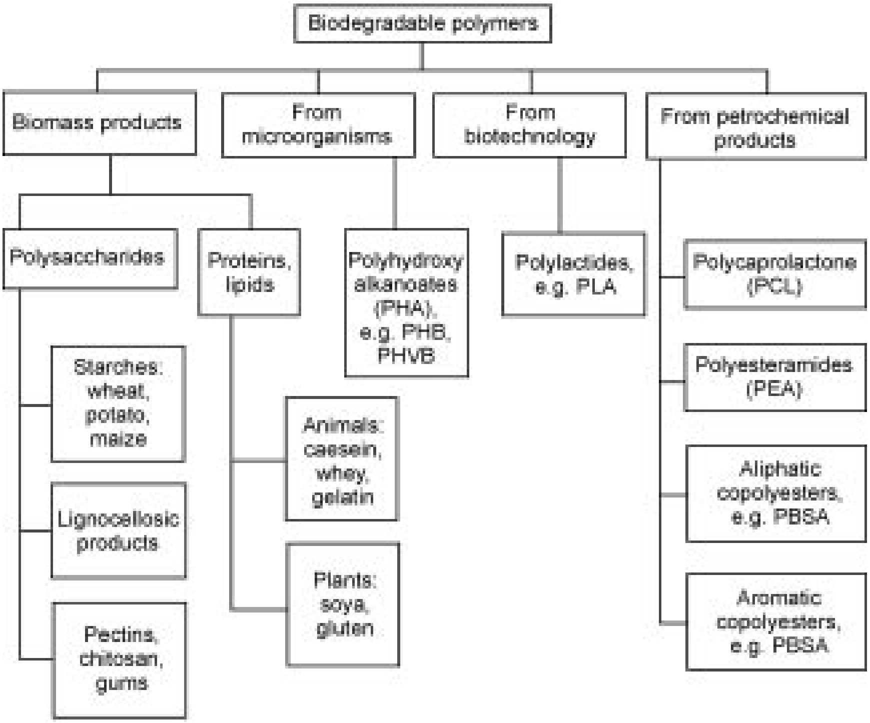
At a time when the world is switching to everything natural from organic farming to vegetarian diets, terms such as ‘green chemistry’ and ‘biocomposites’ seem to be the mantra of the times. Research efforts are currently being harnessed in developing a new class of fully biodegradable ‘green’ composites by combining natural/biofibres with biodegradable resins. The major attractions about green composites are that they are environmentally-friendly, fully degradable and sustainable. At the end of their life they can be easily disposed of or composted without harming the environment. Green composites may be used effectively in many applications such as mass-produced consumer products with short life cycles or products intended for one-off or short-term use before disposal. A number of natural and biodegradable matrices available to use in green composites are listed in Table 2.2. Starch and modified resins have also been used as matrix to form green composites. The reinforcement of biofibres in

Table 2.2 Natural and biodegradable matrices

Natural	Synthetic
Polysaccharides	Poly(amides)
Starch	Poly(anhydrides)
Cellulose	Poly(amide-enamines)
Chitin	Poly(vinyl alcohol)
Proteins	Poly(vinyl acetate)
Collagen/gelatin	Polyesters
Casein, albumin, fibrogen, silks	Poly(glycolic acid)
Polyhydroxyalkanoates	Poly(lactic acid)
Lignin	Poly(caprolactone)
Lipids	Poly(orthoesters)
Shellac	Poly(ethylene oxides)
Natural rubber	Poly(phosphazines)

green composites has been highlighted by Bismarck *et al.*[2] Figure 2.1 shows a classification of biodegradable polymers in four families.[3]

Except the fourth family, which is of fossil origin, most polymers (families 1–3) are obtained from renewable resources (biomass). The first family is agro-



2.1 Classification of biodegradable polymers.[3]

polymers (e.g. polysaccharides) obtained from biomass by fractionation. The second and third families are polyesters, obtained respectively by fermentation from biomass or from genetically modified plants (e.g. polyhydroxyalkanoate, PHA) and by synthesis from monomers obtained from biomass (e.g. polylactic acid, PLA). The fourth family comprises polyesters, totally synthesised by the petrochemical process (e.g. polycaprolactone, PCL; polyesteramide, PEA; aliphatic or aromatic copolyesters).

Another important biocomposites category is based on agro-polymer matrices, mainly focused on starchy materials. Plasticised starch, the so-called 'thermoplastic starch' (TPS), is obtained after disruption and plasticisation of native starch, with water and plasticiser (e.g. polyol) by applying thermo-mechanical energy in a continuous extrusion process. Unfortunately, TPS shows some drawbacks such as a strong hydrophilic character (water sensitive), rather poor mechanical properties compared with conventional polymers and an important post-processing variation of properties.

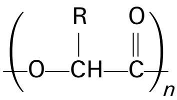
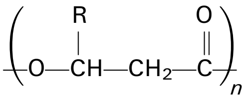
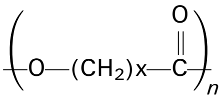
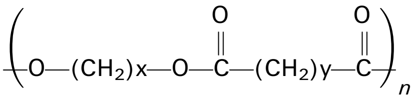
2.4 Aliphatic polyesters

Aliphatic polyesters are classified into two types based on the mode of bonding of constituent monomers, i.e. poly(alkylene dicarboxylate)s which are synthesised by a poly-condensation reaction of diols and dicarboxylic acids and polyhydroxyalkanoates, which are polymers of hydroxy acids, HO–R–COOH, as repeating units. Again hydroxy acids are classified into α-, β- and γ-hydroxy acids in respect of bonding position of the –OH group from the –COOH end group. All such structures are represented in Table 2.3.

2.4.1 Poly(α-hydroxy acid)

Recently PLA has been highlighted because of its availability from renewable resources such as corn. PLA is a hydrophobic polymer because of the incorporation of the $-CH_3$ side groups when compared with poly(glycolic acid) (PGA). PLA is synthesised by the condensation polymerisation of D- or L-lactic acid or ring opening polymerisation of the lactide. The physical properties and biodegradability of PLA can be regulated by employing a comonomer component of hydroxy acids or racemisation of D- or L-isomer, whereas PLA homopolymer such as poly(L-lactic acid) (PLLA) is a hard, transparent and crystalline polymer having a melting point of 170–180 °C and a glass transition temperature of about 53 °C.[4] PLLA, a highly crystalline polymer, is more resistant than PGA to hydrolysis owing to the methyl substituent's steric shielding effect of the ester group. PLA is primarily used for medical applications including sutures, drug delivery, vascular grafts, artificial skin and orthopaedic implants. All PLA resins are manufactured using renewable agricultural resources, such as corn or sugar beets. They are composed of chains of lactic acid that are produced by converting

Table 2.3 Unit structures of typical types of biodegradable aliphatic polyesters

Chemical structure	Example
 $\left(-O-\overset{\underset{\vert}{R}}{C}H-\overset{\underset{\Vert}{O}}{C}-\right)_n$ Poly(α-hydroxy acid)	R = H Poly(glycolic acid), PGA R = CH_3 Poly(L-lactic acid), PLLA
 $\left(-O-\overset{\underset{\vert}{R}}{C}H-CH_2-\overset{\underset{\Vert}{O}}{C}-\right)_n$ Poly(β-hydroxyalkanoate)	R = CH_3 Poly(hydroxyl butyrate), PHB R = CH_3, C_2H_5 Poly(β-hydroxybutyrate-co-valerate), PHBV
 $\left(-O-(CH_2)x-\overset{\underset{\Vert}{O}}{C}-\right)_n$ Poly(α-hydroxyalkanoate)	X = 5, Poly(ϵ-caprolactone), PCL
 $\left(-O-(CH_2)x-O-\overset{\underset{\Vert}{O}}{C}-(CH_2)y-\overset{\underset{\Vert}{O}}{C}-\right)_n$ Poly(alkylene dicarboxylate)	Poly(ethylene succinate), PES Poly(butylene succinate), PBS Poly(butylene succinate-co-butylene adipate), PBSA

starch into sugar, which is then fermented. By removal of water, lactide is formed which is then converted into PLA resins through solvent-free polymerisation. Current commercial applications include compostable food and lawn waste bags, yoghurt cartons, seeding mats and non-woven mulch to prevent weed growth. Although recently microorganisms or enzymes that can degrade PLA have been reported, the number of carbon atoms between ester bonds in the main chain may be responsible for the major non-enzymatic hydrolytic degradation of poly(α-hydroxy acid).

2.4.2 Poly(β-hydroxyalkanoate)s

PHAs are synthesised biochemically by microbial fermentation, which may be produced in the future by transgenic plants. Poly(β-hydroxybutyrate) (PHB) is a biotechnologically produced polyester that constitutes a carbon reserve in a wide variety of bacteria[5] and has attracted much attention as a biodegradable thermoplastic polyester.[6,7] It can be degraded to water and carbon dioxide under environmental conditions by a variety of bacteria and has much potential for applications of environmentally degradable plastics. However, it suffers from some disadvantages compared with conventional plastics, for example brittleness and a narrow processability window. To improve these properties, various copolymers containing hydroxyalkanoate units other than 3-hydroxybutyrate (3HB) have been biosynthesised. PHB and the copolymer, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), are produced by Monsanto and sold under the trade name Biopol®.

PHBV polymers were first manufactured by ICI in 1983 and were originally intended as biodegradable substitutes for oil-based polyolefins in films, bottles and plastic containers. In 1990 the manufacture of blow-moulded bottles using Biopol® for packaging shampoo was started in Germany by Wella AG, Darmstadt. PHBVs are highly crystalline polymers with melting points and glass transition temperature similar to polypropylene. Owing to characteristics of biodegradability through non-toxic intermediates and easy processability, PHBV polymers are being developed and commercialised as ideal candidates for the substitution of non-biodegradable polymeric materials in commodity application.[8] However, the prohibitive cost, the small difference between thermal degradation and melting temperature and especially the low impact resistance around room temperature and below due to high crystallinity and relatively high glass transition (T_g), have prevented its larger commercial application.

PHB is known to be susceptible to thermal degradation at temperatures close to its melting point. This degradation occurs almost exclusively via a random chain scission mechanism involving a six-membered ring transition state. Lehrle and coworkers[9] have reported that under certain conditions random chain scission cannot be responsible exclusively for the formation of the observed degradation products. In particular, it was shown that primary products are involved in a number of secondary reactions and isomerisations and, indeed, that tetramer is formed principally as a result of such secondary reactions.[10] The 3-hydroxypentanoic acid (trivially known as 3-hydroxyvaleric acid or 3HV) and 3-hydroxybutyrate acid (3HB) of PHBV copolymer can be produced by adding propionic acid to the nutrient feedstock supplied to the bacteria. The copolymer compositions containing up to 30 mol% of 3HV can be produced by controlling the feedstock and the conditions.

Biopol® is also produced commercially by a fermentation process using glucose and propionic acid as carbon sources for the microorganisms. The mole percentage of valerate in the polymer sample is limited by the toxicity of the propionic acid to the microorganisms used, *Alcaligenes eutrophus*. However, polymers with compositions up to 95 mol% 3HV have been obtained by adding controlled mixture of pentanoic acid and butyric acid to the feedstock.[11] The comonomer reduces the crystallinity and also the melting point of the homopolymer. The melting point (T_m) of the copolymer decreases from the calculated 180 °C with increasing 3-hydroxyvalerate content and reaches a minimum value of 75 °C at approximately 40 mol% 3HV. Again, as the 3HV content increases towards pure poly(3-hydroxyvalerate) (3PHV), the melting point increases; thus at 95 mol% 3HV the melting point increases to 108 °C. The impact strength, flexural modulus melting temperature and the rate of crystallisation of PHBV copolymers have been shown to be regulated by the content of 3HV units.[12]

Not only are poly(β-hydroxybutyrate) and the copolymer of 3-hydroxy butyrate with 3-hydroxyvalerate produced by bacteria, but other bacterial polyesters are also available. The occurrence of different hydroxyalkanoic acids reflects the low substrate specificity of polyhydroxyalkanoic acid synthesis, which are the key enzymes of polyhydroxyalkanoic acid biosynthesis. In spite of the excitement of more than different constituents of biosynthetic PHA, the commercial exploitation of this variety remains limited, since few PHA are available in sufficient amounts to allow the evaluation of the physical, chemical and biological material properties of these polyesters. Microbiologists can contribute significantly in the near future to solve this dilemma.

2.4.3 Poly(α-hydroxyalkanoate)

PCL is partially crystalline linear polyester with a low T_g of -60 °C and a low T_m of 60 °C. It is prepared from cyclic ester monomer, lactone, by a ring opening reaction with a catalyst such as stannous octanoate in the presence of an initiator that contains an active hydrogen atom. PCL is a tough and semi-rigid material at room temperature having a modulus between those of low-density polyethylene (LDPE) and high-density polyethylene (HDPE). It has been shown that PCL is degraded by enzymes, lipases, secreted from microorganisms.[13] PCL is compatible with many organic materials and polymers and thus it is used in many polymer formulations as compatibilisers. Its low T_g (high chain flexibility) leads to its use as soft blocks for segmented polyurethanes. Recent findings showed that PCL can provide water resistance in starch-based formulations, which may lead to future application of large quantities of this polymer in this area.

2.4.4 Poly(alkylene dicarboxylate)

This is a type of biodegradable aliphatic polyester, which has been developed by Showa Highpolymer under the trade name ‘Bionolle’. Different grades of Bionolle are:

- polybutylene succinate, PBS (#1000 series);
- poly(butylene succinate-co-butylene adipate), PBSA (#3000 series);
- poly(ethylene succinate), PES (#6000 series).

Bionolle polymers with high molecular weight were invented in 1990 and produced through polycondensation reaction of glycols (such as ethylene glycol and butanediol-1,4) with aliphatic dicarboxylic acids (such as succinic acid and adipic acid and others).[14,15] If higher molecular weight is needed, coupling reaction is carried out with a small amount of coupling agents as chain extenders.[16,17]

Bionolle is a white crystalline thermoplastic with melting point of about 90–120 °C (similar to LDPE), glass transition temperature of about −45 to −10 °C (between PE and polypropylene, PP), density of about 1.25 g/cm^3 (similar to polyethyleneterephthalate, PET), tensile strength between PE and PP, stiffness between LDPE and HDPE and heat of combustion below 6 kcal/g, i.e. about one-half of polyolefins. Bionolle has excellent processability and can be processed on polyolefin processing machines at temperatures of 160–200 °C, into various products such as injected, extruded and blown ones.[18–23] A new grade Bionolle (coded #1900 series), which has a long chain branch, and high recrystallisation rate, has been developed, for use in the preparation of stretched blown bottles and highly expanded bottles as well as foams. The biodegradability of Bionolle polymers depends upon their structures and also the environment in which they are placed. The biodegradability of different grades of Bionolle buried in activated sludges, soils and compost has been studied.[24] As per the findings, Bionolle #3000 showed the best biodegradability in soils, while Bionolle #6000 showed best biodegradability in activated sludges.

2.5 Polyester amides

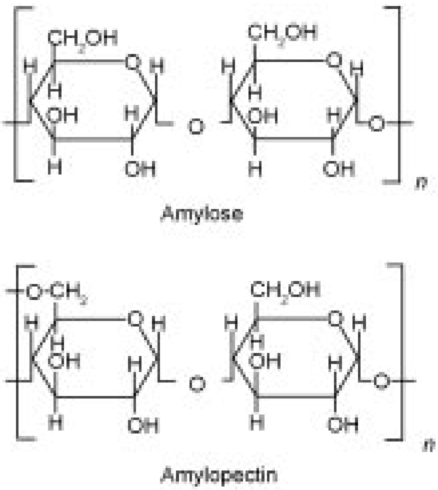
Aliphatic polyester amides have been suggested and recently investigated as a potential family of polymers with good mechanical and thermal properties, as well as processing facilities and susceptibility to degradation.[25] A series of biodegradable aliphatic polyester amides derived from 1,6-hexanediol, glycine and diacids with a variable number of methylene groups has been synthesised and characterised. The synthesis and some physicochemical properties of polyester amides derived from 1,6-hexanediol, sebacic acid and α-amino acid such as glycine, alanine or phenylalanine have been reported. Saotome *et al.*[26] have synthesised a series of polyester amides based on 1,2-ethanediol, adipic acid and an amino acid as glycine, leucine or phenylalanine. The degradation studies with proteolytic enzymes (*chymiotripsine* and *elastase*) indicated that only the polymers containing glycine were not degraded by any of the tested enzymes. They also reported[27] that inclusion of phenylalanine in the glycine-derived polyesteramides enhances their degradability with *chymiotripsine*. Again the decomposition temperatures of such polyester amides were always higher than the corresponding melting temperatures, suggesting that these polymers can be processed from the melt. Enzymatic incubation with *papain* demonstrated the biodegradability of all the polyester amides of the series. In all cases, the polymers showed a high susceptibility to enzymatic degradation.

The German government asked for research and development on biodegradable thermoplastics with good performance and processing behaviour, and in 1990 Bayer presented its first grade of polyester amide (BAK 1095) to the public.[28] During 1997 Bayer launched another grade, BAK 2195. BAK 1095 is based on caprolactam (Nylon 6), butanediol and adipic acid, whereas BAK 2195 is synthesised from adipic acid and hexamethylene diamine (Nylon 6,6) and adipic acid, with butanediol and diethylene glycol as ester components. Since the production process of BAK is solvent- and halogen-free, the polymer is free of halogens, aromatic compounds and toxic heavy metals. Although the processing conditions are similar to polyolefins, the biggest difference being the shape of the granules, the granulation technique is under constant development by Bayer to provide easily processable granules. BAK 1095 has mechanical and thermal properties resembling to those of polyethylene. The resin is also noted for its high toughness and tensile strain at break. It can be processed into film and also into extruded or blow-moulded parts. It is suitable for thermoforming and can be coloured, printed, hot-sealed and welded.

The crystallisation temperature of BAK 1095 is 66 °C and it crystallises relatively slowly, so it is not ideal for injection moulding. BAK 2195 resin is an injection-moulding grade biodegradable thermoplastic that exhibits greater stiffness. This resin has higher melting point (175 °C) than BAK 1095 (m.p. 125 °C) and also higher crystallisation temperature, i.e. 130 °C. The property profile of BAK 2195 can also be extended through the addition of fillers and reinforcing substances, such as starch, natural fibres, wood flour and minerals. The combined performance of both BAK grades and the compounds opens a wide range of applications such as disposable plant pots, agricultural films, biowaste bags, plant clips, cemetery decoration and one-use dishes. BAK 1095 breaks down into water, carbon dioxide and biomass under aerobic conditions. The degradation rate is comparable to that of other organic materials that are composted.

2.6 Starch plastics

Starch is produced in plants and is a mixture of linear amylose (poly-α-1,4-D-glucopyranoside) and branched amylopectin (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside). The amount of amylose and amylopectin varies with the source. The chemical structures of amylose and amylopectin are shown in Fig. 2.2. The exact structure of starch granules is not yet fully understood. Amylose is the minor component of starch ranging from 20 to 30%. The amylopectins are responsible for the crystalline properties of starches. The relative amounts, structures and molar masses of amylose and amylopectin in starches are determined by means of genetic and environmental control during biosynthesis, and hence wide variation occurs among plant raw materials. Corn is the primary source of starch, although potato, wheat and rice starch also have markets in Europe and the United States. Starch is one of the least expensive biodegradable materials available in the world market today. It is a versatile biopolymer with immense potential for use in the non-food industries. Starch converted to



2.2 Structures of amylose and amylopectin.

thermoplastic material (starch plastics) offers an interesting alternative for synthetic polymers where long-term durability is not needed and rapid degradation is an advantage.

The properties and applications of starch and starch plastics have been reviewed recently by Shogren.[29] Starch can be made thermoplastic through destructurisation in the presence of specific amounts of plasticisers (water and/or poly-alcohols) in specific extrusion conditions. Thermoplastic starch products with different viscosity, water solubility and water absorption have been prepared by altering the moisture content, amylose/amylopectin ratio of raw product and the temperature or the pressure in the extruder. Thermoplastic starch alone can be processed as a traditional plastic; however, its sensitivity to humidity makes it unsuitable for many applications. The thermoplastic starch alone is mainly used in soluble foams, such as loose-fillers, expanded trays, shape-moulded parts and expanded layers, as a replacement for polystyrene.

BIOTEC of Germany has conducted promising research and development along the lines of starch-based thermoplastic materials. The company's three product lines are Bioplastm granules for injection moulding, Bioflexm film, and Biopurm foamed starch. Under the Mater-Bi trademark, Novamont of Italy today produces four classes of biodegradable materials. Each class is available in several grades and has been developed to meet the needs of specific applications. The current production capacity of Novamont is 8000 tonnes/year. Mater-Bi can be processed using conventional plastic technologies such as injection moulding, blow moulding, film blowing, foaming, thermoforming and extrusion. The physical-mechanical properties of Mater-Bi are similar to those of conventional plastics such as polyethylene and polystyrene. Mater-Bi is not only recyclable but also as biodegradable as pure cellulose. The biodegradability of Mater-Bi products has been measured according to standard test methods approved by international organisations (ISO, CEN, ASTM). The compostability of some Mater-Bi grades has been certified by the 'Ok Compost' label. Mater-Bi can be used in a wide range of applications such as disposable items.

2.7 Thermoplastic composites

2.7.1 Polyethylene composites

Extensive studies were reported on the effect of incorporation natural fibre in PE matrix. As mentioned earlier, the fibre–matrix adhesion in thermoplastic composites can be improved by using compatibilisers such as maleated ethylene, maleated propylene and a few acrylic-grafted linear polymers. For HDPE/cellulose fibre composites (at 10% and 30% fibre concentration), the best improvement in tensile strength and modulus was achieved with maleated ethylene. The enhancement in the properties was attributed to the coupling reaction (ester linkage) between the maleated ethylene and the hydroxyl group of cellulose. The influence of coupling agents on the mechanical properties of HDPE/wood fibres has also been studied by Raj *et al.*[30] They observed that incorporation of wood fibres in HDPE resulted in an increase in the stiffness and decrease in tensile strength for untreated wood fibres. Treatment of wood fibres with silane coupling agent and polyisocyanate resulted in an increase in tensile strength. They also compared the tensile and impact properties of LLDPE/wood fibre composites with mica and glass fibre composites and have shown that the potential advantage of using wood fibres as reinforcement is in terms of material cost and specific properties.

In 1993, Joseph *et al.*[31] investigated the effect of fibre length, fibre orientation and processing conditions on the tensile properties. They found that the tensile properties of sisal/LDPE composites were sensitive to fibre length, fibre content and fibre orientation. Unidirectional alignment of the fibre enhanced the strength and modulus of the composites along the axis of fibre alignment by more than twice compared to randomly oriented fibre composites. Again Joseph *et al.*[32] reported the effect of chemical treatment on the tensile properties of sisal/polyethylene composites (both randomly and unidirectionally oriented). They analysed the mechanisms of different treatment methods such as alkali treatment, isocyanate treatment, i.e. treating fibre surface with urethane derivative of cardanol (CTDIC), peroxide treatment, i.e. benzoyl peroxide (BP) and permanganate treatment ($KMnO_4$). It appears that the increase in the tensile property values due to these treatments are in the order: CTDIC > BP > $KMnO_4$ > alkali.

Electrical properties of sisal/LDPE have also been studied with respect to the effects of frequency, fibre content and fibre length on the dielectric parameters.[33] Sisal/LDPE composites of 1 mm fibre length and 30 wt% fibre content were found to have the highest values of dielectric constants at all frequencies. The dielectric constant, dielectric loss factor and electrical conductivity of 25 wt% sisal/LDPE can be increased considerably by adding 5% carbon black. The dielectric parameters of LDPE composites reinforced with raw and treated (alkali, stearic acid, benzoyl peroxide, dicumyl peroxide, permanganate, isocyanate and acetylation) sisal fibres have also been studied by Paul *et al.*[34] It is noted that in the case of treated and untreated sisal/LDPE composites, the dielectric constant values were found to decrease following chemical treatments as a consequence of the low sorption of water by the treated fibre. The volume resistivity values for treated sisal/LDPE composites are higher than those for raw sisal fibre/LDPE composites. The volume resistivity values for permanganate-treated sisal/LDPE composites depend upon the concentration of permanganate solution used. The experimental tensile properties of sisal/LDPE composites with different fibre volume fractions have been compared with existing theories of reinforcement such as parallel and series, Hirsch, Cox, Halpin–Tsai, modified Halpin–Tsai and modified Bowyer and Bader models by Kalaprasad *et al.*[35] Also the influence of short glass fibre addition on the mechanical properties of short sisal fibre reinforced LDPE composites has been discussed by Kalaprasad *et al.*[36] They observed that by the addition of a small volume fraction of short glass fibre into the above system enhanced the tensile strength of longitudinally oriented composites by more than 80%. It was also observed that water absorption tendency of the composite decreases with the process of hybridisation.

George *et al.*[37] reported on the processing characteristics, viscoelastic properties and mechanical behaviour of pineapple leaf fibres (PALF)/LDPE composites. The effects of fibre orientation, fibre loading and fibre length on the viscoelastic properties of PALF/LDPE composites have been studied.[37] Longitudinally oriented composites show the maximum value of the storage modulus. Dynamic storage and loss modulus increase with fibre loading and level off beyond 20% due to fibre–fibre interactions. The melt viscosity was found to increase with loading. Various chemical treatments have been made to improve fibre–matrix interfacial adhesion. Treatments based on polymethylene-poly(phenyl isocyanate) (PMPPIC), silane, and peroxide increase the viscosity of the system due to high fibre–matrix interfacial interaction. The water absorption behaviour of PALF/LDPE composites has been investigated[38] with special reference to fibre loading, the nature of the fibre–matrix interface, and temperature. It is found that the uptake of water increases with fibre loading owing to the increased cellulose content. The chemically modified fibre composite exhibits a reduction in water uptake because of better interfacial bonding. The maximum improvement is observed in the case of isocyanate treated composites. A reduction in tensile properties for the composites was observed after immersion in water for different time intervals due to the plasticisation effect of water. Flexural strength and modulus of composite samples after exposure to UV light were studied. In the case of the LDPE alone the decrease in strength and modulus is marginal. Addition of PALF does not have any significant effect on the UV resistance.

The impact performance of chopped bagasse/ethylene vinyl acetate (EVA) composites was evaluated and compared with the behaviour of bagasse filled with PP and PE matrix. The investigation proved that incorporation of bagasse strongly reduces the deformation capacity of EVA polymers. The impact strength was independent of the bagasse size, but varied with the volume fraction.[39]

2.7.2 Polypropylene composites

Similar to PE, PP is widely used as a matrix for composite fabrication. In the last few decades, detailed investigation has been undertaken on the successful use of PP as matrix for composites. Arib *et al.*[40] investigated the tensile and flexural behaviours of pineapple leaf fibre/PP composites as a function of volume fraction. They found that tensile strength and modulus increase as a function of fibre content. Albano *et al.*[41] studied the effect of acetylated and non-acetylated sisal fibre on the thermal degradation of blends of PP and polyolefins, specifically: PP/HDPE, PP/HDPE/functionalised ethylene propylene rubber (EPR), and PP/HDPE/non-functionalised EPR. The studies showed that the starting temperature of the decomposition of the fibre, whether treated or not, is maintained at almost at the same level. When PP and PP/HDPE and PP/HDPE/functionalised and non-functionalised EPR blends were mixed with treated and non-treated sisal fibre, a sudden decrease in activation energy was observed. This can be explained because mixing acetylated fibre with polymer results in high polymer–filler interaction, which favours the thermal stability of the compounds.

To prepare sisal/PP composites Joseph *et al.*[42] optimised mixing parameters by varying the mixing time, rotor speed and chamber temperature. Under optimum mixing conditions melt-mixed composites showed better tensile properties than those of solution-mixed composites. The fibre breakage and damage during melt mixing were analysed from fibre length distribution curves and optical photomicrographs. Treatments with chemicals such as sodium hydroxide, maleic anhydride and permanganate were carried out to improve the bonding at the fibre–polymer interface.[43] A large amount of fibre breakage was observed during melt mixing of sisal fibres used for the reinforcement of a polypropylene. The dynamic mechanical properties of short sisal/PP composites containing both untreated and treated fibres have also been studied by Joseph *et al.*[44] with reference to fibre loading, fibre length, chemical treatments, frequency and temperature. The incorporation of short sisal fibre into PP increased the storage modulus and loss modulus but the mechanical loss factor decreased. The treated fibre composites show better properties than an untreated system. Selzer[45] studied the effect of environmental influences on the mechanical properties of sisal fibre reinforced polymer composites. Dependencies between moisture, acid as well as alkali attacks were determined and mechanical properties of sisal/PP composites were evaluated. They concluded that the bending properties of sisal/PP composites were sensitive to environmental attack. Le Thi *et al.*[46] reported that the grafting of the fibres by PP-g-maleic anhydride (MA) enhanced both the impact strength and the breaking stress of the composites.

Rana *et al.*[47] observed an increase in impact strength of jute/PP composites as a function of fibre loading. They also found that both impact and tensile properties showed increasing trend with the compatibiliser but the reverse was true for the flexural properties. The influence of the fibre–matrix adhesion in jute/PP on the material's behaviour under fatigue and impact loadings was investigated by Gassan and Bledzki.[48] It was shown that a strong interface is connected with a higher dynamic modulus and reduction in stiffness degradation with increasing load cycles and applied maximum stresses. The specific damping capacity resulted in higher values for the composites with poor bonded fibres. Furthermore, the stronger fibre–matrix adhesion reduced the loss-energy by non-penetration impact tested composites by roughly 30%. The microstructure and mechanical properties of polypropylene composites containing flax and wheat straw fibres were discussed by Hornsby *et al.*[49] Compared with unfilled PP, addition of flax and wheat straw caused a significant increase in tensile modulus, particularly, in the case of flax fibres, which also gave higher tensile yield strength and charpy toughness, despite a lack of interfacial bonding. Tensile strength was increased further through inclusion of 5% by weight of maleic anhydride-modified PP, which was shown to promote adhesion between fibres and matrix

A new type of bamboo/PP composite was prepared by Chen *et al.*[50] and its mechanical properties were tested. The tensile modulus, tensile strength and impact strength were all increased significantly by the addition of MA-g-PP. Oil palm empty fruit bunch (OPEFB)-filled PP composites were produced by Rozman *et al.*[51] The OPEFB filler was chemically modified with MA. The effects of the filler size and chemical modification of OPEFBs on the tensile and dimensional stability properties of OPEFB/PP composites were studied. The composites with MA-treated OPEFBs showed higher tensile strength than the untreated ones. The MA-treated PP (MAPP) composites showed lower water absorption and thickness swelling than those with untreated OPEFBs. A systematic study of the effect of surface treatments on the properties of PP/cellulose fibre has been carried out by Bataille and his group.[52] The results indicated an increase in modulus with increase in the fibre content. The addition of coupling agents and/or MAPP improved the interfacial adhesion, thereby leading to improved properties. Sain *et al.*[53] reported that the use of bismaleimide modification for improving the properties of PP/wood fibre composites. Wright and Mathias[54] reported synergistic reinforcement of balsa wood composites using ethyl-α-(hydroxyl methyl)acrylate (EHMA) and styrene.

The significant improvements in the properties were ascribed to the strong interaction between the fibre and the matrix polymer, as confirmed by solid-state nuclear magnetic resonance (NMR) and scanning electron microscopy (SEM). The composite also exhibited improved dimensional stability.

2.7.3 Polystyrene composites

Nowadays the production of PS, which has low cost, good mouldability, excellent colour range, transparency, rigidity and low water absorption, is much faster. Its unacceptably brittle nature has led the current research field to create PS with more improved properties. Only limited studies were reported regarding the usage of PS as matrix for natural fibres. The thermal behaviour of PS composites reinforced with short sisal fibres was studied by Nair *et al.*[55] by means of thermogravimetric and dynamic mechanical analysis (DMA). The thermal stability of the composites was found to be higher than that of sisal fibre and the PS matrix. The effects of fibre loading, fibre length, fibre orientation and fibre modification on the dynamic mechanical properties of the composites were evaluated. Fibre modifications were carried out by benzoylation, PS MA coating and acetylation of the fibre and the treatments improved the fibre–matrix adhesion. PS/sisal composites are thermally more stable than unreinforced PS and sisal fibre. The T_g values of the composites are lower than that of unreinforced PS and may be attributed to the presence of some residual solvents in the composites entrapped during the composite preparation.

2.8 Thermosetting composites

Thermoset resins are brittle at room temperature and have low fracture toughness values and also, owing to the crosslinking thermoset, cannot be reshaped. The most frequently used thermosetting resins in high-performance advanced composites are the phenolic, epoxies, etc. These resins exhibit both excellent solvent and high temperature resistance. Compression moulding is the most widely accepted and convenient method to make these composites, whether the fibre is long or short. The mechanical properties of this kind of composites have been obtained by various authors.

2.8.1 Natural-fibre/polyester composites

Various workers have reported on the successful usage of natural fibre into thermosetting plastics. Sanadi *et al.*[56] showed that tensile strength and elastic modulus of the composites containing up to 40% fibre volume fraction (V_f) increase linearly with V_f and is in good agreement with the rule of mixtures. The work of fracture, as determined by Izod impact test, also increases linearly with V_f. Analysis of the energy absorption mechanisms during impact fracture shows that fibre pull-out and interface fracture are the major contributors to the high toughness of these composites. Satyanarayana *et al.*[57] studied the mechanical properties of chopped sisal/polyester composites prepared by the compression moulding technique. It was found that the specific modulus of the composite was 1.90 compared with 2.71 for glass fibre reinforced plastics, while the specific strength was of the same order as that of polyester resins (34–41 MPa). The impact strength was 30 J/m^2, which is three times higher than that of polyester and 30% less than glass fibre reinforced plastics. Later, Pavithran *et al.*[58] reported the impact properties of sisal/polyester composites and compared the work of fracture of these composites with those of other natural-fibre-containing composites. It can be seen that sisal fibre composites have the maximum work of fracture followed by pineapple leaf fibre composite. They also studied the variation in impact properties of various natural-fibre composites with microfibrillar angle of the fibre and compared the impact properties of unidirectionally oriented sisal/polyester composites with those of composites having ultra-high-density polyethylene (UHDPE) and glass fibres.

Joseph *et al.*[59] observed that in all the composites (sisal fibre reinforced polymer composites of several thermoset resin matrices such as polyester, epoxy, phenol formaldehyde (PF) and in LDPE) the mechanical and fracture behaviour increases as a function of fibre loading. However, the optimum length of the fibre required to obtain an increase in properties varied with the type of matrix. It was observed that among polyester, epoxy and PF composites of sisal fibre, a phenolic-type resin performed as a better matrix than epoxy and polyester resins with respect to tensile and flexural properties due to the high interfacial bonding in phenolic composites. Singh *et al.*[60] studied the effect of several chemical treatments, such as organotitanate, zirconate, silane and *N*-substituted methacrylamide, on the physical and mechanical properties of sisal/polyester composites. Gupta *et al.*[61] analysed the nature of interfacial adhesion between chemically modified sisal/polyester composites.

The effect of fibre pretreatment and water absorption on the impact properties of sisal fibre reinforced polyester and epoxy matrices was studied by Rong *et al.*[62,63] They indicated that fibre surface treatment has a strong effect on the impact behaviour of composites and the effects are different for different matrices. It is observed that fibre pull-out is the major contributor to the energy absorption. Hill and Abdul Khalil[64] determined the effect of environmental exposure on the properties of polyester matrix composites reinforced with acetylated coir fibres and oil palm empty fruit bunch fibres. A comparison of properties was made with silane and titanate-treated fibre composites. It was seen that water sorption was substantially reduced and structural integrity maintained in contrast to composites in which no fibre treatment was used. Silane treatment of fibres was also found to give good protection to composites. Titanate treatment was not found to be as effective as silane. Rout *et al.*[65] investigated the effect of the addition of surface-modified coir fibres on the mechanical properties of polyester. Significant improvement in tensile properties was observed in the case of alkali-treated composites whereas better flexural strength was observed in the case of bleached coir/polyester composites.

The mechanical property of jute fabric reinforced polyester composite was studied by Gowda *et al.*[66] The composites were found to have better strength than wood composites, though not as high as conventional composites. The lowering of the tensile strength up to 25% indicates their susceptibility water absorption and shear failure. Zhu *et al.*[67] carried out the studies of banana fibre strands reinforced polyester composites and reported that the fracture toughness of composites was about 1.6 times greater than polyester matrix. Also, when the fibre length is continuous and at sufficiently high content, the banana fibre is seen to act as good reinforcement in polyester matrix.

The effect of hybridisation in polyester composites has been studied. The impact performance of sisal/glass polyester composite was improved by using glass core sisal shell laminates instead of sisal core glass shell laminates. Mishra *et al.*[68] found a quality enhancement of PALF through different surface modifications such as dewaxing, alkali treatment, cyanoethylation and grafting of acrylonitrile on to dewaxed PALF. The best improvement in tensile strength was observed in the case of 10% acrylonitrile grafted PALF. Aquino *et al.*[69] studied the mechanical properties of pissava fibre/resin matrix composites. The use of pissava fibres as reinforcement in resin matrix composite materials was found to be very promising. They suggested that modified interphase prevents fibre/fibre contacts, hence removing the source of high stress concentration in the final composite.

Recently alkalised long/random hemp and kenaf fibre in polyester resin has been developed.[70] The authors used the hot press method to form composites. A general trend was observed whereby alkalised and long fibre composites gave higher flexural modulus and flexural strength compared with composites made from as-received fibres. Alkalised long kenaf/polyester composites possessed superior mechanical properties to alkalised long hemp/polyester composites. For the hemp/polyester composites a high flexural modulus and a high flexural strength are associated with a low work of fracture. Mishra *et al.*[71] showed that addition of relatively small amount of glass fibre to the PALF and sisal/polyester matrix enhanced the mechanical properties of the resulting hybrid composites. Different chemically modified sisal fibres have been used in addition to glass fibres as reinforcements in polyester matrix to enhance the mechanical properties of the resulting hybrid composites. The surface modification of sisal fibres such as alkali treatment produced optimum tensile and impact strengths, while cyanoethylation resulted in the maximum increase in flexural strength of the hybrid composites. It has been observed that water uptakes of hybrid composites are less than that of unhybridised composites. A brief review on other recent works regarding short natural fibre reinforced polyester composites are given in Table 2.4.[66,72–87]

Table 2.4 Recent works on natural-fibre reinforced polyester composite

System	Treatment	Measurements	Result	Ref
Banana/polyester	Silane	Polarimetry study/DMA	The overall polarity is found to be maximum for fibres treated with the silane A151. Modification affected the dynamic mechanical properties and T_g is shifted towards higher temperature	72
PALF/polyester	Untreated, mercerisation	Mechanical property	Increased as fibre content, treatment	73
Jute fabric/ polyester	Untreated	Mechanical property	The composites are a good substitute for wood in indoor applications	66
Jute fibre/ polyester	Untreated	Mechanical property	Dependent on the secondary chemical bonding between jute fibre and polyester	74
Polyester/wood flour	Untreated, mercerisation	Mechanical property	Increased as fibre treatment	75
Bagasse/aliphatic polyester	Mercerisation	Mechanical property	Increased up to an fibre content of 65 vol%, treatment increased mechanical property	76
Date palm/ polyester	Untreated, mercerisation	Mechanical property Water absorption	Mechanical property increased, treatment decreased water absorption	77
Hemp/jute fibre/ polyester	Untreated non-woven	Fracture toughness	Provided a more quantitative assessment of the relative toughness of bast fibre reinforced unsaturated polyester laminates	78
Sisal/polyester	Dewaxing, mercerisation, vinyl monomer grafting, bleaching	Mechanical property	Increased after every treatment	79
Banana/sisal/ polyester	Hybrid effect	Mechanical properties	A positive hybrid effect is observed in the flexural properties. The tensile strength is found to be increased when the volume fraction of banana is increased. A negative effect is observed for impact properties	80

Table 2.4 Continued

System	Treatment	Measurements	Result	Ref
Banana/polyester	Random untreated	DMA	Storage modulus, loss modulus and dissipation factor varies as temperature, fibre load and frequency	81
Jute/polyester	Bleaching	Mechanical DMA	Mechanical properties are very high. Dynamic, storage modulus is exceptionally high	82
Banana/sisal/polyester	Layering pattern	DMA	Bilayer composite showed higher damping property while intimately mixed and banana/sisal/banana composites showed increased stiffness compared to the other pattern	83
Banana/polyester	Mercerisation Silane	DMA	Storage modulus, loss modulus and dissipation factor varies as temperature, fibre load and frequency	84
Kenaf/polyester	Modification of polyester Mercerisation	Mechanical Thermal DMA	Modification of polyester affected the mechanical and dynamic properties	85
Hemp/sisal/jute/kapok	Mercerisation Acetylation	Mechanical Differential scanning calorimetry (DSC) X-ray diffraction (XRD)	Effectively changes the surface topography of the fibres and their crystallographic structure	86
Flax/polyester	Influence of flax processing parameters	Mechanical properties	Processing of the fibres has an influence on their performance. Treatment improved mechanical properties	87

2.8.2 Natural-fibre/phenol formaldehyde composites

Phenolic resins show superior fire resistance to other thermosetting resins. They also have considerably lower cost than many other high-performance resins. Because of these advantages, several investigations have used PF as a matrix for the composite fabrication. Sreekala *et al.*[88] investigated the use of surface modification of oil palm fibres as reinforcement in PF resin. The fibres were subjected to different chemical modifications such as mercerisation, acrylonitrile grafting, acrylation, latex coating, permanganate treatment, acetylation and peroxide treatment. They came to a conclusion that treatment of fibre changes in stress–strain characteristics, tensile strength, tensile modulus and elongation at break of the composites. The incorporation of the modified fibres resulted in composites having excellent impact resistance. Fibre coating enhanced the impact strength of untreated composite by a factor of four. A brief review on other recent works regarding short natural-fibre-reinforced PF composites is given in Table 2.5.[89–93]

2.8.3 Natural-fibre/epoxy composites

Epoxies have good adhesion, mechanical properties, low moisture absorption, chemical resistance, little shrinkage and ease of processing. These excellent properties make this family of compounds one of the best matrix materials for many composites. Paramasivam and Abdulkalam[94] investigated the feasibility of developing polymer-based composites using sisal fibres due to the low cost of production of composites and amenability of these fibres to winding, laminating and other fabrication processes. The tensile strength of sisal/epoxy composites was found to be 250–300 MPa, which was nearly half the strength of fibre glass/epoxy composites of the same composition. Because of the low density of the sisal fibre, however, the specific strength of sisal composites was comparable to that of glass composites. The unidirectional modulus of sisal/epoxy composites was found to be about 8.5 GPa. Recently Bai *et al.*[95] studied the failure mechanisms of continuous sisal/epoxy composites. They examined the microfailure behaviour and interfacial debonding of composites using SEM after four-point bend tests. It was reported that the sisal fibre bundle–epoxy interface had a moderate high strength, but the adhesive strength between the microtubular fibre and the bonding material appeared to be small. An improvement in the mechanical properties of alkalised jute fibre reinforced epoxy composites was observed by Gassan and Bledzki.[96] By this process, shrinkage of the fibres during treatment had significant effects on fibre structure and, as a result, on the mechanical properties of the fibres. Regarding fibre–matrix adhesion, the rougher surface morphology after NaOH treatment did not lead to any improvement but the composite strength and stiffness generally increased. The Young's modulus of the composites was linearly dependent on fibre content for both

Table 2.5 Recent works on natural-fibre reinforced phenol formaldehyde composite

System	Treatment	Measurements	Result	Ref
Banana/glass/PF	Untreated	Comparison of mechanical properties	Banana/PF composites exhibit superior mechanical properties, which can be compared with synthetic fibres like glass in terms of specific properties	89
Oil palm/glass/PF	Untreated Hybrid	Comparison of mechanical properties	Overall performance of the composites was improved by the glass fibre addition	90
Oil palm/glass/PF	Fibre content Hybrid fibre ratio	DMA	Incorporation of oil palm fibre shifts the T_g towards lower temperature. The T_g of hybrid composites is lower. The highest value of mechanical damping is observed in hybrid composite	91
Banana/sisal/hemp/ Novalac resin	Maleic anhydride	Mechanical Water absorption	Mechanical property increases. Treatment decreases water absorption	92
Jute/cotton/phenolic	Fibre orientation, roving/fabric characteristics	Mechanical DMA	Properties dependent on fibre orientation, content, adhesion and fabric characteristics	93

untreated and treated fibre composites. Furthermore, the use of treated fibres and of higher fibre contents, both led to a decrease in fatigue behaviour and progress in damage in the composites. Impact damping was distinctly affected by the shrinkage state of the fibres during the NaOH treatment because of its influence on yarn toughness.

The effect of fibre treatment on the mechanical properties of unidirectional sisal/epoxy composites was reported by Rong *et al.*[97] Treatments, including alkalisation, acetylation, cyanoethylation, the use of silane coupling agent, and heating, were carried out to modify the fibre surface and its internal structure. When the treated fibres were incorporated into an epoxy matrix, mechanical characterisation of the laminates revealed the importance of two types of interface: one between fibre bundles and the matrix and the other between the ultimate cells. In general, fibre treatments can significantly improve adhesion at the former interface and also lead to ingress of the matrix resin into the fibres, obstructing pull-out of the cells. In a novel work, Oksman *et al.*[98] studied the longitudinal stiffness and strength as well as morphology of unidirectional sisal/epoxy composites manufactured by resin transfer moulding (RTM). Horseshoe-shaped sisal fibre bundles were non-uniformly distributed in the matrix. In contrast to many wood composites, the lumen was not filled by polymer matrix. Technical sisal fibres showed higher effective modulus when included in the composite material than in the technical fibre. Ganan *et al.*[99] evaluated the mechanical and thermal properties of sisal/epoxy matrix composites as a function of modification of sisal fibre by using mercerisation and silane treatments. Both treatments clearly enhanced thermal performance and also mechanical properties of fibres. Mercerisation, above all when combined with silanisation, led to significant enhancement on mechanical properties of composites. A brief review on other recent works regarding short natural-fibre reinforced epoxy composites is given in Table 2.6.[100–107]

2.8.4 Natural-fibre/vinyl ester composites

Ray *et al.*[108] subjected jute fibres to alkali treatment with 5% NaOH solution for 0, 2, 4, 6 and 8 h at 30 °C. The modulus of the jute fibres improved by 12, 68 and 79% after 4, 6 and 8 h of treatment, respectively. The tenacity of the fibres improved by 46% after 6 and 8 h treatment and the percentage breaking strain was reduced by 23% after 8 h treatment. For 35% composites with fibres treated for 4 h, the flexural strength improved from 199.1 to 238.9 MPa (by 20%), modulus improved from 11.89 to 14.69 GPa (by 23%) and laminar shear strength increased from 0.238 to 0.283 MPa (by 19%). On plotting different values of slopes obtained from the rates of improvement of flexural strength and modulus, against NaOH treatment time, two different failure modes were apparent before and after 4 h of NaOH treatment. In the first region between 0 and 4 h, fibre pull-out was predominant, whereas in the second region between 6 and 8 h,

Table 2.6 Recent works on natural-fibre reinforced epoxy composite

System	Treatment	Measurements	Result	Ref
Sisal/epoxy	Silane Mercerisation	Mechanical property Water absorption	Improved wettability, mechanical properties and water resistance	100
Banana/epoxy	Woven form	Flexural strength	Depends upon fibre architecture	101
Hemp/flax fibre/ epoxy/phenolic resin	6 M urea 50% Polyvinyl alcohol solution	Mechanical property	Increased the stiffness Improved the stiffness and strength	102
Hildegardia/epoxy/ 10% polycarbonate	Mercerisation	Flexural properties	Flexural properties increase	103
Hildegardia populifolia/ polycarbonate toughened epoxy resin	Fabric content Orientation of the fibres Mercerisation Silane	Mechanical	The tensile properties improved with fabric content but decreased with an increase in the orientation angle	104
Oil palm fibre/ epoxy	Untreated	Fatigue behaviour	Increasing in fatigue resistance as the stress ratio increased	105
Sisal/vinyl sisal/epoxy (textile)	Silane/permanganate treatment	Fracture toughness	Fibre surface treatments can improve the fracture toughness	106
Jute/epoxy unidirectional	Mercerisation	Mechanical and processing methods	Mild, batchwise treatments result in the increase of both longitudinal and transverse properties. Treatment also increased the mechanical property	107

transverse fracture occurred with minimum fibre pull-out. In another investigation by Ray *et al.*[109] by dynamic mechanical analysis proved that mercerisation of the jute fibre increases the fibre–matrix adhesion thereby increasing the storage modulus of the composites.

2.9 Biofibre–rubber composites

A short fibre rubber composite can be defined as a compounded rubber matrix containing discontinuous fibres that are distributed within the rubber to form a reinforcement phase. Incorporation of fibres combines the elastic behaviour of rubber with the strength and stiffness of the reinforcing fibre. Short fibres are also used to improve or modify certain thermodynamic properties of the rubber for specific applications or to reduce the cost of the fabricated articles. The addition of short fibres in rubber imparts increased strength and stiffness to the matrices. The primary effects of biofibre reinforcement on the mechanical properties of natural rubber composites include increased modulus, increased strength with good bonding at high fibre concentrations, decreased elongation at failure, improved creep resistance, increased hardness and a substantial improvement in cut, tear and puncture resistance. Natural rubber is a very strong matrix because of its strain-induced crystallisation. Generally it has been seen that the tensile strength initially drops to a certain amount of fibre and then increases. The critical volume of fibre varies the fibre aspect ratio and fibre–matrix interfacial adhesion. At low fibre concentrations, the fibre acts as a flaw in the rubber matrix and the matrix is not restrained by enough fibres, causing highly localised strains to occur in the matrix at low stress. This makes the bond between fibre and rubber break, leaving the matrix diluted by non-reinforcing debonded fibres. As the fibre concentration increases, the stress is more evenly distributed and the strength of composite increases. The incorporation of fibre into the rubber matrix increases the hardness of the composite, which is related to strength and toughness. The close packing of fibres in the compounds increases the density while resilience decreases.

Rubber is the second most widely used matrix for sisal fibre composites behind PE. The main research areas are concerned with the effect of fibre length, orientation, loading, type of bonding agent and fibre–matrix interaction on the properties of composites, which include mechanical properties, rheological behaviour, thermal ageing, γ-irradiation and ozone resistance. Experimental results show that for best balance of properties, the fibre length is about 6 mm. This is the same as the sisal/PP composites. Orientation effects are as expected. The efficiency of sisal as reinforcement in rubber matrices is achieved by modifying the surface topology of sisal fibre by suitable chemical treatment or by selecting a bonding system. It has been observed that 18% mercerisation treatment of sisal fibre enhanced the bonding of fibre with the rubber matrix.[110–113] Interfacial adhesion between sisal and styrene-butadiene rubber (SBR) has been improved by hydration, mercerisation, acetylation, benzoylation, PS-MA treatment of sisal fibres, and by incorporation of resorcinol hexamine bonding system. The mechanical properties increase upon various chemical treatments that are in the order: PS-MA coating < mercerisation < acetylation < benzoylation. Varghese *et al.*[112] studied the effect of acetylation and bonding agent on the ageing properties of sisal fibre reinforced natural rubber composites, which included thermal ageing, γ-radiation and ozone resistance. High fibre-volume fraction showed better resistance to ageing, especially with fibre surface treatment. Increasing the dosage of gamma radiation was found to increase the extent of the ageing process.

The rheological behaviour of short sisal fibre reinforced SBR composite has been reported by Kumar *et al.*[114] The effects of shear rate, fibre loading, temperature and the extent of interface bonding on the viscosity of the system have been examined. All the system showed pseudoplastic behaviour, leading to the decrease of viscosity with increasing shear rate. The incorporation of treated fibres increased the melt viscosity and, of the various chemical treatments, the benzoylated fibre reinforced composite showed maximum viscosity. The relative viscosity of the composites was also found to increase with an increase of the fibre loading. The reinforcement of coir fibre in natural rubber has been extensively studied by Geethamma *et al.*[115] Upon incorporation of coir fibre, it was seen that the tensile strength decreased sharply with increase in fibre loading up to 30 parts per hundred of resin (phr) and then showed a slight increase for composites containing 40 and 60 phr fibre loading. This trend was observed in both longitudinal and transverse directions. The extent of coir fibre orientation from green strength measurements was determined. It was observed that orientation was lowest when fibre loading was small and increased with loading. Maximum orientation was observed at 30 phr loading.

The effect of fibre concentration and modification of fibre surface in oil palm fibre reinforced rubber composites on the mechanical properties was investigated by Ismail *et al.*[116] They observed the general trend of reduction in tensile and tear strength with increasing fibre concentration. SEM studies showed that for rubber composites filled with untreated fibre, the adhesion between the fibre and matrix is poor, while for treated fibre improved adhesion between the fibre and rubber matrix is evident. In another work Ismail *et al.*[117] studied the fatigue and hysteresis behaviour of oil palm wood flour (OPWF) filled natural rubber composites. The stress at any strain decreased with increasing OPWF loading in the composites. As the filler loading increased, the poor wetting of the OPWF by the rubber matrix gave rise to poor interfacial adhesion between the filler and rubber matrix. Results also indicate that the composite with the highest loading of OPWF was the most sensitive towards changes in strain energy, and hence exhibited the highest hysteresis. Thermal ageing not only reduced the fatigue life, but also increased the hysteresis of the composites.

In an interesting study, researchers have used a novel fibre – isora fibre in natural rubber.[118] Isora fibres are present in the bark of the *Helicteres isora* plant and are separated by the retting process. The effects of different chemical treatments, including mercerisation, acetylation, benzoylation and treatment with toluene diisocyanate and silane coupling agents, on isora fibre properties and mechanical properties were analysed. Isora fibre was seen to have immense potential as reinforcement in natural rubber.

Researchers have also designed novel rubber biocomposites by using a combination of leaf and fruit fibre in natural rubber.[119] The incorporation of sisal and coir fibre in natural rubber was seen to increase the dielectric constant of the composites. These hybrid biocomposites were found to have enormous applications as antistatic agents. In an innovative study, a unique combination of sisal and oil palm fibres in natural rubber has been utilised to design hybrid biocomposites. It was seen that the incorporation of fibres resulted in increased modulus.[120] Chemical modification of both sisal and oil palm fibres was imperative for increased interfacial adhesion, which resulted in enhanced properties. Viscoelastic, water sorption, dielectric and stress relaxation characteristics were also studied.[121,122]

Da Costa *et al.*[123] incorporated rice husk ash into natural rubber, and curing was done using a conventional vulcanisation system. Physical testing of the natural rubber vulcanisates involved the determination of tensile, tear, and abrasion resistances, and hardness. Fourier transform infrared (FTIR) analysis was done to verify the presence of the characteristic functional groups of precipitated silica in MHA (milled husk ash) and THA (treated husk ash). The effect of the coupling agent, bis(3-triethoxysilylpropyl)-tetrasulphane (Si-69), on the curing and physical properties of the vulcanisates was investigated. For comparison, two commercial fillers, precipitated silica (Zeosil-175) and carbon black (N774), were also used. Although the presence of the silane-coupling agent did not bring the expected increase in properties, treated husk ash showed exceptional performance in terms of tensile strength and abrasion resistance of the filled vulcanisates.

Many researchers have examined the dynamic mechanical behaviour of fibre reinforced polymeric composites.[121,124–130] Jacob *et al.*[121] studied the dynamic behaviour of sisal/oil palm hybrid fibre reinforced natural rubber composites. The storage modulus was found to increase with weight fraction of fibre. In the case of chemically modified fibres, storage modulus and loss modulus were found to vary as a function of the fibre surface modification. The viscoelastic properties of short coir fibre reinforced natural rubber composites was investigated by Geethamma *et al.*[124] It was found that composite with poor interfacial bonding tend to dissipate more energy than that with good interfacial bonding. DMA of soy protein reinforced SBR composites was performed by Jong.[125] The addition of soy protein to the rubber composites generated a significant effect. The physicomechanical properties of α-cellulose filled SBR composites have been studied by Haghighat *et al.*[126] Martins and Mattoso[127] reported the viscoelastic characteristics of sisal fibre reinforced tyre rubber composites. They showed that mercerisation/acetylation treatment increases dynamic mechanical properties. The results showed that these composites are potential for non-structural applications. The DMA of fly ash filled natural rubber modified with cardanol derivatives were studied by Menon *et al.*[128] The stabilising effect of lignin filler on natural rubber was examined by Kosikova *et al.*[129] using DMA. It is observed that the dynamic mechanical properties of natural rubber vulcanisates were considerably improved by the addition of lignin. Mechanical and dynamic mechanical properties of rice husk ash filled natural rubber compounds were studied by Da Costa *et al.*[130] The T_g values of filled rubber vulcanisates shifted to higher temperatures, showing the presence of crosslinks, which restrict the mobility of polymer chains. The interactions between fillers and rubber phase also account for the higher mechanical and dynamic mechanical properties.

2.10 Biodegradable composites

As growing environmental concerns are making plastics a target of criticism owing to their lack of degradability, biodegradable polymers are considered an eco-friendly option to manage waste. They constitute a loosely defined family of polymers that are designed to degrade through the action of living organisms. They offer a possible alternative to traditional non-biodegradable polymers whose recycling is impractical or uneconomical. The problem of solid waste disposal in a context where land availability for the purpose is limited, the litter problem and the pollution of the marine environment are becoming matters of concern for developing countries as well as industrialised countries. As a result, interest in biodegradable plastics is being revived by new technologies developed by major players such as Bayer, DuPont and Dow Cargill. But the main hindrance to the growth of biodegradable plastics is performance limitation and also high cost. The real challenge of biodegradable polymers lies in finding more applications in order to achieve economies of scale. Research efforts are currently being harnessed in developing a new class of fully biodegradable 'green' composites by combining (natural/bio) fibres with biodegradable resins. The major attractions of green composites are that they are environmentally friendly, fully degradable and sustainable; that is, they are truly 'green'. After use they can be easily disposed of or composted without harming the environment. Green composites may be used effectively in many applications such as in mass-produced consumer products with short life cycles or products intended for one-off or short-term use before disposal. Green composites may also be used for indoor applications with a useful life of several years. Starch and modified resins have also been used as the matrix to form green composites. The reinforcement of biofibres in green composites has been highlighted by Bismarck *et al.*[2]

Researchers have also developed green composites using jute fabric as reinforcement in Biopol® matrix.[131] Chemical modification of the fabric was carried out to improve interfacial properties. The characterisation of biodegradation in flax and cotton fibre-reinforced biodegradable polyester amide composites was investigated by Jiang and Hinrichsen.[132] It was seen that after a microbiological induction period of 3 days, all the investigated samples showed a certain biodegradation, although with different degradation rates. In another study, biocomposites[133] were fabricated using a non-woven fibre mat (90% hemp fibre with 10% thermoplastic polyester binder) as reinforcement, and unsaturated polyester (UPE) resin as well as blends of UPE and functionalised vegetable oils as the polymer matrix having a fibre content of 30 vol%. The structure–property relationships of this system as well as the thermomechanical properties of these composites were measured. The notched Izod impact strength of biocomposites from bio-based resin blends of UPE and functionalised vegetable oil and industrial hemp fibre mat were enhanced by 90% as compared with that of the pure UPE–industrial hemp fibre mat composites. The tests also showed an improvement in the tensile properties of the composite. The biodegradability of wood-fibre reinforced Biopol composites was investigated by Peterson *et al.*[134] A significant finding was that the wood fibre–Biopol composites were highly biodegradable, often degrading faster than pure Biopol specimens. The results suggest that an optimum mass fraction of wood fibres exist for maximising degradation and this appears to be around 15%. The authors are also of the opinion that the wood fibres act as conduits for bacteria, thus enabling greater access and improved degradation rates.

In an interesting study, the usefulness of lignocellulosic waste flours, i.e. spruce, olive husk and paper flours, as a source of filler for the preparation of cost-effective and biodegradable polymer matrix composites was studied by Tserki *et al.*[135] The biodegradable polyester Bionolle 3020 was used as matrix. Surface treatment, acetylation and propionylation, and the addition of MA-grafted Bionolle as compatibiliser were done in order to promote the interfacial adhesion of waste flour/matrix. Tserki *et al.* observed that compatibiliser addition resulted in materials with improved mechanical properties, while flour treatment with acetic and propionic anhydride significantly reduced material water uptake. In addition, waste flour incorporation into the polymeric matrix was found to increase the biodegradation rate. The same trend was also observed by Tserki *et al.*[136] in flax, hemp and wood reinforced Bionolle 3020 composites. Zini *et al.*[137] used flax fibres as reinforcing agents for biodegradable polyesters (Bionolle and poly(lactic acid) plasticised with 15 wt% of acetyltributyl citrate, *p*-PLLA). It was also seen that the fibre surface chemistry must be suitably modified to strengthen the fibre–matrix interface.

In an innovative piece of research, commercial L-polylactide was first converted to film and then used in combination with jute fibre mats to generate biodegradable composites by a film stacking technique.[138] Degradation of the polylactide during the process was investigated using size exclusion chromatography. The tensile properties of composites produced at temperatures in the

180–220 ºC range were significantly higher than those of polylactide alone. Size exclusion chromatography revealed that only minor changes in the molecular weight distribution of the polylactide occurred during the process. In an innovative study, novel biodegradable films were fabricated from chitosan and PLA by Sébastien *et al.*[139] It was found that composite films offered a great advantage in preventing the surface growth of mycotoxinogen stains because of their antifungal activity. However, the physicochemical properties of such heterogeneous films dramatically limit their further use as packaging material. The crystallisation behaviour of composites based on PLA and different cellulose reinforcements, viz. microcrystalline cellulose, cellulose fibres and wood flour, has been reported by Mathew *et al.*[140] The effect of these reinforcements on the crystallisation of PLA was studied. The effectiveness of natural fibre as reinforcement for PLA was studied by Oksman *et al.*[141] Flax fibres were used as reinforcement and composites were prepared using a twin-screw extruder followed by compression moulding. Preliminary results showed that properties of PLA and flax fibre composites are promising.[142] Prior to composite manufacturing, the flax fibres were extracted with NaOH and acetone to remove lignin, pectin and waxes from the cellulose. Surface wetting, as well as the morphology of the fibres, were studied by SEM and optical microscopy. The composites of acetone-washed fibres were found to have higher moduli than the unwashed.

Khondker *et al.*[143] investigated the fabrication process of long-fibre reinforced unidirectional thermoplastic composites made using jute yarns (both untreated and treated). Tubular braiding technique was used to produce an intermediate material called ‘microbraid yarn’ (MBY) with jute yarn as the straightly inserted axial reinforcement fibre and polymer matrix fibre being braided around the reinforcing jute yarns. Microbraid yarns were then wound in a parallel configuration on to a metallic frame and compression-moulded to fabricate unidirectional composite specimens containing PLA as matrix.

Lee and Wang[144] investigated the effects of lysine-based diisocyanate (LDI) as a coupling agent on the properties of biocomposites from PLA, PBS and bamboo fibre (BF). They observed that the tensile properties, water resistance, and interfacial adhesion of both PLA/BF and PBS/BF composites were improved by the addition of LDI, but thermal flow[145] was hindered due to crosslinking between polymer matrix and BF. Enzymatic biodegradability of PLA/BF and PBS/BF composites was investigated using enzymes Proteinase K and Lipase PS, respectively. It was seen that the composites could be quickly decomposed by enzyme and the addition of LDI delayed the degradation. Green composites composed of regenerated cellulose (lyocell) fabric and biodegradable polyesters PHBV, PBS and PLA were prepared by Shibata *et al.*[146] and their properties studied. The tensile modulus and strength of all the biodegradable polyester/lyocell composites were found to increase with increasing fibre content. The biodegradation test revealed that the lyocell fabric in PLA/

lyocell composite degraded while pure PLA film was found to be almost unchanged after 120 days. The effect of surface treatment on abaca fibre reinforced biodegradable polyester composites was reported by Shibata *et al.*[147] Esterifications using acetic anhydride and butyric anhydride, alkali treatment and cyanoethylation were performed as surface treatments on the fibre. The flexural modulus of all the fibre reinforced composites increased with fibre content.

Arbelaiz *et al.*[148] developed composites by mixing biodegradable PCL with short flax fibre bundles. In order to improve fibre–matrix adhesion, PCL-g-MA was used as compatibiliser. Composites fabricated with flax fibre bundles and PCL-g-MA matrix showed the highest tensile and flexural strength. SEM of fractured surfaces confirmed the adhesion improvement between flax fibre bundles and the PCL-g-MA matrix. Results obtained by thermogravimetric analysis (TGA) showed that fibre addition and matrix modification slightly reduced the thermal stability of composites. In an interesting study, the biodegradation characteristics of different aliphatic polyesters reinforced with untreated and acetic anhydride (AA) treated abaca fibre were analysed by Teramoto *et al.*[149] using soil burial test. The polyesters used were PCL, PHBV, PBS and PLA. The authors observed that in the case of PCL composites, the presence of untreated abaca or AA-abaca did not affect the weight loss in a significant manner because PCL itself has relatively high biodegradability. However, the addition of abaca fibres caused the acceleration of weight loss in cases of PHBV and PBS composites. It was also observed that untreated abaca fibre reinforced PHBV and PBS composite specimens crumbled within 3 months. This result was in marked contrast to the fact that neat PHBV and PBS specimens retained the original shape even after 6 months.

An interesting report described the development of high-strength biodegradable 'green' composites from Manila hemp fibre bundles and a starch-based emulsion-type biodegradable resin.[150] The tensile and flexural strengths of the composites increased with increasing fibre content up to 70%. The effects of the fibre compression and the length distribution on the flexural properties of short kenaf fibre reinforced biodegradable composites were investigated by Shibata *et al.*[151] Two types of kenaf fibre, differing in density, were used. These fibres were mixed with a corn starch-based resin, and the composite specimens were fabricated by hot press forming. The flexural modulus values did not exhibit much difference despite the variation in density. De Carvalho *et al.*[152] developed wood pulp reinforced thermoplastic starch composites and investigated various properties. It was found that the addition of wood pulp led to a large increase in the elastic modulus and tensile strength and that these effects are very dependent on the glycerol content. The water absorbed by the composites was sharply reduced by the addition of pulp, and seemed to be independent of the amount of glycerol and pulp content. SEM of fracture surfaces revealed that wood pulp was well dispersed in the matrix and strongly bonded to it.

The effects of starch content and ageing on the mechanical properties of starch/poly (hydroxyester ether) (PHEE) composite materials were characterised by Lawton *et al.*[153] Native corn starches were extruded with PHEE. Composites were aged for up to 20 months at either 23 °C or 50% relative humidity (RH), or over calcium sulphate, to keep the composites dry. The tensile strength of the composites was affected by the type of starch filler that they contained. Composites containing native or crosslinked starch had significantly greater tensile strength than composites containing octenylsuccinated starch. The authors were of the opinion that the octenylsuccinate modification of the starch granule affected the adhesion between the starch and PHEE. In an interesting study, environmentally friendly starch biocomposites were successfully developed using a colloidal suspension of cottonseed linter cellulose crystallite as a filler to reinforce glycerol plasticised starch.[154] Chiellini *et al.*[155] investigated the biodegradation behaviour of cast films based on waste gelatin. The authors observed that waste gelatin (WG) based films showed a high degree of biodegradability under soil burial conditions. Furthermore, blending of WG with polyvinyl alcohol (PVA) followed by the addition of a lignocellulosic material as filler, as well as a limited amount of crosslinking agent such as glutaraldehyde, could modulate the durability of the film both in terms of physical persistence and biodegradation rate.

In another study involving poly(propylene carbonate), starch–g-poly(methylacrylate) (S–g-PMA) copolymer was used to reinforce PPC. Starch–g-poly(methylacrylate) copolymer was prepared by ceric ammonium nitrate-initiated polymerisation of methyl acrylate on to corn starch.[156] Tensile tests showed that the S–g-PMA incorporation improved the stiffness and tensile strength of composites significantly. Thermogravimetric results indicated that the S–g-PMA addition led to an improvement in the thermal stability of resulting composites. The biodegradability of composite sheets composed of biodegradable polymers and paper was investigated using a soil burial test by Kanie *et al.*[157] The authors added paper strengthening agents such as poly(amidoamine-epichlorohydrin) (PAE) and polyvinylamines (PVAm). They observed that the weight loss of composite sheets with PAE/PVAm reached 65% after 30 days, whereas the weight losses of composite sheets and genuine paper were 82% and 90%, respectively, over the same time period.

In an innovative study, the biodegradability of protein-filled polymer composites using dielectric measurements was investigated by Tchmutin *et al.*[158] The composites comprised a metallocene-based linear LDPE and a biopolymer, hydrolysed protein (HP), which was isolated from the chrome-tanned solid leather waste of the tanning industry by enzymatic hydrolysis. Biodegradation experiment was conducted in an aqueous phase of malt extract medium by an enzyme, *Aspergillus oryzae*, for 3 weeks. The authors observed that the biodegradation coefficients determined using dielectric measurements were in good agreement with the weight loss of the composites. The authors also observed that at above 20% concentration of hydrolysed protein, biodegradation extended to the interior regions of the composite. At concentrations below 20%, biodegradation was seen to be restricted in the surface areas. Ozaki *et al.*[159] developed biodegradable composites from waste wood and PVA. These composites displayed good mechanical properties and higher durability than solid wood.

Researchers recently investigated the effect of stearic acid on tensile and thermal properties of ramie fibre reinforced soy protein isolate (SPI) resin green composites.[160] It was observed that part of the stearic acid crystallised in SPI resin and that the crystallisability was affected by the addition of glycerol as a plasticiser. The fabricated green composite was found to have enormous potential for certain indoor applications. In an interesting study, Chabba *et al.*[161] modified soy flour (SF) by crosslinking it with glutaraldehyde. The crosslinked soy flour (CSF) polymer was characterised for its tensile and thermal properties. The effect of glycerol on the mechanical properties of the soy flour was also characterised and optimised. CSF polymer showed improved tensile properties and thermal stability, compared with unmodified SF resin, for use as a resin to fabricate composites. Unidirectional green composites using flax yarn and CSF resin were fabricated and characterised for their tensile and flexural properties. The composite specimens exhibited fracture stress and Young's modulus of 259.5 MPa and 3.71 GPa, respectively, and flexural strength of 174 MPa, in the longitudinal direction. Recently green composites were fabricated using pineapple leaf fibre and soy-based plastic.[162] The addition of compatibiliser (polyester amide grafted glycidyl methacrylate (PEA-g-GMA)) was seen to increase the mechanical properties of composites. In another interesting study involving biocomposites, the effect of alkali treatment on the thermal properties of Indian grass fibre reinforced soy protein green composites was studied by the same group.[163] The characterisation of Phytagel® modified SPI resin and unidirectional flax yarn reinforced green composites was undertaken by Lodha and Netravali.[164] The incorporation of Phytagel® in SPI resin led to an overall 10-fold increase in the tensile fracture stress and a nine-fold increase in Young's modulus of the SPI resin along with a seven-fold decrease in fracture strain. The dynamic mechanical properties such as storage and loss modulus of the modified resin increased and the glass transition temperature also increased by about 56 °C.

Among many natural products cashew nut shell liquid (CNSL) has attracted the attention of researchers because of its versatility in preparing a wide spectrum of oligomers, resins and high-temperature resistant polymers.[165] The presence of a phenolic hydroxyl group and non-conjugated double bonds in the parent side chain has the advantage of reacting with a large number of active groups leading to crosslinked structures and polymerised products. The main constituents of CNSL are ancardic acid, cardanol, cardol and 6-methyl cardol. Several other reports are there in the literature regarding the preparation of polymers from cardanol. Among these, resin co-polymers synthesised by condensing cardanol with formaldehyde and some substituted aromatic compounds, urea and thiourea are of importance.[166]

2.11 Characterisation of surfaces and interfaces

The characterisation of the interface gives relevant information on interactions between fibre and matrix. Studies of interfacial contributions in wood fibre reinforced polyurethane composites was conducted by Rials *et al.*[167] Recently the chemical and physical characterisation of the interphase has been discussed in an article by Kim and Hodzic.[168] The authors are of the opinion that the gap between physicochemical investigation and bulk material testing is bridged by implementation of novel techniques such as nano-indentation, nano-scratch tests and atomic force microscopy. The various methods that are available for characterisation of the interface are as follows.

2.11.1 Micromechanical techniques

For the micromechanical characterisation of the interface properties, techniques such as pull-out, fragmentation and micro-indentation are usually used. These test techniques do not simulate a situation that can be found in a real composite material but the loading conditions are relatively simple so that the interface properties can be rather easily derived. All these techniques evaluate the bonding strength between the fibre and matrix.

Stamboulis *et al.*[169] employed the single fibre pull-out technique for interfacial characterisation of dew retted and upgraded Duralin flax fibre reinforced thermoplastic composites. The duralin fibres were treated for improved moisture resistance. The interfacial shear strength of dew retted and upgraded duralin fibres in LDPE, HDPE and MA-modified PP were determined. Joseph *et al.*[89] have conducted an interesting study on the comparison of interfacial properties of banana fibre and glass fibre reinforced PF composites. They observed that the interfacial shear strength is higher for the banana/PF system than for the glass/PF system. This was attributed to the hydrophilic nature of cellulose and PF resin. Another study utilising single fibre pull-out was attempted by Van de Velde *et al.*[170] The authors used dew retted hackled long flax treated with propyltrimethoxy silane, phenyl isocyanate and MAPP. The studies revealed that composite prepared with flax fibre treated with MAPP exhibited the highest interfacial shear strength (IFSS). The interfacial adhesion of sisal fibre with different thermoset matrices (polyester, epoxy and phenol formaldehyde) and a thermoplastic resin (LDPE) was investigated by Joseph *et al.*[171] The authors found that interfacial bonding was maximum in sisal fibre reinforced phenol formaldehyde composites due to chemical bonding between phenol formaldehyde prepolymer and in lignocellulose.

The interfacial adhesion of flax fibre reinforced PP and PP ethylene propylene diene terpolymer blends were investigated by Manchado *et al.*[172] In this study both the matrices were modified with maleic anhydride. They observed that the addition of small proportions of MA to the matrices significantly increased the shear strength. The authors were of the opinion that introduction of functional groups in the matrix reduced the interfacial stress concentrations, preventing the fibre–fibre interactions that are responsible for premature composite failure. Also in the presence of MA functional groups the esterification of flax fibres takes place, increasing the surface energy of the fibres to a level closer to that of the matrix. Hence a better wettability and interfacial adhesion are obtained.

Pull-out tests were conducted by Sydenstricker *et al.*[173] in sisal fibre reinforced polyester biocomposites. Sisal fibre was modified by sodium hydroxide and *N*-isopropyl-acrylamide solutions. It was observed that all the chemical treatments were effective and best results were obtained with the 2% *N*-isopropyl-acrylamide treatment. Yuan *et al.*[174] investigated the effect of air-plasma and argon treatment on IFSS between sisal fibre and PP by means of single fibre pull-out. They found that optimum treatment parameters were shortest plasma treatment time, medium power level and medium chamber pressure. Under these conditions the IFSS of air plasma treated sisal fibres was found to be higher than argon plasma treated fibres. The interfacial compatibility between sugar cane bagasse fibre and polyester upon chemical modification was investigated by García-Hernández *et al.*[175] The authors used the fibre pull-out technique to evaluate IFSS. They observed that IFSS was higher for treated composites than for untreated ones.

The drawback of the single fibre pull-out test is that it involves only a single fibre. As the role of neighbouring fibres is not taken into account, the thermal stresses and the polymer morphology around the fibre are not the same as in a real composite. Real composites contain multiple fibres and the pull-out fibre is surrounded by a composite medium. In single fibre model composites, the effect of the composite medium surrounding the pull-out fibre has been ignored. Therefore, owing to the influence of the composite medium surrounding the pull-out fibre, the interfacial debonding process in multifibre composites and the interfacial properties obtained therefrom, would very likely deviate from those of the single-fibre composite pull-out test.

2.11.2 Microbond test

The procedure involves the deposition of a small amount of resin on to the surface of a fibre in the form of one or more discrete micro-droplets. The droplets form concentrically around the fibre in the shape of ellipsoids and retain their shape after appropriate curing. Once cured, the micro-droplet dimensions and the fibre diameter are measured with the aid of an optical microscope. The embedded length is fixed by the diameter of the micro-droplet along the fibre axis, which is dependent on the amount of resin deposited on the fibre.

Most of the development studies for the microbond method have been carried out with E- glass fibres having a diameter range of 10–15 μm. Craven *et al.*[176] evaluated the interface of *Bombyx mori* silkworm silk–epoxy composite by microbond test. After the resin has cured, it is sheared from the fibre by two parallel plates attached to a microvice. They observed that the mean IFSS of silk/epoxy composite is 15 MPa. It was found that silk fibres could offer useful reinforcement to an epoxy system due to its high tensile strength and extensibility. In another study, Luo and Netravali[177] characterised the interfacial properties of green composites made from pineapple fibres and poly(hydroxy butyrate-co-valerate) resin. The IFSS value was found to be very low. Another interesting study on the IFSS of green composites was conducted by Lodha and Netravali[178] in which the authors prepared green composites comprising ramie fibre and soy protein isolate. A problem that is associated with the microbond technique is that the maximum debonding force value is influenced by interfacial friction in already debonded regions and, therefore, these parameters are not purely ‘adhesional’ but depend, in an intricate way, on interfacial adhesion and friction.

The specimen preparation for the micro-droplet test whereby a single fibre is pulled out of a small droplet of resin suffers from several difficulties. For instance, the reliability of the data is affected by the shape of the droplet. Symmetric, round droplets are easier to test and analyse than droplets with flat surfaces, produced when the specimens solidify on a flat substrate. Also the size of the droplet is critical. If the length of the droplet exceeds a critical value, the fibre will fracture prior to debonding and pull-out. An additional complication with some thermoset materials is that the anticipated curing characteristics may not manifest themselves in a droplet of small size, and hence comparison on a microstructural level between micro- and macro-specimens may not be possible. Another defect is that this test is not applicable to matrices that are soft.

2.11.3 Fragmentation test/single fibre composite (SFC) test

In this method, a single fibre is embedded in a polymer and broken into small pieces. The fibre is neither pushed nor pulled directly, and so fibre Poisson effects are similar to those occurring in a fibre composite. Unlike the other methods, it produces only one result for the IFSS, which is the average for the many fragments produced. The use of Raman spectral lines has made it possible to estimate fibre strains and hence the IFSS can be estimated directly from the fibre’s Young’s modulus. This makes the test much more powerful.

Zafeiropoulos *et al.*[179] characterised the interface in flax fibre reinforced PP composites by means of single fibre fragmentation test. Flax fibre was modified by means of two surface treatments: acetylation and stearation. The authors observed that acetylation improved the stress transfer efficiency at the interface.

Stearic acid treatment was also found to improve the stress transfer efficiency but only for shorter times. Tripathy *et al.*[180] used the single fibre fragmentation test for determining the critical fibre length and IFSS of jute fibre reinforced epoxy composites. In an interesting study, Valadez-Gonzalez *et al.*[181] have shown that there is a maximum quantity of silane coupling agent that can be deposited on henequen fibre. The authors analysed the tensile and micromechanical properties of the composite material. They observed that the interaction between the fibre and matrix was stronger when the fibre surface was physically modified and combined with silane coupling agent. The IFSS, which was determined from the single fibre fragmentation test, was seen to increase, to reach a maximum at the intermediate concentrations of silane and then to decrease with the increase in silane concentration. The interfacial properties and microfailure degradation mechanisms of bioabsorbable fibre reinforced PLLA composites were studied by Park *et al.*[182] using fragmentation technique and non-destructive acoustic emission (AE) technique. The IFSS between bioactive glass fibre and PLLA was found to be much higher than in chitosan fibre/PLLA systems.

In the SFC, the failure strain of the matrix must be much larger than the failure strain of the fibre to promote multi-fragmentation of the fibre. This requires the use of matrices, which can undergo large deformations. Consequently commercial resins utilised in actual composite systems which typically have low strains to failure cannot be used for this test. Therefore the IFSS determined is not directly applicable to the actual composite system. Another problem is that the embedding matrix can inhibit fibre fracture, which initiates from surface flaws. The magnitude of this effect is dependent on the type of matrix or embedding resin. Therefore, it is important to utilise the actual fibre and resin of a given composite system to determine the IFSS.

2.11.4 Spectroscopic techniques

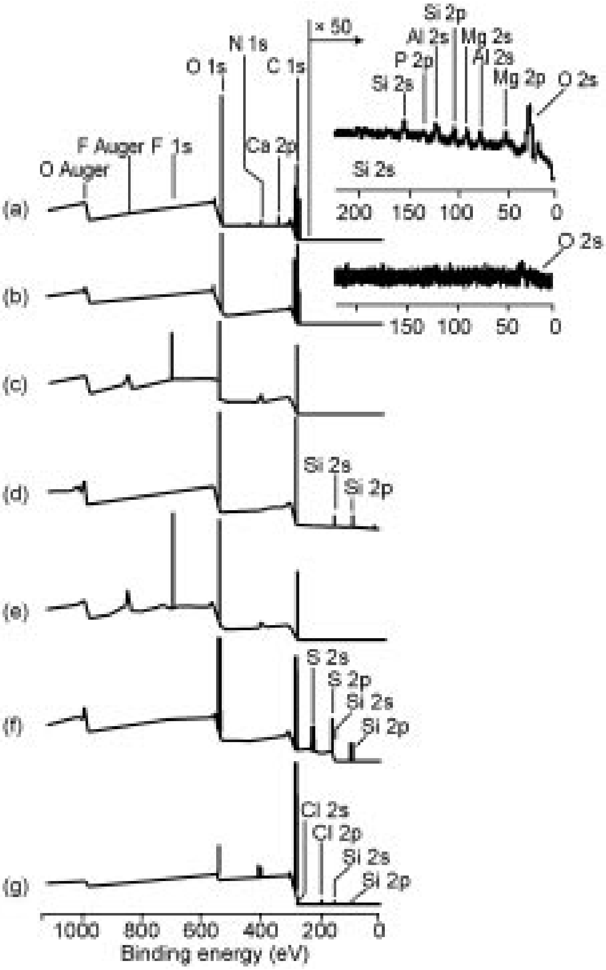
Electron spectroscopy for chemical analysis

Electron spectroscopy for chemical analysis (ESCA) is an extremely powerful tool for studying solid surfaces. This technique has an information depth of 1–5 nm and therefore it is capable of examining only the outer layers or surfaces of fibres. Carbon fibres and coated glass fibres have been characterised by X-ray photoelectron spectroscopy (XPS). ESCA has been used to determine the surface composition of cellulose and wood fibres. Joly *et al.*[183] used XPS analysis to study the C/O ratio for cellulosic fibres treated with isocyanate. Felix and Gatenholm[184] modified the surface properties of cellulose fibre using a PP-MA copolymer. They used XPS to identify the chemical structure and found that the coupling agent was localised at the surface of the fibres. Valadez-Gonzalez *et al.*[185] used XPS and FTIR to confirm the existence of a chemical bond between the silane coupling agent and henequin fibre. The effect of silane coupling agents on radiata pine fibre reinforced PE was investigated by Pickering *et al.*[186] Radiata pine fibres are readily available from pulping operations for paper production and from production of fibre for board manufacture. Two silanes, namely γ-aminopropyl triethoxy silane and dichlorodiethyl silane, were employed for surface modification of radiata pine wood fibre. XPS and NMR were used to characterise the modification of the pine fibre. The XPS results based on the elemental and functional composition of the untreated and treated wood fibres indicated that modification of fibre surface has taken place for most of the samples. The NMR analysis gave firm evidence of a reaction producing ether linkages between the hydroxyl groups on the wood fibre and silane. An investigation of modified and unmodified flax fibres using XPS was performed by Zafeiropoulos *et al.*[187] The authors subjected flax fibres to two treatments, viz. acetylation and stearation, and the effects of these treatments were analysed by ESCA. They observed that the surface of flax fibre had an appreciable coverage of hydrocarbon compounds but no aromatic compounds were detected. In the case of acetylation treatment it was found that ester bonds were present on fibre surface after treatment.

Pothan *et al.*[188] investigated the change in the surface composition of the raw and chemically modified fibre using XPS. Surface characterisation by XPS showed the presence of numerous elements on the surface of the fibre. Investigation of the surface after alkali treatment on the other hand showed the removal of most of the elements. Silane treatment was found to introduce a considerable amount of silicon on the surface of the fibre. The [O]/[C] ratio was found to decrease in all cases except for the fluorinated and vinyl silane treated fibres. Detailed investigation of the deconvoluted C 1s spectra revealed the change in the percentage atomic concentration of the various elements on the fibre surface. The XPS results were found to agree perfectly with the solvatochromic and electrokinetic measurements. A series of XPS survey spectra of raw and chemically modified banana fibres is given in Fig. 2.3.

Fourier transform infrared spectroscopy

The FTIR technique has also been used to characterise the surface of the fibre from which information can be obtained about the interfacial adhesion.[189] George *et al.*[190] characterised the interface and modified fibre surface of pineapple leaf fibre reinforced PE composites using IR. The effect of different chemical modifications on aspen fibres on the interfacial characteristics of aspen fibre reinforced HDPE composite was conducted by Colom *et al.*[191] The interaction between aspen fibres and HDPE was improved by the addition of two coupling agents, maleated PE (epolene C-18) and γ-methacryloxy-propyl trimethoxy silane (silane A-174). The highest absorbance value corresponds to the untreated composites and the lowest value to that of composite modified with maleated polypropylene (PPMA). Hristov *et al.*[192] performed another study



2.3 Series of XPS survey spectra of raw and chemically modified banana fibres: untreated banana fibres (a), fibres after a treatment with 0.25% NaOH (b), fibres after acetylation (c), fibres grafted with the silane A174 (d), fibres grafted with the fluorosilane F8261 (e), fibres grafted with the sulphur-containing silane Si69 (f), and fibres treated with C18T (g). The insets are cuts of the survey spectra of untreated (a) and NaOH-treated (b) banana fibres showing the presence or absence of accompanying elements in the sample surfaces.

employing FTIR to examine the interface of wood fibre reinforced polypropylene composites. The authors modified PP matrix with PPMA and poly(butadiene styrene) rubber. From the spectra of the treated composite they concluded that the compatibiliser was attached to the wood fibres either by ester or hydrogen bonds.

The chemical modification of various fibres was analysed using different spectroscopic and microscopic methods by Mwaikambo and Ansell.[193] FTIR was one of the techniques used by the authors to analyse hemp, sisal, jute and kapok fibres, which were treated with NaOH. The results showed that kapok was the most reactive of all fibres, followed by jute, sisal and hemp. Alkalisation was seen to improve adhesion between fibre and resin thereby increasing mechanical and thermal stability of composites. The influence of 4,4′-thiodiphenol (TDP) on the interfacial properties of flax fibre reinforced poly(3-hydroxybutyrate) was studied by Wong *et al.*[194] The additive TDP was known to form hydrogen bonds with many functional groups. FTIR revealed hydrogen bonding occurred in the composites, which consequently brought about advantageous changes in the mechanical properties of the composites. The advantages of FTIR mean less experimental complexity and a more easily interpretable spectrum. It is also much more precise than the infrared technique. The disadvantages are lower sensitivity and the need to use compact samples.

Laser Raman spectroscopy

The development of the laser Raman spectroscopic (LRS) method has led to the assessment of the stress field at the interface level. The technique relies on the fact that Raman bands corresponding to the vibrational modes of bonds in the fibre, shift towards a lower wavenumber upon the action of strain and stress and this is thought to be due to direct molecular straining/stressing. This has been used to map stresses along fibres embedded in matrix resin to determine the IFSS. Recently Raman spectroscopy has also been used to investigate the deformation micromechanics of natural and regenerated cellulose fibres.[195] Studies have also been carried out in the case of composites but it was found that bonding across the ends of the fibres gave rise to good stress transfer and it was difficult to evaluate the properties of the interface. Eichorn and Young[196] used Raman spectroscopy to follow the composite micromechanics of hemp fibres and epoxy resin micro-droplets. The authors observed that the 1095 cm^{-1} cellulose Raman band has been shown to shift under the application of strain and stress towards a lower wavenumber, indicative of molecular deformation. It has also been shown that it is possible to map the stress of a hemp fibre inside an epoxy resin droplet on the surface. This technique has also shown that an IFSS for epoxy and hemp fibres is comparable to aramid/epoxy and glass/epoxy systems, but coupled with good adhesion of the fibre ends may lead to low fracture toughness of a natural-fibre composite.

Nuclear magnetic resonance spectroscopy

High-resolution NMR spectroscopy is a very powerful technique to measure and characterise polymer tacticity, helicity, and molecular weight, composition and diffusion coefficient of polymers. Solid-state ^{13}C NMR spectroscopy using cross-polarisation and magic angle spinning is especially useful for characterising wood and wood/polymer composites. Detailed information that can be obtained includes composition, glass transition temperature, melting transitions, percentage crystallinity and number and type of crystalline phases. In general, solid-state NMR involves proton–carbon cross-polarisation to enhance the ^{13}C signal high-power decoupling to eliminate dipolar line broadening due to protons and spinning of the sample about the magic angle with respect to static field to reduce chemical shift anisotropy effects. Imaging NMR, with improvement of lateral resolution, will offer many opportunities for non-destructive studies of interfaces. NMR resonance imaging has also been used as a method of void detection in carbon fibre reinforced polymer composites.[197]

2.11.5 Microscopic techniques

Environmental scanning electron microscopy

Conventional SEM requires high vacuum, dry specimens and usually electrically conductive surfaces. Coating the surface of non-conductive specimens with a conducting material such as gold or carbon has been necessary. This has precluded the viewing of wet or oily materials. The environmental SEM (ESEM) allows wet, oily and electrically non-conductive specimens to be observed without special preparation and at relatively high pressures. The ESEM has proven useful for investigating wood–polymer interactions at fracture surfaces and polymer distribution in the wood–polymer composites (WPCs). Jahn *et al.*[198] used ESEM to visualise the microstructural fibre properties variation as a function of alkali concentrations during mercerisation.

Atomic force microscopy

Atomic force microscopy (AFM) is a useful technique to determine the surface roughness of fibres. The force modulation mode gives a qualitative statement about the local sample surface elasticity using an oscillating cantilever tip that indents into the sample surface. The amplitude of this deflection is measured as a function of the tip position when the cantilever tip indents cyclically into the surface. Mader and coworkers[199] used this technique to determine the physical properties of the interfaces. In an innovative study Michaeli *et al.*[200] characterised the interfacial adhesion between flax fibre and unsaturated polyester (UP) resin with AFM. In an interesting study Dupres *et al.*[201] investigated the wetting behaviour and electrostatic properties of hair fibre by AFM. Surface potential imaging was used to characterise local polarities. The wetting properties were analysed by imaging hair samples on which different liquids were spread. The authors observed that non-polar liquids preferentially wetted the cuticle edges of the hair fibre while polar liquids did not wet any region of the cuticle. Water was found to penetrate the bulk of the hair fibre.

2.12 Other techniques

2.12.1 Contact angle measurements

Contact angle measurement is probably the most common method of solid surface tension measurement. The three most commonly used methods of contact angle measurement are the sessile drop, the captive bubble and the Wilhelmy plate technique. In the sessile drop experiment, a droplet of a properly purified liquid is put on the solid surface by means of a syringe or a micropipette. The droplet is generally observed by a low-magnification microscope, and the resulting contact angle is measured by a goniometer fitted in the eyepiece. In the captive bubble technique, an air or liquid drop is put on the sample surface immersed in a liquid medium by means of a U-shaped needle. Advancing and receding angles are measured as in the above technique. In the Wilhelmy plate technique the advancing and receding angles are calculated from the force exerted as the sample is immersed or withdrawn from a liquid. The contact angle in a fibre reinforced polymer melt is given by the following relationship:

$$\cos\theta = F/p = g\,\Delta m/p\,\gamma \qquad 2.1$$

where θ = contact angle; F = force/unit length; p = fibre perimeter; γ = surface tension of the used test liquid; g = gravitational constant; Δm = change in mass before and after immersion of fibre in polymer melt. The main advantages of the Wilhelmy plate technique over more conventional methods are the control of the interfacial velocity and that measurement can also be performed on small diameter fibres.

The effects of different chemical treatments on the fibre–matrix compatibility in terms of surface energy was analysed by Cantero *et al.*[202] Composites were prepared with two kinds of flax fibres (natural flax and flax pulp) and PP. The applied treatments were MA, MAPP and vinyl triethoxy silane (VTSO). Two techniques were used to determine the surface energy values: the dynamic contact angle method for long flax fibres and the capillary rise method for irregular pulps. The three chemical modifications were found to reduce the polar component of surface energy of the fibres. MAPP treatment was found to produce the best surface energy values for all the percentages.

2.12.2 Zeta potential measurements

Electrophoresis, electro-osmosis and streaming potential are basically three electrokinetic phenomena that are currently exploited to measure the zeta potential of the surfaces of polymers. All these phenomena have in common distinguishable moving and stationary phases. In electrophoresis and electro-osmosis an electric field is applied and the movement of colloidal particles (electrophoresis) or of a solution (electro-osmosis) is observed. In streaming potential or streaming current measurements the liquid phase is moved by an applied pressure and the ensuing potential or current are measured. Every measurement of the concentration or pH dependence needs a well-defined starting point. For most fibre materials the zeta potential shows a parabolic curve-like trend, which is caused by the adsorption properties of the solid for potential determining ions as well as by specifically adsorbed ions. Since the zeta potential as a property of the electrochemical double layer cannot depend on the geometry of the investigated capillary bundle, like a fibre bundle, it is necessary to characterise the pore geometry as well. The presence of acidic or basic dissociable surface functional groups can be estimated by measuring the pH dependence of the zeta potential. Zeta potential measurements provide interesting results when applied to the effect of coupling agents in the filling and reinforcement of polymers. Bismarck *et al.*[203] also carried out zeta potential measurements on modified jute fibres. It was found that jute fibres, as expected, contained dissociable acidic surface functional groups. Similar studies were also conducted by Pothan *et al.* on modified banana fibres.[204]

2.12.3 Solvatochromism

The sum of all possible interactions between a surface group and an adsorbed molecule or ion is termed as the surface polarity. In well-behaved regular solvents the thermal motions of the solvent molecules surrounding the solvatochromic probe dye cause an average polarity. Consequently, a specific probe dye reflects the specific sum of interactions being operative between the relevant surface groups and the relevant sites of the probe molecule. The thermal motions at the surface of the solid material attached to the probe dye will be lower than that of the probe dye contacting the liquid. The probe dye should interact with the site on the surface corresponding to a minimum of the free energy.

Pothan *et al.*[205] characterised chemically modified banana fibre surfaces using three carefully chosen probe dye indicators, dicyano-bis(1,10-phenanthrolin) iron II, Michlers ketone and aminobenzodifuranone. The hydrogen bond donating acidity α, the basicity β, the dipolarity/polarisability π^*, the acceptor number AN, and the $E_T(30)$ parameter values were determined in a few cases for the chemically modified fibres. It was found that the hydrogen bond donating acidity is found to be the lowest for fibres treated with the silane A174 after pre-treatment with 0.5% NaOH. The highest value of AN is found to be for fibres treated with the silane A151. The $E_{(30)}$ parameter, which is indicative of the overall polarity, is found to be maximum for fibres treated with the silane A151. The probe dye aminobenzodifuranone has been proved to be the best for identifying the acidic and basic centres in chemically modified banana fibre.

2.12.4 Stress relaxation

The term relaxation denotes the process of establishment of statistic equilibrium in a physical or physicochemical system and its rate depends upon the probability of transition of system from one stage of equilibrium to another. Meaningful data on the behaviour of the materials can be obtained by accelerated testing methods. Stress relaxation is one of the widely employed testing methods for composites, since stress relaxation represents the basic time-dependent response of the material from which other time-dependent responses derive. The stress relaxation modulus of polymers is increased by rigid fillers and decreased by elastomeric ones up to the point where dewetting or crazing becomes pronounced. The rate of stress relaxation for rigid and elastomeric fillers increases after the onset of dewetting. The stress relaxation rate has been chosen as a way of ranking adhesion between fibres and matrix. The slope of the stress relaxation curve is chosen as a measure of the level of adhesion between the fibre and matrix. Flink and Stenberg[206] used stress relaxation experiments to measure the adhesive strength of cellulose fibres with natural rubber by analysing the relaxation mechanism. Bhagawan *et al.*[207] studied the stress relaxation behaviour of short jute fibre reinforced rubber composites

In a recent study the theoretical expressions for describing the stress relaxation rates of cellular materials were derived analytically by Lin and Huang[208] based on a cell wall relaxation–bending model. Theoretical results indicated that the stress relaxation rates of hexagonal honeycombs and open-cell and closed-cell foams, depend on their relative density, the imposed strain and the stress relaxation parameters of the solid material from which they are made. It was also found that cellular materials have the same activation energy and power-law stress relaxation exponent as solid cell walls. In another interesting study Sinha and Sinha[209] observed that controlled isothermal 'constant-strain' stress relaxation tests (SRT) at different strains led to the conclusion that SRT cannot provide the anticipated viscous strain rate over a wide stress range; the stress exponent for power-law creep was found to depend on strain. The recovery phase after SRT showed that delayed elasticity, not the viscous flow, controls relaxation processes during the primary stages of stress relaxation irrespective of the level of constraint. Viscous flow controls stress relaxation only at longer times, exhibiting 'apparently' asymptotic approach to a quasi-stable stress rate. Sinha and Sinha also made theoretical predictions for the time-dependent recoverable (delayed elastic) and permanent components of strain as functions of time and imposed strain. In a study concerning natural fibre, Pothan *et al.*[210] investigated the stress relaxation behaviour of banana fibre reinforced polyester composites with special reference to the effect of fibre loading, fibre treatment, hybridisation with glass fibre and also as woven fabric composites. It was observed that incorporation of fibre in the polyester matrix reduces the rate of relaxation. The nature of the relaxation curve was found to depend on the quantity of fibre as well as the surface characteristics of fibre used as reinforcement. Another important observation was that of the various chemical modifications chosen in the study, the decrease in stress was found to be the lowest for composites made out of banana fibre treated with NaOH. Stress relaxation values of woven glass and banana fibre composites were found to be lower than that of short fibre composites.

Geethamma *et al.*[211] looked into the stress relaxation properties of coir fibre reinforced natural rubber composites. The authors observed that the relaxation mechanism of both the unfilled compound and the composites was influenced by the strain rate. At a high strain rate, the rate of stress relaxation was found to be low because of the major contribution of elastic components in the system. The rate of relaxation was highest for the natural rubber compound, and it decreased with coir fibre loading from 30 to 60 phr. This indicated decreased entropy of the elastomeric matrix because of the incorporation of fibres.

2.12.5 Inverse gas chromatography

The most frequently used technique for the determination of thermodynamic and acid/base characteristics is inverse gas chromatography (IGC). In IGC compounds, usually solvents, of known properties, characterise the unknown fibre surface. IGC measurements can be carried out in two different ways. Usually linear or ideal IGC infinite concentrations of n-alkane are injected into the column containing the fibre to be characterised. The net retention volume (V_N) can be calculated by:

$$V_N = (t_r - t_0)Fj_0 \tag{2.2}$$

where t_r is the retention time and t_0 the reference time, F the flow rate of the carrier gas and j_0 is a correction factor taking into account the pressure difference between the two ends of the column. The dispersion component of the surface tension of the filler can be calculated from the retention volumes of n-alkanes:

$$-RT \ln V_n = Na(\gamma_{LV}\, \gamma_s^d)^{1/2} \tag{2.3}$$

where V_n is the net retention volume of the alkane, a is the surface area of the adsorbed molecule, γ_{LV} the surface tension of the solvent and N is the Avogadro number. The product of RT and the logarithm of the retention volume of normal alkanes is a linear function of a $(\gamma_{LV})^{1/2}$. If the measurements are carried out with polar solvents, the deviation from this straight line is proportional to the acid–base interaction potential of the solid surface. Adsorption isotherms of the probe compound on the fibre surface can be determined with non-linear or finite dilution IGC.

When the surface of a solid is only partially wetted by a liquid, it forms a droplet with a definite contact angle (θ). The interaction of the components is expressed by Young's equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \tag{2.4}$$

where γ_{SV} is the surface tension of the solid in contact with the vapour of the liquid, γ_{LV} is the surface tension of the liquid and γ_{SL} is the interfacial tension.

Due to wetting, γ_{SV} is smaller than the surface tension of the solid measured in vacuum (γ_{So}), the difference is the spreading pressure (π_e), i.e.:

$$\gamma_{So} - \gamma_{SV} = \pi_e \qquad 2.5$$

The value of π_e is very small for low energy surfaces, but it cannot be neglected for fibres. On the contrary, π_e can be used for the calculation of the thermodynamic characteristics of their surface. The spreading pressure can be determined from the adsorption isotherm in the following way:

$$\pi_e = RT \int \tau \, d \ln P \qquad 2.6$$

where p is the vapour pressure and τ the moles of vapour adsorbed on a unit volume of the fibre. If the measurement is carried out with polar solvents, the dispersion component of the surface tension of the fibre can be determined from the spreading pressure:

$$\pi_e = 2(\gamma_s^d \gamma_{LV})^{1/2} - 2\gamma_{LV} \qquad 2.7$$

This equation is derived from Young's, the Dupre and the Fowkes equations by assuming complete wetting ($\cos\theta = 0$). Measurements with polar solvents give the polar component of the surface tension, but acid–base constants and the corresponding work of adhesion can also be calculated from them:

$$W_{AB}{}^{spec} = 2\gamma_{LV,p} + \pi_{e,p} - 2(\gamma_s^d \gamma_{LV,p}^d)^{1/2} \qquad 2.8$$

where $W_{AB}{}^{spec}$ is the polar or acid/base component of W_{AB} and the p subscript indicates a polar solvent. Finite dilution IGC is more tedious to carry out than the linear IGC.

Shakeri and Tabar-Haidar[212] investigated the surface characteristics of treated pulp paper fibre using IGC. The effectiveness of the various surface treatments was monitored by IGC adsorption curves using n-alkanes and acid–base probes. The empirical acid (KA) and base (KD) characteristics (i.e. electron donor/acceptor abilities) of untreated and treated pulp papers fibres were determined using Schultz's method and were correlated with the surface chemical compositions determined from FTIR spectroscopy. The results indicated that the surface of untreated pulp paper fibres had an acidic characteristic due to the electron acceptor character of the hydroxyl protons. The dispersive component of the free energy as well as the acid–base properties of cellulose fibre surfaces, before and after modification by corona treatment was determined by IGC.[213]

2.12.6 Swelling studies

The extent of fibre alignment and strength of fibre–polymer interfacial adhesion were analysed from the swelling measurements. The extent of interaction between polymer and fibre can be analysed using the Kraus equation:[214]

$$\frac{V_{\mathrm{ro}}}{V_{\mathrm{rf}}} = 1 - m\left[\frac{f}{1-f}\right] \qquad 2.9$$

where V_{ro} = volume fraction of polymer, f = volume fraction of fibre, m = polymer–fibre interaction parameter and f = volume of filler/total volume of recipe.

The diffusion mechanism in polymers is essentially connected with the ability of the polymer to provide pathways for the solvent to progress in the form of randomly generated voids. As the void formation decreases with fibre addition, the solvent uptake also decreases. Information about anisotropy caused by the orientation of fibres and matrix/fibre adhesion can be obtained from anisotropic swelling studies. This provides an idea about the extent of fibre orientation also. Geethamma *et al.*[215] estimated the extent of fibre orientation and fibre–matrix interfacial adhesion in coir reinforced natural rubber composites.

2.13 Applications

The main application of the natural-fibre reinforced composites is in the automotive industry area, which has developed various new components based on natural-fibre composites. In Europe, plant fibre composites are mainly used by the automotive industry.[216] In 1996 the total reported use of natural fibres did not exceed 4.0 ktonne; by 1999 this had increased to more than 21 ktonne as reported by the suppliers to the European automotive industry.[217] Projections for 2005 and 2010 suggest that the total application of biofibres in the European automotive sector could be more than 100 000 t by 2010.[218] Biofibre reinforcement in blended thermoplastics or resinated thermoset compression mouldings is now generally accepted for applications as door-liners/panels, parcel shelves and boot-liners. The automotive components with biofibre reinforced composites can be expected to increase steadily with increased model penetration. But the new invention is that, nowadays, biofibre composites are used also in the exterior components of an automotive. DaimlerChrysler's innovative application of abaca fibre in exterior under-floor protection for passenger cars has been recently recognised.[219,220] Other exterior parts (front bumper, under-floor trim of bus) from flax fibre reinforced composites will follow within a short time.[221] The automotive company Ford (Germany) is using kenaf fibres imported from Bangladesh in the Ford Mondeo and the door panels of the Ford Mondeo are manufactured by kenaf reinforced PP composites. Nowadays, 27 components of a car are manufactured from biofibre reinforced composites with a total weight of 43 kg (73% more than the previous weight) for the newest Mercedes S class.

2.14 Conclusions

The interest in natural-fibre reinforced polymer composites is growing rapidly owing to their great performance, significant processing advantages, biodegradability, low cost and low relative density. In addition, natural fibres are important renewable resources in many countries and natural-fibre-based polymer composites form a new class of materials, which have good potential as future substitutes for scarce wood, therefore providing a solution to environmental issues such as reduction of both synthetic and agricultural wastes. Many studies have been reported in the literature and reviewed in this chapter, showing the importance of the interface and the influence of various types of surface modifications on the physical and mechanical properties of natural-fibre reinforced composites. Brief reviews about the different types of matrices used for the composite fabrication as well as fabrication methods are also highlighted. Challenges still exist in the development of more suitable cost-effective fabrication techniques as well as composites having superior mechanical properties using natural fibres as reinforcement. Nevertheless, the progress so far obtained in this field has allowed the application of natural-fibre polymer composites in many sectors such as in consumer items and, more importantly, in the automotive industry.

2.15 References

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3

Engineering the fibre–matrix interface in natural-fibre composites

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3.1 Introduction

It is well known that the interface between the reinforcing agent and the matrix plays a pivotal role in determining the mechanical properties of composite materials. As a result it is not surprising that extensive research has been carried out in the past in order to understand the interfacial bond and assess its effect on the mechanical behaviour of composites. A strong interface creates a material that displays exemplary strength and stiffness but that is very brittle in nature with easy crack propagation through the matrix and fibre. A weaker interface reduces the efficiency of stress transfer from the matrix to the fibre and consequently the strength and stiffness are not as high, but in contrast toughness is increased (Matthews and Rawlings, 1999). Assessing the interface in composites has been the topic of significant research in the past. An excellent overview on the topic of the interface in composites along with an extensive discussion of interfacial characterisation has been given by Kim and Mai (1998).

Natural-fibre composites are distinct from artificial fibres. The main problem in the case of natural-fibre composites is that natural fibres are highly heterogeneous materials both physically and chemically. Owing to this, different strategies are employed to successfully tailor and assess the interface. This chapter discusses the interface in natural-fibre composites and also highlights the peculiarities of these systems. The chapter first discusses methods of interfacial modification (Sections 3.2–3.4), and, second, experimental techniques for interfacial bond assessment in terms of mechanical behaviour are discussed (Sections 3.5 and 3.6). The chapter finishes with a concise section of closing remarks and some future perspectives. The main focus, however, is on the use of model composites and micromechanical testing, rather than macromechanical testing. The reason for this choice is that the complete listing of all the literature on natural-fibre composites and relevant interfacial tailoring methods would inevitably result in a full book, rather than a chapter. Hence, surface modification methods and representative references from the literature are exclusively focused on micromechanical assessment and not on mechanical testing in general.

3.1.1 Strategies for engineering the fibre–matrix interface in natural-fibre composites

Natural fibres consist mainly of cellulose, which is a natural polymer rich in hydroxyl groups. The remaining components of natural fibres (i.e. hemicelluloses, pectins and lignin) are also molecules rich in hydroxyl, carboxyl and other functional groups. Consequently, the fibres are usually strong polar materials and exhibit significant hydrophilicity. In contrast, most polymer matrices tend to be apolar and mostly hydrophobic. As a result there are significant problems of compatibility between the fibre and the matrix, leading to poor dispersion, a weak interface and ultimately inferior quality composites. Such compatibility problems have to be tackled with the use of appropriate methods to improve adhesion between the fibre and the matrix. There are essentially two different possible general strategies to achieve this goal, the first being to alter the fibre surface and the second being to modify the matrix properties. In both cases, however, the major objective is to improve the wettability of the matrix on the fibre surface and promote adhesion by the induction of chemical bonding and/or the tuning of surface energy. However, one particular aspect that has to be specifically considered for natural-fibre composites is cost. The application of any adhesion-promoting method inevitably increases the manufacturing cost of the end products, and since one of the key advantages of natural fibres is their low cost it is obvious that it should be kept at low levels. The next section describes adhesion-promoting methods, highlighting their advantages and disadvantages.

3.2 Physical methods for surface modification

Physical treatments alter the structural and surface properties of the fibres without the use of chemical agents. The only notable exception is mercerisation, which involves the use of sodium hydroxide. Aside from mercerisation, three other methods can be classified as physical treatments: corona, plasma and heat treatments. Physical treatments do not alter extensively the chemical composition of the fibres, and therefore the interface is generally enhanced via an increased mechanical bonding between the fibre and the matrix. One the most attractive features of physical methods is the fact that they are 'clean' since they do not involve chemicals.

3.2.1 Corona treatment

Corona treatments exploit the corona effect, i.e. the formation of high-energy electromagnetic fields close to charged thin wires or points, with consequent ionisation in their proximity, even at atmospheric pressure and relatively low temperature. In the ionised region, excited species (ions, radicals, etc.) are present and the latter are active in surface modification, typically by the introduction of oxygen-containing functional groups (Garbassi *et al.*, 1998). In addition, prolonged treatment times may result in a fibre with a significantly rough surface. A typical corona apparatus consists of two electrodes (usually made of aluminium) and a dielectric spacer (usually made of quartz). The corona method has been applied by various research groups on natural-fibre composites, especially in composites involving polyolefins as the matrix (Dong and Sapieha, 1991; Belgacem *et al.*, 1994).

The corona treatment has many advantages over other methods of surface modification. The main one is that it does not require chemicals and therefore is a 'clean' technique. The necessary instrumentation of the corona treatment can also be modified so that it can become a continuous process in industry.

3.2.2 Plasma treatment

Plasma treatment is another physical treatment method, similar to corona treatment. The method exploits the property of plasma to induce changes on the surface of a material. In general, during the treatment an ionised region is formed, with its composition depending on the gas feed, always including high-energy photons, electrons, ions, radicals and excited species. In term of apparatus the main difference as compared with the corona treatment is the need for a vacuum chamber and gas feed to maintain the appropriate pressure and composition of the gaseous mixture (Garbassi *et al.*, 1998). Low-temperature plasmas require low pressure to be sustained and this in turn has a negative impact on cost as high vacuum is expensive. Even though it possible to use different gases, oxygen plasma has been the most popular in use with synthetic polymers. It has also been popular for natural polymers such as cellulose materials, although not to the same extent as it has been for synthetic polymers.

Felix *et al.* (1994) modified cellulose fibres (regenerated rayon, Svenska Rayon AB) with cold oxygen plasma and characterised the interface in the system cellulose/linear low-density polyethylene (LLDPE). Using single fibre fragmentation tests they showed that after only 15 s of treatment the interfacial shear strength (IFSS) was increased by 200%. They also measured the surface free energies of treated and untreated fibres and reported that the surface free energy of treated rayon fibres was increased. Furthermore, they showed that the oxygen plasma treatment reduced the surface roughness. As a possible explanation for the significant improvement of the interfacial shear strength, they suggested that hydroperoxide groups, which are assumed to be intermediates in the formation of different oxygen-containing functional groups during oxygen plasma or corona treatment, may initiate grafting of the matrix chains on to cellulose. Felix *et al.* found support for their theory by analysing the surface of treated rayon fibres with X-ray photoelectron spectroscopy (XPS) and proved the existence of hydroperoxide groups on them that could initiate grafting of the matrix chains.

3.2.3 Mercerisation

Mercerisation is one of the oldest methods of treating cellulose textile fibres. It has been applied mostly to cotton textiles. At present there is also a tendency to use mercerisation for the modification of cellulose fibres, which are going to be used as reinforcing agents in composite materials. The treatment involves soaking the fibres in a dilute solution of sodium hydroxide (NaOH). Different degrees of modification are obtained by varying the concentration of the alkaline solution, the temperature and the length of treatment. The mercerisation treatment improves the fibre surface adhesive characteristics by removing natural and artificial impurities, thereby producing a rough surface topography. Additionally, X-ray scattering examination of native and mercerised cotton fibres has shown that mercerisation changes the cellulose crystalline form in a complex solid-state mechanism, increasing the amount of amorphous cellulose at the expense of crystalline cellulose (Ott, 1943). Mercerisation also leads to fibre fibrillation, that is, breaking down the composite fibre bundle into smaller fibres, increasing the effective surface area available for contact with the wet matrix. It is also known that mercerisation greatly enhances the reactivity (or accessibility) of cellulose (Lai, 1996).

Bisanda and Ansell (1991) applied this treatment to sisal fibre/epoxy composites. They were able to show that mercerisation greatly improves the resin pick up, i.e. the wettability, and causes a 21% rise in the compressive strength of the composite. Similar results were also reported by Boynard *et al.* (2003) for sponge gourd fibre (*Luffa cylinderica*) reinforced polyester composites. Fibre treatment with NaOH resulted in composites with enhanced flexural properties as compared with untreated fibre ones, and this was attributed to the removal of the outer surface layer and to extensive fibrillation.

Fibre fibrillation is an interesting alternative method of modifying the fibre surface. Karlsson *et al.* (1996) caused fibre fibrillation on regenerated cellulose by immersion in water with subsequent shaking, rather than mercerisation. They then showed that the fibrillation process does not significantly affect the mechanical properties of the fibre. They also showed, by applying the single fibre fragmentation test in the system cellulose/LLDPE, that the IFSS increased proportionally to the degree of fibrillation. In order to explain this increase they suggested that the fibrillation on the fibre surface improved the adhesion via better mechanical interlocking.

3.2.4 Heat treatment

Heat treatment involves heating the fibres or processing the composites at temperatures close to those at which the components of natural fibres begin to degrade. When cellulose is heated it undergoes physical and chemical changes. Physical properties affected include the enthalpy, weight, strength, colour and crystallinity. Chemical changes include reduction of the degree of polymerisation by bond scission, creation of free radicals, formation of carbonyl, carboxyl and peroxide groups (especially in the presence of air), evolution of water (dehydration) and carbon dioxide and finally, at elevated temperatures around 300 °C, decomposition (Shafizadeh, 1985). The thermal degradation of cellulose is strongly influenced by the ambient atmosphere and pressure, and the rate depends on whether degradation products are present (sealed systems) or are being removed continuously (open systems). The presence of reaction products can in turn accelerate the degradation process (Stamm, 1964). During the processing of cellulose-containing composites the degradation products are, at least partially, localised at the interface or diffuse into the polymer melt, where they may react with the polymer matrix and the cellulose fibre. The degradation products may cause oxidation of the polymer matrix, similar to that which is usually achieved by flame, corona or cold plasma treatments. The controlling factors of the treatment are the time, the temperature and the composition of the gaseous atmosphere in the oven.

Sapieha *et al.* (1989) investigated the mechanical properties of composites made of untreated cellulose fibres (alpha-cellulose, Sigma Chemical Co.) and low-density polyethylene (LDPE) as a function of processing parameters. They reported that the yield strength of the fabricated composites increased rapidly with the processing temperature and reached a maximum at 225 °C (for constant processing time). The increase in strength was accompanied by discoloration and the appearance of two infrared absorption bands at 1718 and 1735 cm^{-1}. These two bands are not typical of either polyethylene or cellulose. Sapieha *et al.* suggested that the two bands reflect the existence of ketonic, acidic and ester groups attached to polyethylene and/or cellulose, possibly formed because of thermal degradation of cellulose and oxidation of polyethylene. In another study Liu *et al.* (1994) characterised the interface in cellulose fibre/polystyrene (PS) composites. They used three different types of cellulose fibres: cotton, rayon and wood. One of the methods they used to modify the surface was heat treatment. They applied the microbond test and reported a slight improvement in the IFSS following heat treatment.

Concluding, heat treatment seems to be an interesting alternative and has many intriguing advantages, such as simplicity, low cost and no chemicals; it is also easy to carry out. The disadvantage is that it is a rather difficult method to fully control and needs high precision to achieve the desired effects.

3.3 Chemical methods for modification of surfaces

When two materials are incompatible it is often possible to bring about compatibility by introducing a third material that has properties intermediate between those of the other two to act as a compatibiliser. Compatibilisers are more commonly known as coupling agents. In addition, in many cases it is also often possible to alter the surface characteristics of materials after treatment with chemical agents. Considering natural fibres, several chemical methods have been employed, aiming at increased compatibility and improved adhesion with polymer matrices. These chemical methods can be divided into four major categories:

- esterification-based treatments;
- silane coupling agents;
- graft copolymerisation;
- treatments with various chemicals.

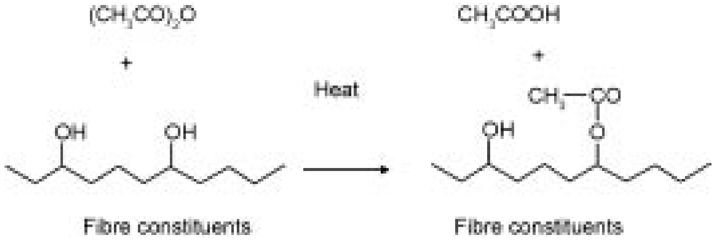
3.3.1 Esterification-based methods

Esterification-based methods refer to the use of a variety of chemicals that have the ability to form ester bonds with the fibre surface. Since cellulose fibre surfaces are rich in OH groups the chemicals used are carboxylic acids and their derivatives (anhydrides, chlorides, etc.). The main idea is to coat the OH groups of the fibres that are responsible for their hydrophilic character with molecules that have a more hydrophobic nature. Four chemical processes have been mostly employed for esterification: acetylation, benzylation, propionylation and treatment with stearates. Of these four methods, acetylation is by far the most popular. It is worth noting that treatment with maleic anhydride grafted polymers (such as polypropylene) also belongs to esterification, but since the chemical is a long chain polymer this method will be discussed in Section 3.3.3 on graft copolymerisation.

Hon and Chao (1993) modified wood fibres by benzylation and prepared composites with PS as a matrix. It is known that benzylation does not alter the shape of the fibres (Westerlind *et al.*, 1987). The benzylated cellulose fibres were prepared in a two-stage reaction. In the first stage, the fibres were immersed in a sodium hydroxide solution and alkali cellulose (mercerised) was formed. In the second stage benzylchloride was added, which after reaction yielded benzylcellulose. The degree of substitution can be varied by changing the reaction time at constant temperature. Using dynamic mechanical thermal analysis (DMTA), Hon and Chao demonstrated that polystyrene and benzylated wood fibres are compatible and fully miscible with one another. In another study Westerlind *et al.* (1987) produced benzylated rayon fibres for reinforcing isoprene rubber and reported that even a low degree of substitution, with a few benzyl groups in the surface structure, has a profound effect on the mechanical properties of the single rayon fibres. The untreated rayon fibre strength was 180 MPa and immersion of the fibres for 2 h in the NaOH solution reduced the tensile strength to 115 MPa. The introduction of benzyl groups to the structure further decreased the strength to 80 MPa at very low degrees of substitution, whereas higher degrees of substitution did not affect the fibre strength appreciably. Benzylation has one intriguing advantage: it promotes compatibility with polymers containing aromatic rings (e.g. polystyrene). This is due to the π–π interaction between the electrons of the benzyl molecule and the electrons of the aromatic ring of the matrix.

Acetylation is another method of modifying the surface of natural fibres and making it more hydrophobic. In addition, acetylation is one of the most studied reactions of lignocellulosic materials. Cellulose acetate was discovered in 1865, and partially acetylated cellulose products were commercialised as acetate rayon fibres and cellulose acetate plastics in the early 1900s (Billmeyer, 1984). The first attempt to acetylate wood flour and sawdust took place in 1928 (Rowell *et al.*, 1986). The principle of the method is to react the hydroxyl groups (–OH) of the fibre constituents with acetyl groups (CH_3CO–). The reaction is known to proceed to full esterification of all the three hydroxyls of anhydro-d-glucose when it is carried out in a homogeneous phase (i.e. when cellulose is dissolved), but in the case of fibres and wood where the reaction is heterogeneous that is very rarely the case (Nevell and Zeronian, 1985). Hence, a highly non-uniform product may be obtained. The reaction is catalysed by bases or acids and a large number of catalysts have been used in the past including pyridine, sulphuric acid, potassium and sodium acetate, γ-rays, etc. (Rowell *et al.*, 1986). However, the use of catalysts poses many problems. Strong mineral acids or acid salts are known to cause hydrolysis of cellulose resulting in damage of the fibre structure, and pyridine is toxic with a very unpleasant odour and difficult to remove after the reaction is completed.

The hydroxyl groups that react are those of the minor constituents of the fibre, i.e. lignin and hemicelluloses, and those of amorphous cellulose (Fig. 3.1) (Sjostrom, 1981). That is because the hydroxyl groups in crystalline regions with close packing and strong interchain bonding are completely inaccessible. Acetylation has been shown to reduce swelling of wood in water (Rowell, 1984), and also to be beneficial in reducing moisture absorption for natural fibres. Reduction of about 50% of moisture uptake for acetylated jute fibres and of up to 65% for acetylated pine fibres has been reported in the literature (Bledzki and Gassan, 1999). Liu *et al.* (1994) studied the effect of acetylation in natural-fibre composites (cotton, rayon, wood with PS as matrix) and they showed by using

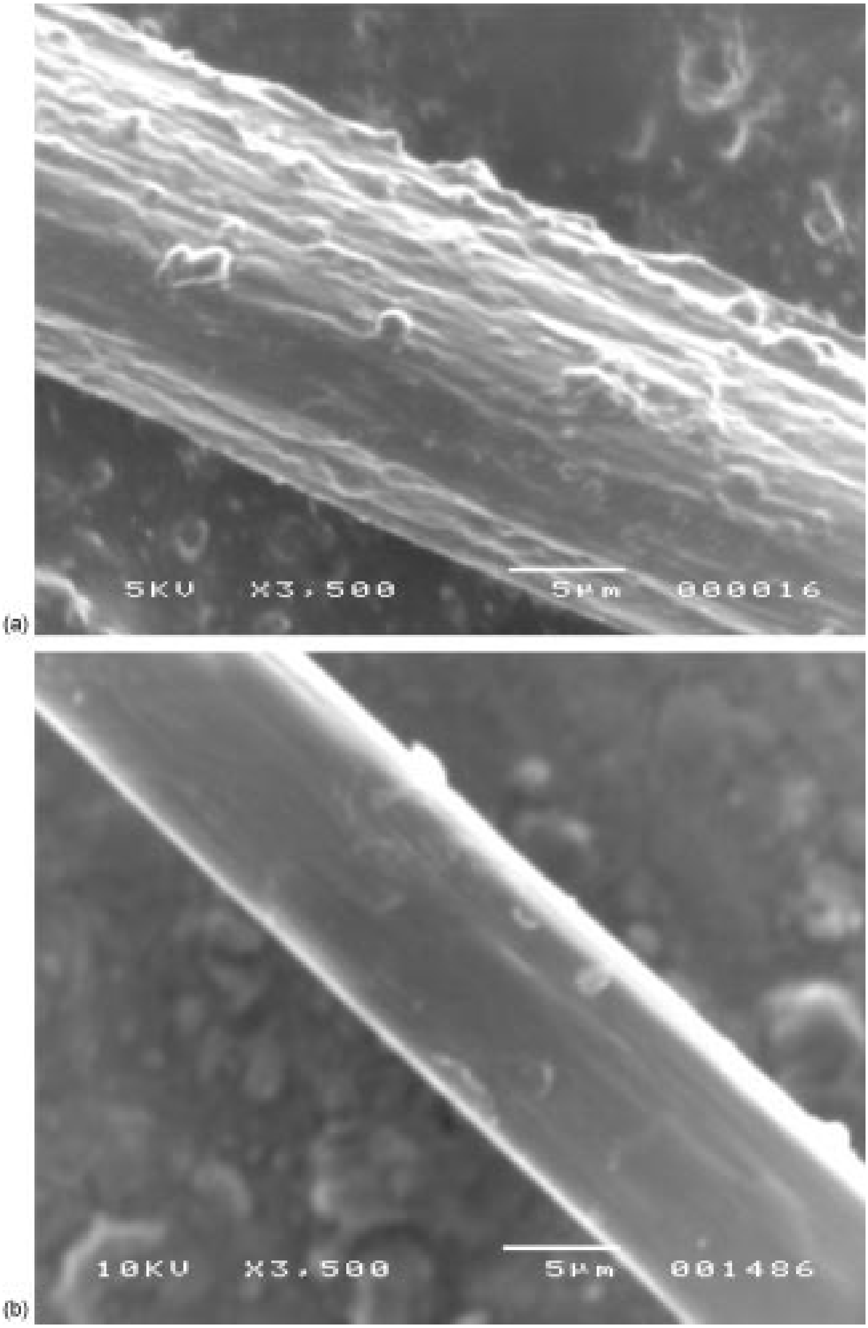


3.1 Schematic representation of the acetylation chemical reaction with cellulose fibre constituents.

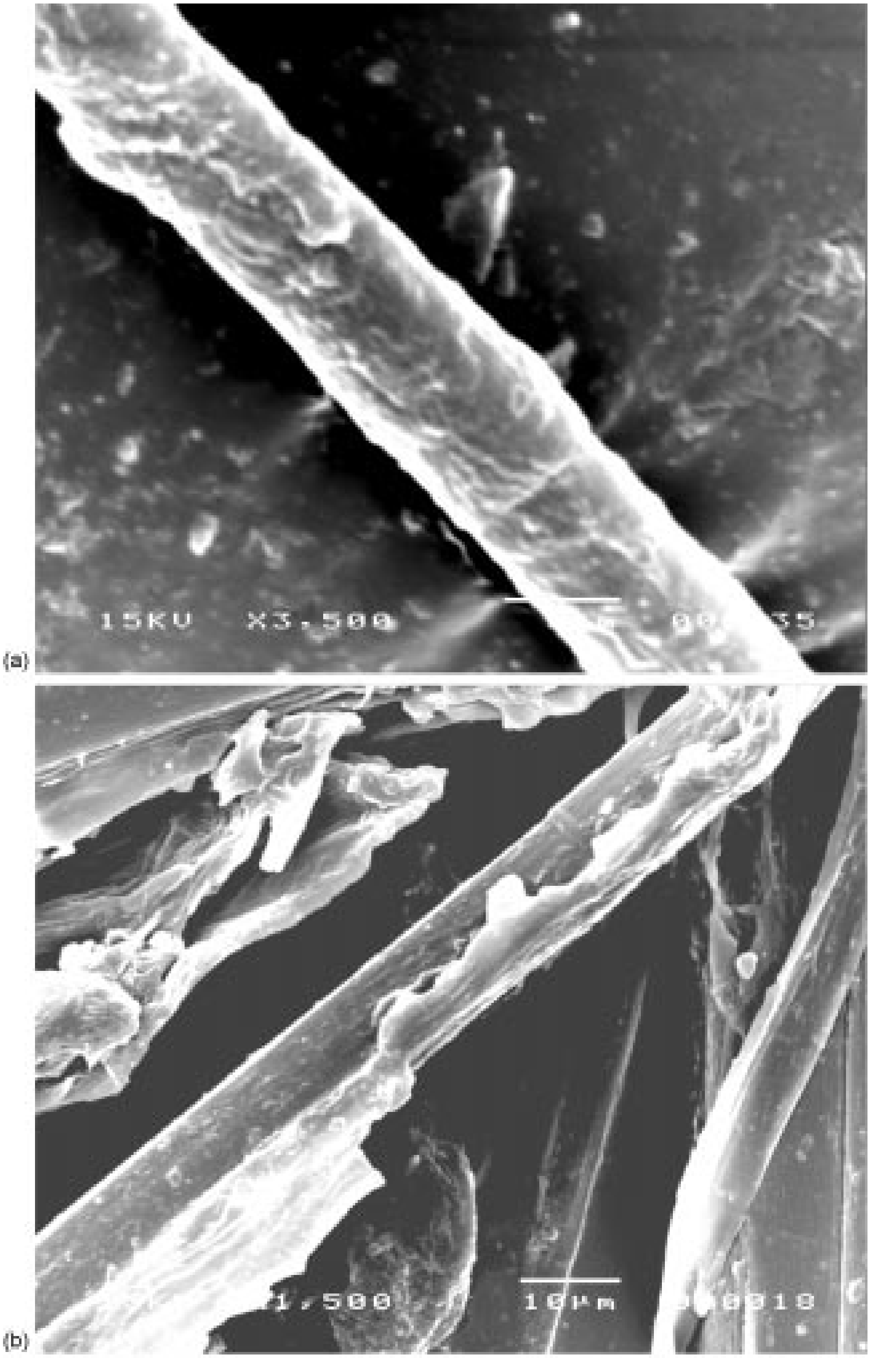
the microdebond test that acetylated fibres showed increased IFSS. Furthermore, they reported that acetylation increased the surface free energy of the fibres. Zafeiropoulos and coworkers conducted a systematic study on acetylation for improving adhesion in natural fibre composites (Zafeiropoulos *et al.*, 2002a,b, 2003; Tserki *et al.*, 2005a,b). The main fibres used were flax fibres but hemp and cotton were also investigated.

Acetylation resulted in profound changes for the fibres. In particular, the topography of the flax fibres was significantly altered after acetylation. In Figs 3.2 and 3.3 micrographs of two different grades of flax fibres may be seen, dew retted flax and 'green' flax, respectively. Dew retted flax is flax that has undergone retting, which is a bacterial process usually carried out after harvest in the field (Kirby, 1963). 'Green' flax is as-received flax from the harvest without any treatment. As seen in Fig. 3.2 the dew retted fibres have increased surface roughness, which is removed after acetylation. The situation differs though in the case of the green flax (Fig. 3.3). The as-received fibres are covered by a surface layer consisting of waxy substances (a result confirmed by XPS) (Zafeiropoulos *et al.*, 2003), which is completely removed after acetylation. This surface layer was found to have increased adhesion with polypropylene (Zafeiropoulos *et al.*, 2002b) but overall the interface was weaker because this layer acted as a weak boundary layer and failure occurred between this layer and the fibre, rather than at the interface between the fibre and the polymer matrix. In addition, it was found that acetylation increased the surface free energy of flax for both grades of fibre (dew retted and green) (Zafeiropoulos *et al.*, 2002a).

Experimental investigation of the untreated and treated flax fibres with XPS, Fourier transform infra-red spectroscopy (FTIR) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) revealed the presence of acetyl ester bonds on the surface of the fibres after acetylation (Zafeiropoulos *et al.*, 2003; Tserki *et al.*, 2005b). Hemp and cotton fibres also exhibited a stronger interface with polypropylene after acetylation and analysis with FTIR and XPS also revealed the presence of acetyl ester bonds on the fibre surface (Tserki *et al.*, 2005a,b). It is worth noting that acetylation was also found to yield flax fibres with enhanced thermal stability (Zafeiropoulos *et al.*, 2000). In particular, with the use of thermal gravimetric analysis (TGA) both the onset of degradation (that is the temperature when the material starts experiencing loss of weight) and the temperature at which 2% of weight loss was reached were found to be higher for the acetylated fibres as compared with the untreated fibres (Zafeiropoulos *et al.*, 2000). Additionally, when the fibres were kept at a temperature of 200 °C it was shown that the acetylated fibres were able to retain their stability for longer (Zafeiropoulos *et al.*, 2000), a feature that can be of paramount importance, since compounding with thermoplastic matrices is usually carried out at high temperatures above the melting point of the matrix. The results are summarised in Table 3.1 along with results on stearated fibres, which will be discussed later on in the present section.



3.2 SEM micrographs of untreated (a) and acetylated (b) dew retted flax fibres (reprinted with permission from Zafeiropoulos *et al.*, 2002a).



3.3 SEM micrographs of untreated (a) and acetylated (b) green flax fibres (reprinted with permission from Zafeiropoulos *et al.*, 2002a).

Table 3.1 Thermal stability results for treated and untreated flax fibres

(a) Dynamic TGA test

Type of flax	Initial degradation temperature T_i (°C)	Temperature at 2% weight loss (dynamic test) (°C)
Dew retted	236.2	226.3
Green	227.8	210.9
Acetylated dew retted	252.1	237.2
Acetylated green	230.2	227.4
Stearic acid treated dew retted	240.2	235.0
Stearic acid treated green	225.2	217.6

(b) Static TGA test (Ar atmosphere)

Type of flax	Percentage weight loss at 200 °C after 2 h	Time when 2% weight loss was reached (min)
Dew retted	2.6	73.4
Green	4.5	30.0
Acetylated dew retted	1.51	>120
Acetylated green	4.5	33.3
Stearic acid treated dew retted	2.51	53.9
Stearic acid treated green	3.83	49.1

(c) Static TGA test (Air atmosphere)

Type of flax	Percentage weight loss at 200 °C after 2 h	Time when 2% weight loss was reached (min)
Dew retted	3.61	45.2
Green	6.44	23.6
Acetylated dew retted	3.36	48.3
Acetylated green	6.4	26.2
Stearic acid treated dew retted	2.89	71.9
Stearic acid treated green	5.39	21.4

An investigation of the effect of acetylation on the strength of single fibres with single fibre tensile testing (Zafeiropoulos and Baillie, 2007; Zafeiropoulos *et al.*, 2007) revealed that acetylation had no significant impact on the fibre strength of flax fibres. The effect of surface treatments on fibre strength in natural-fibre composites is an important aspect that requires attention, since the fibre bulk structure may also be altered, especially when the treatment involves extended reaction times or aggressive chemicals. In such cases the result may be increased interfacial strength but decreased fibre strength, which can in turn result in composites with decreased mechanical properties. Finally, an extended investigation with the use of single fibre fragmentation testing using isotactic polypropylene (iPP) as the matrix (Zafeiropoulos *et al.*, 2003; Tserki *et al.*, 2005a; Zafeiropoulos, 2007) revealed that acetylation resulted in composites with enhanced stress transfer efficiency.

In the same manner it is possible also to use different acids and acid derivatives to achieve surface modification based on esterification. Tserki and coworkers (Tserki, 2005a,b,c, 2006a,b) modified different natural fibres (flax, hemp, wood and cotton) as well as wood flour using propionic anhydride (propionylation). The principle of the method is the same as with acetylation, the only difference being that propionic anhydride has one more methyl group than the acetic anhydride. FTIR and XPS experiments showed that ester bonds were present on the surface of the natural fibres after propionylation, confirming that the surface modification was successful (Tserki *et al.*, 2005b). Single fibre fragmentation testing using iPP as the matrix revealed that the interface stress transfer efficiency was significantly improved after propionylation. However, even though the effect of propionylation on hemp/polypropylene composites was similar to the effect of acetylation, acetylation was found to strengthen the interface more than propionylation in the case flax/iPP composites (Tserki *et al.*, 2005a). Zafeiropoulos and coworkers (2002a) modified flax fibres with the use of stearic acid. Stearic acid is a long chain fatty acid ($C_{17}H_{35}COOH$) that has been used in the past as a sizing agent in the paper-making industry (Swanson, 1978; Takeyama and Gray, 1982; Arnson *et al.*, 1989). FTIR (Swanson, 1978) and XPS (Takeyama and Gray, 1982) analyses have been employed to analyse stearated cellulose and the results indicated that stearic acid had formed stable ester bonds with the hydroxyl groups of cellulose. In these cases the sizing process was carried out in heterogeneous solutions having dissolved stearic acid in a solvent. However, the method developed by Zafeiropoulos and coworkers (2002a) involves sizing the fibres with the use of stearic acid vapours in order to eliminate the negative environmental impact of the solvents. The drawback of the vapour phase sizing method, however, is that stearic acid is most probably physically adsorbed on the fibre surface rather than forming stable ester bonds, due to its decreased reactivity. FTIR and XPS analyses were inconclusive as to if stable ester bonds had been formed, but ToF-SIMS revealed the presence of stearic acid molecules on the fibre surface (Zafeiropoulos *et al.*, 2003). Single fibre testing showed that at long treatment times the strength of flax fibres decreases during stearation (Zafeiropoulos and Baillie, 2007; Zafeiropoulos *et al.*, 2007). Single fibre fragmentation testing of flax/iPP model composites showed that the interface stress transfer is enhanced after stearation (Zafeiropoulos *et al.*, 2002b).

Esterification methods have the advantage that they are relatively straightforward to apply on an industrial scale. Depending on the chemicals used the treatment may have only a limited impact on the cost (e.g., acetic anhydride is a relatively cheap chemical). The main disadvantage of the method is, however, the use of chemicals which render the method ‘dirtier’ than physical modifications.

3.3.2 Silane coupling agents

Organosilanes are by far the largest group of coupling agents used today in the composites industry. They have been developed to couple glass fibres and virtually any mineral (mica, chrysotile, etc.) which is used to reinforce composites (Mittal, 1992). Most of the silane coupling agents can be represented by the following formula: $Y(CH_2)_nSiX_3$, where $n = 0$ to 3, Y is an organofunctional group usually selected for reactivity with a given matrix, and X is the hydrolysable alkoxy group on silicon.

The organofunctional organic group Y in the coupling agent causes the reaction with the polymer. This reaction could be copolymerisation and/or the formation of an interpenetrating network. The curing reaction of a silane-treated substrate enhances the wetting by the resin. Generally, silanes are very effective with thermosetting resins owing to the formation of covalent bonds between the Y group and the matrix during curing. In the case of thermoplastics, where the polymerisation process is finished, silanes do not contribute much to adhesion. However, if the organofunctional group has the potential to produce free radicals under certain conditions, e.g. by use of peroxide initiators, grafting with polymer chains may be achieved. In addition, silanes may reduce the number of hydroxyl groups on the surface of polar materials such as natural fibres rendering them more hydrophobic. Analogous to glass fibres, silanes have been used as coupling agents for natural fibre composites by several groups (Brebner and Schneider, 1985; Schneider and Brebner, 1985; Battaile *et al.*, 1989; Kokta *et al.*, 1989; Maldas *et al.*, 1989; Raj *et al.*, 1989a,b; Mieck *et al.*, 1995a,b; Rong *et al.*, 2001).

Kokta *et al.* (1989) sized wood flour with three different silanes, the A-172, A-174 and A-1100 (γ-aminopropyltriethoxy silane, Union Carbide). The concentration of silane was 3.0% by weight of the fibre. Composites from iPP and wood flour were prepared and their properties were evaluated. Silane treatment did not improve the mechanical properties of the composites. Tensile strength and elongation decreased, while the Young's modulus increased only by augmenting the filler concentration level. Daneault and coworkers sized wood fibres with silanes A-172, A-174 and A-1100, and prepared composites with PS (Maldas *et al.*, 1989) and LLDPE (Raj *et al.*, 1989b). They reported that the silane treatment did not increase, or only slightly increased, the mechanical properties of the composites. Mieck *et al.* (1995a) used silane treated flax fibres to reinforce iPP. They reported that although silanes with alkyl organofunctional groups did not improve the fibre–matrix adhesion, silanes that carry functional groups capable of reacting by formation of free radicals under processing conditions led to remarkable improvement. Mieck *et al.* used a methanol solution of A-172 silane (a silane that has a vinyl organofunctional group, i.e. contains a double bond able to produce free radicals) and dibutyl dilaurate of tin, and found a 60% increase in shear strength. As initiators they used dicumyl peroxide and dibenzoyl peroxide.

Silane treatments are relatively straightforward to apply and the chemistry involved is fairly well understood. However, the disadvantage of the method is that it still involves chemicals and silanes are relatively expensive agents, having a negative impact on cost.

3.3.3 Graft copolymerisation

The most effective and the most popular method for chemically modifying cellulose fibres is graft copolymerisation. This method involves the reaction of the cellulose molecules with appropriate substances such as styrene monomer, methyl methacrylate, acid anhydrides and isocyanates, which are compatible with the polymeric matrix. The reaction may proceed via two different mechanisms. In the first mechanism polymerisation is initiated on the fibre surface (e.g., by free radical). The free radicals are formed by 'cracking' the cellulose molecules, and this again can be done with several different ways. The second mechanism involves a direct reaction between the cellulose molecules and the chosen chemical compounds and is the most important.

Graft copolymerisation can be divided into the following three subcategories:

- Treatment with triazine coupling agents.
- Treatment with isocyanates.
- Treatment with maleic anhydride.

Treatment with triazine coupling agents

Zadorecki and Flodin (1985a) treated bleached softwood Kraft paper fibres (Klippans Finpappersbruck AB) with three derivatives of trichloro-s-triazine (2-octyloamino 4,6-dichloro-s-triazine, methacrylic acid, 3-(4,6-dichloro-s-triazine-2-yl) aminopropyl ester, 2-diallylamino 4,6-dichloro-s-triazine) and prepared composites by impregnating the fibres in unsaturated polyester resins. The tensile properties of composites prepared from treated and untreated fibres were studied before and after exposure to water. Zadorecki and Flodin measured the contact angles between the fibres and water and showed that all treatments resulted in hydrophobic surfaces (the contact angles changed from 0 to over 120 for untreated and treated fibres respectively). The tensile strength was increased after treatment under both dry and wet conditions. Scanning electron microscopy (SEM) micrographs of tensile fractured surfaces showed that for untreated fibres debonding occurred at the interface, while for treated fibres no debonding occurred and only fractured fibres were present. In another study Zadorecki and Flodin (1985b) investigated the interface of wood fibre/polyester composites under water exposure. Using UV microscopy, SEM and optical microscopy, they were able to show that deterioration of mechanical properties of cellulose/polyester composites is due to the formation of cracks at the interface during drying, but not during water absorption. However, when covalent bonds are present at the interface, as in the case of triazine treated fibres, then the formation of cracks is totally prevented.

Treatment with isocyanates

Isocyanates, characterised by the –N=C=O group, have been used extensively in the wood industry as binders from the late 1970s. The –N=C=O group is capable of reacting with almost any active hydrogen under either acid or, preferably, alkaline conditions. The most commonly utilised reaction of isocyanate chemistry is with a hydroxyl group to yield a urethane. The urethane structure, also called carbamate, is fundamental to many polymers utilising isocyanates. The reactions of isocyanates are strongly influenced by catalysts and temperature. Catalysts include most base metal complexes, including the organic compounds of tin, titanium, cobalt and lead (Johns, 1982).

Raj *et al.* (1988) used different isocyanates (polymethylene (polyphenylene) isocyanate (PMPPIC), toluene-2-4-diisocyanate (TDI), 1-6 hexamethylene diisocyanate HDI, ethyl isocyanate) as coupling agents in composites from LLDPE/wood fibres and high-density polyethylene (HDPE)/wood fibres. The effective role of isocyanates as bonding agents was demonstrated by the increase in stress and modulus values of the composites. For example in HDPE/wood fibres, composite strength at yield was increased from 11.2 MPa with untreated fibres to 31.9 MPa with treated fibres (for a fibre content of 40% wt in both cases). The PMPPIC-treated composites showed better results than other isocyanates and this was attributed to higher reactivity of polymeric isocyanate with the substrate. The isocyanate group forms covalent bonds, urethane bonds as mentioned before, with hydroxyl groups of cellulose. The other part of the isocyanate can be interlinked by van der Waals type of bonding with the hydrophobic polymer matrix.

Raj *et al.* (1989a) treated cellulose fibres with PMPPIC (Polyscience Inc.) and maleated propylene wax (Epolene E43, Eastman Chemicals) and prepared composites with LLDPE. The concentration of fibre in the composite was varied from 10 to 40% by weight. Raj *et al.* reported that composites with untreated fibres showed a decrease in tensile strength with increase in fibre concentration. In contrast, when PMPPIC treated fibres were used, the strength increased significantly, particularly at higher percentages of fibre in the composites. The increased strength was attributed to the formation of urethane bonds between the coupling agent and the cellulose fibres, and to the improvement of wetting that the PMPPIC coating provides in the composite. Maldas and Kokta (1989) studied the effect of ageing conditions on the mechanical properties of wood fibre/PS composites using isocyanates as coupling agents. The mechanical properties and dimensional stability of these composites were evaluated under various conditions, including variation of the testing temperature (from −40 °C to 25 ºC), exposure to boiling water and heating in an oven at 105 ºC. In all cases the treated fibre composites showed superior mechanical properties and dimensional stability compared with non-treated fibre filled composites. The enhancement of the mechanical properties of the composites at sub-zero temperature suggests that there was excellent interfacial contact between the cellulose fibre and polystyrene which are divergent in polarity. Again this was due to the formation of covalent bonds between the cellulose and isocyanate coupling agent which hydrophobises the fibre surface. Furthermore, because both PMPPIC and polystyrene contain benzene rings, an increased interaction between them is expected. That is due to the interactions of delocalised π-electrons of the benzene rings (van der Waals type of interactions) of both polymers.

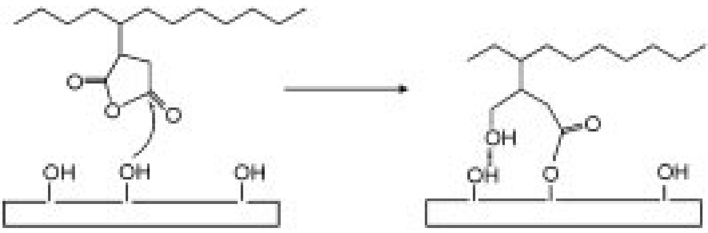
Isocyanate treatments have the advantage of allowing good control of the interfacial properties. However, the main drawback of the method is the toxicity of the chemicals involved.

Treatment with maleic anhydride

The most important and by far the most popular grafting method is the application of MA (maleic anhydride) modified polymers (and especially polypropylene) as compatibiliser in vegetable fibre composites. The nature of adhesion in this system has been studied thoroughly by Felix and Gatenholm (1991). They showed that chemical bonds, of esteric nature, as well as hydrogen bonds are formed between the MA functional groups of polypropylene and the hydroxyl groups of cellulose. The reaction scheme is shown in Fig. 3.4.

There are numerous studies in the literature in which the effect of MA grafting on the mechanical properties of vegetable fibre composites has been investigated and it is impossible to list all of them here. Hence, a few representative studies are discussed here with emphasis on earlier work, since in these studies the underlying mechanisms have been first described.

Shiraishi and coworkers (Kishi *et al.*, 1988; Takase and Shiraishi, 1989; Han *et al.*, 1989, 1991; Han and Shiraishi, 1990) prepared composites with cellulose fibres and MA grafted polypropylene (MAPP) and reported that the tensile



3.4 Schematic representation of the maleic anhydride chemical reaction with cellulose fibre constituents.

strength and Young's modulus were increased in comparison with composites without MA. They also showed by using TEM (transmission electron microscopy) that MAPP was localised on the surface of the fibres and had not penetrated the cell wall. Joly *et al.* (1996) studied the interface of treated cellulose fibres with MAPP/iPP composites and reported that the IFSS measured with the microbond test increased almost 70% in comparison with untreated cellulose fibre composites. Mieck *et al.* (1995b) prepared composites from MAPP treated flax and iPP and found that the tensile strength of the composites increased by 25% in comparison with that of the untreated flax/iPP composites. Hornsby *et al.* (1997) prepared composites from linseed flax fibres and iPP (25% wt) and MAPP (5% wt). They showed that the tensile strength of the composites with MAPP was increased by about 7%.

Treatment with MAPP also improves wetting of the fibres. The presence of grafted polymer chains on cellulose markedly reduces the polarity of the fibres and promotes wetting by the viscous polymer matrix. Apart from the positive effect that this treatment has on the interface it also positively affects processing of vegetable fibre composites. Owing to the reaction of surface cellulose hydroxyls there is a decrease in intermolecular hydrogen bonds between the fibres, which allows the fibres to be better dispersed in the matrix (Woodhams *et al.*, 1984). Mondragon and coworkers (Biagiotti *et al.*, 2004; Arbelaiz *et al.*, 2005) modified flax fibres using MA as well as MAPP and investigated the effect of these two treatments on the interface of flax/iPP composite materials. With the use of single fibre pull-out tests they showed that the interface was marginally improved for the MAPP-treated samples (the IFSS increased from 7.77 to 8.94 MPa), but for the treatment with maleic anhydride alone they observed a marginal decrease in the IFSS (from 7.77 to 6.06 MPa). Contact angle measurements revealed that both treatments reduced the total surface free energy of flax fibres, but the treatment with MAPP reduced also the polar component of the surface free energy from 19.87 to 1.41 mJ/m^2, rendering the flax fibres very apolar.

Treatment with MA polymers is probably the best available method for natural-fibre composites. The chemistry and the mechanisms involved in the modification of the interfacial properties are not well understood, but the treatment consistently delivers composites with superior properties. The main drawback of the treatment is that it increases cost.

3.3.4 Various chemical treatments

Apart from the well-known and popular surface treatments, i.e. graft copolymerisation and silanes, that will be described later on in this chapter, research groups have tried many other chemical methods aiming to enhance the adhesion in natural-fibre composites. The present section presents a concise overview of the most notable but somewhat rare different chemical methods that have been employed in natural-fibre composites.

Hua and coworkers (1987a,b) used formaldehyde and dimethylomelamine (DMM) to modify the surface of cellulose fibres and manufactured composites with polyester as a matrix. Both treatments reduced the water absorption of composites (the water uptake of the composites was reduced by 46 to 52%, with respect to the initial water uptake). The wet strength of the composites improved by more than 50%. TEM micrographs (Hua *et al.*, 1987b) showed that the major part of the melamine resin had penetrated into the cell wall of fibres and reacted with the cellulose molecules, which caused the reduction of water sensitivity.

Sterzynski *et al.* (1995) treated flax fibres with dimethylurea (DMU) and prepared composites with iPP. Mechanical tests showed that strength at yield, tensile modulus and elongation at yield were increased with increasing DMU content deposited on the fibres. Furthermore, they observed that treatment with DMU led to a better dispersion of flax fibres in the matrix. The latter may be explained from the reaction of DMU with the OH groups of the fibres that subsequently almost eliminated any fibre–fibre interaction resulting from intermolecular hydrogen bonds.

The use of phenol formaldehyde (PF) resin as a compatibilising agent for cellulose fibres is also very interesting. PF resin is chemically similar to lignin. It contains methylol groups that can react with hydroxyl groups, forming stable ether bonds, while at the same time it contains hydrophobic polymer chains. Chtourou *et al.* (1991) coated wood fibres with PF resin and used them as a reinforcing agent in recycled polyolefins from domestic wastes (4.7% PP, 95.3% PE). The water uptake of composites was found to decrease after PF treatment. After 80 days in water at ambient temperature, the moisture content of the treated fibre composites was about 50% lower than that of the non-treated fibre composite.

3.4 Engineering the interface through control of processing conditions

Even though fibre surface treatments and compatibilisers are the most popular methods for engineering the interface in composites, in certain cases processing can also influence the interface to a great extent. When a fibre is embedded into a thermoplastic melt it may act as a nucleating site for the growth of spherulites. If there are many nucleation sites along the fibre surface, then the resulting spherulite growth will be restricted in the lateral direction, so that a columnar layer, known as transcrystallinity (Keller, 1995), will develop and enclose the fibre. The occurrence of such a layer has been reported for a large combination of semicrystalline thermoplastic matrices and fibres and a full review of the phenomenon may be found in Quan *et al.* (2005). The most intriguing aspect of transcrystallinity is its effect on the interface in composites. Even though a large number of studies have been conducted on transcrystallinity, the phenomenon is still rather poorly understood. In the past many factors have been proposed to explain why transcrystallinity develops, the main ones being:

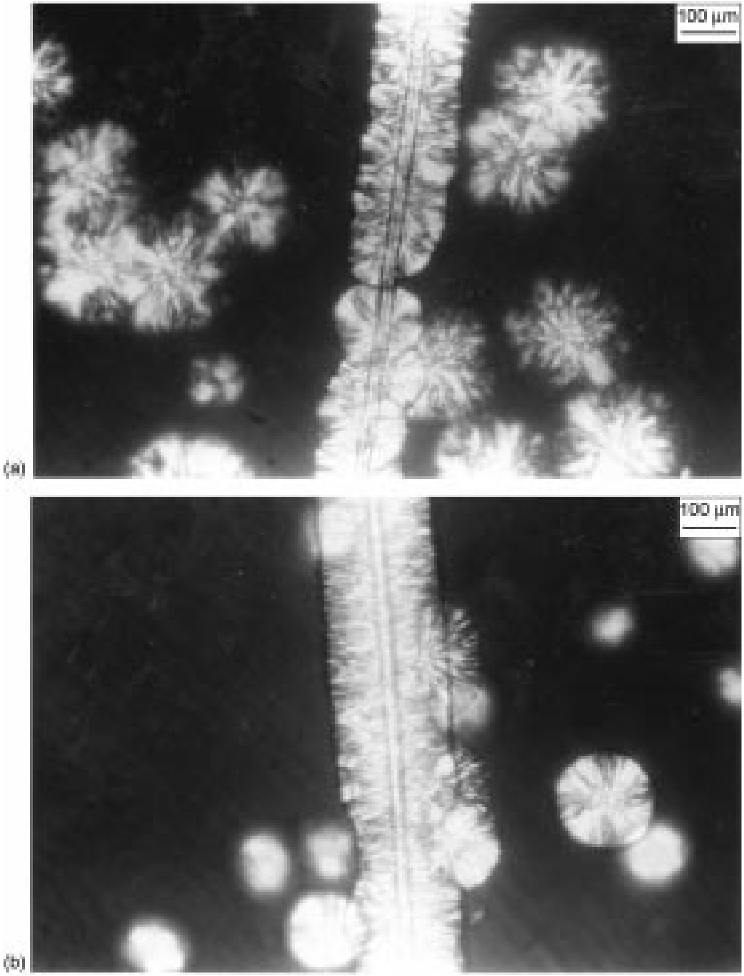
- fibre surface topology;
- fibre surface free energy;
- fibre surface chemistry;
- crystallinity of the fibre surface;
- adsorption of nucleating agents present in the polymer matrix;
- temperature gradient at the interface;
- application of shear to the polymer melt.

While in specific isolated cases, any of the above factors may be dominant, there is no evidence that these factors are of universal validity. However, there is one factor that has been identified as generally inducing transcrystallinity and this is the application of shear to the polymer melt. The generality of the factor has led many researchers to the conclusion that there must always be some sort of shear, either intrinsic at the interface, or external (e.g., due to processing), for transcrystallisation to take place (Cai *et al.*, 1997). Apart from the questions about the origin of transcrystallisation, there are also significant questions about the structure of the transcrystalline layer, but a full discussion of the phenomenon goes beyond the scope of the present chapter and the reader is referred to the review article of Quan *et al.* (2005).

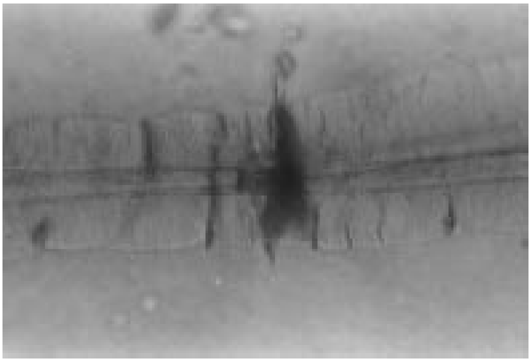
In the case of natural fibres there are abundant nucleation sites on the surface, because the main constituent is cellulose, a highly crystalline natural polymer. The ability of cellulose fibres to induce transcrystallinity has been reported by several research groups (Gray, 1974; Quillin *et al.*, 1993; Felix and Gatenholm, 1994; Bhattacharya and Shembekar, 1995; Wolcott *et al.*, 2000; Sanadi and Caulfield, 2000; Zafeiropoulos *et al.*, 2001a,b). The crystalline structure of cellulose fibres has been identified as playing a significant role in transcystallinity. Gray (1974) conducted the first study on transcrystallinity in natural-fibre composites and he demonstrated that although a variety of natural fibres consisting of native cellulose induced transcrystallinity in iPP, mercerised fibres did not. Gray attributed this different behaviour between native cellulose and mercerised cellulose to the difference in their crystalline structures. It is well known that regenerated cellulose has a different structure (Cellulose II) from that of natural cellulose (Cellulose I) and that mercerisation alters the structure from Cellulose I to Cellulose II. Similar results were also reported by Quillin *et al.* (1993).

A more systematic study was conducted by Felix and Gatenholm (1994) for highly purified cotton fibre/iPP. By applying the single fibre fragmentation test, Felix and Gatenholm showed that there is an increase of the IFSS of the order of 100% when transcrystallinity is present in the system. They attributed this increase to augmented interactions between the fibre and the matrix because of the transcrystalline layer. They suggested that under isothermal crystallisation the iPP chains have time to obtain the most favourable conformation and, because the crystal structures of cellulose and iPP are matching, there is an increased van der Waals interaction between the α-carbon/methyl moieties of the iPP and the oxygen atoms in the electron rich glucosidic linkages in cellulose.

Zafeiropoulos *et al.* (2001a,b) investigated the effect of transcrystallinity on the interface in flax fibre/iPP composites and observed a significant strengthening of the interface when transcrystallinity was present. Besides the case of the untreated flax fibres, surface modifications such as stearation also induced transcrystallinity (Fig. 3.5). Single fibre fragmentation testing revealed that the



3.5 (a) Micrograph showing the creation of a transcrystalline layer around dew retted flax in polypropylene at 145 °C (60 min) (reprinted with permission from Zafeiropoulos *et al.*, 2001a); (b) Micrograph showing the creation of a transcrystalline layer around stearic acid treated dew retted flax in polypropylene at 145 °C (60 min) (reprinted with permission from Zafeiropoulos *et al.*, 2001a).



3.6 Micrograph of the fibre breaks in flax fibre/polypropylene model composites in the presence of a transcrystalline layer (courtesy of N. E. Zafeiropoulos, 2001).

IFSS increased from 12.75 MPa for the samples without transcrystallinity to 23.05 MPa for the transcrystallised samples. In addition to the interfacial stress increase, post-mortem examination of the tested samples with optical microscopy revealed extensive cracking inside the transcrystalline layer (Fig. 3.6). This phenomenon of extensive cracking of the transcrystalline layer has been identified previously by Wagner *et al.* (1992) in the system iPP/glass fibre and was termed 'treeing failure'. The damage consists of an interlamellar crack within the transcrystalline zone, which eventually propagates through spherulites in the matrix.

3.5 Experimental methods for assessing the interface

As has been discussed previously a thorough knowledge of the microstructure–property relationship of the interface region is an essential key to the successful design and proper use of composite materials. It is very desirable to have a reproducible, reliable method for investigating and measuring fibre–matrix adhesion. Several testing methods have been developed for measuring the fibre–matrix adhesion using single fibres. The goal was to measure fibre–matrix adhesion in a way that would be a predictor of composite fibre–matrix adhesion, as well as to understand the fundamental physics and chemistry of adhesion itself. Four main single fibre tests are in existence and being used by most of the research groups investigating the interface of composites. They are the single fibre pull-out test, the microbond or microdebond test, the push-in or micro-indentation tests, and the single fibre fragmentation test. Out of these tests the micro-indentation test has hardly been used on natural-fibre composites and, hence, it will not be discussed in the present chapter. All interfacial tests are summarised in the book of Kim and Mai (1998), to which the interested reader is referred for more information. Finally, natural fibres present certain peculiarities in comparison with synthetic fibres that make the application of single fibre model composites testing trickier. The main reason for this is the high heterogeneity of natural fibres, especially in terms of fibre diameter. Practically all data analysis schemes for model single fibre testing require a constant diameter in order to extract either the interfacial shear stress (τ) or a critical interfacial energy release. The present section discusses interfacial tests and addresses the special aspects concerning natural-fibre composites.

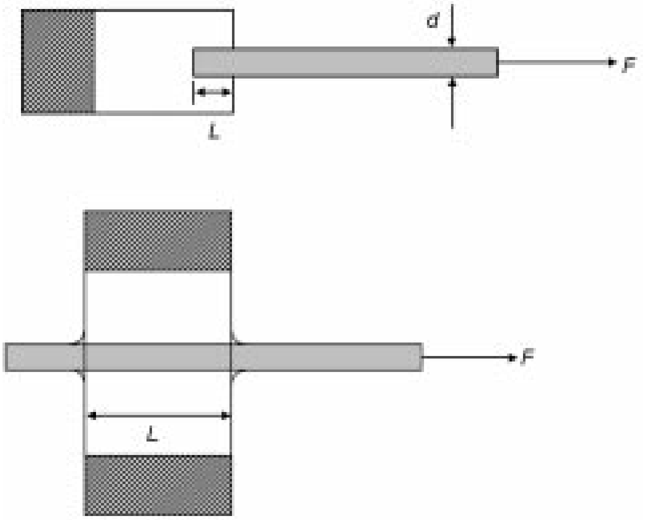
3.5.1 Single fibre pull-out

The pull-out test (Narkis *et al.*, 1988; Drzal and Herrera-Franco, 1990; DiFrancia *et al.*, 1996) is the earliest of the single fibre tests. In this test a single fibre is embedded in a block of matrix (Fig. 3.7). The free end is gripped and an increasing load is applied as the fibre is pulled out of the matrix while the load and displacement are measured. The maximum load, F, measured before detachment of the fibre from the matrix is related to the average value of the fibre–matrix shear strength, τ, through the equation

$$F = \tau\pi dL \tag{3.1}$$

where πd is the fibre circumference and L is the embedded fibre length.

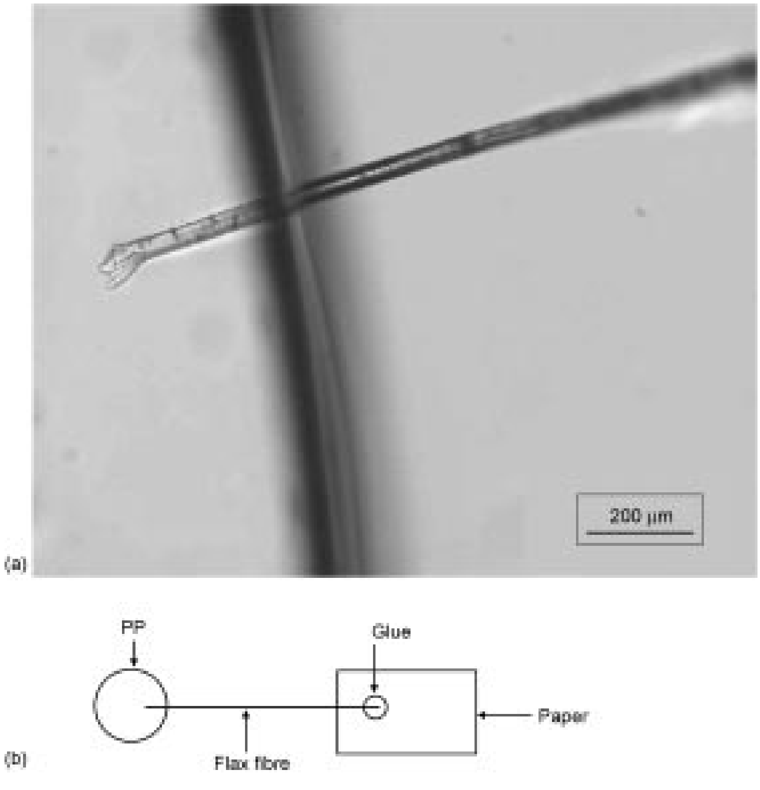
In principle, this is a direct measurement method, but closer inspection shows that the stress at the juncture of the fibre and the matrix creates a normal tensile interfacial force not encountered in an actual composite (DiFrancia *et al.*, 1996). The normal tensile force can act on the interface to reduce the measured shear strength. If the length of fibre embedded in the block of matrix is longer than the



3.7 Schematic representation of the single fibre pull-out test.

critical transfer length for that fibre–matrix combination, the fibre will fracture within the matrix block. This requires the fabrication of thin discs of matrix or very precise control of the depth of the fibre end, because fibre length-to-diameter ratios (aspect ratios) of 50–100 are typical. For 10 μm diameter fibres, this means that the matrix thickness, or fibre end location in a matrix block, should not exceed 500 μm to avoid fibre fracture. It needs to be noted that eq. 3.1 assumes a linear stress transfer profile and more sophisticated models have been developed in the literature to provide more accurate estimations of the average interfacial shear strength τ_i (Kim and Mai, 1998).

Single fibre pull-out is a method that has also been employed with natural-fibre composites by several research groups (Stamboulis *et al.*, 1999; VandeVelde and Kiekens, 2001; Joseph *et al.*, 2002; Manchado *et al.*, 2003; Herrera-Franco and Valadez-Gonzalez, 2005; Arbelaiz *et al.*, 2005; Li *et al.*, 2005; Arbelaiz Garmedia, 2006). A typical arrangement of the test can be seen in Fig. 3.8. The main problem with the test, however, is the high degree of heterogeneity of natural fibres.



3.8 (a) A single flax fibre embedded in molten polypropylene. (b) Schematic diagram of the single fibre pull-out specimen (courtesy of A. Arbelaiz Garmedia, 2006).

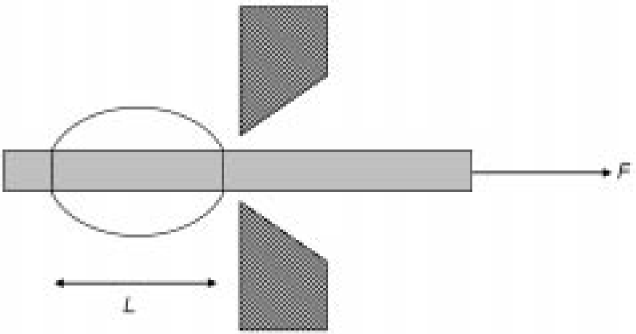
3.5.2 Microbond test

The microbond test, developed by Miller and Gaur (Miller *et al.*, 1987; Gaur and Miller, 1989), is a variation on the pull-out method, adapted to be more suited to the smaller diameter fibres now in use. Instead of embedding the fibre into a resin block, a small droplet of resin is applied to the fibre. This is normally achieved either with a syringe, if the matrix is thermosetting, or by passing a fibre through a small thin film containing a slit so that the fibre is perpendicular to the film surface. Afterwards the whole system is heated so that the thin film melts and produces a small droplet on the fibre. This latter technique is applicable for thermoplastics. Testing is conducted by positioning the specimen between two knife-edges (Fig. 3.9). A tensile force is applied to one of the free fibre ends which pulls the resin droplet against the knife-edges, transferring the load to the interface. The same equation as in pull-out is used to calculate the IFSS from the applied load. The most serious limitation of the test is that droplets as small as 30 μm are often necessary to prevent the fibre breaking when interfaces are well developed. Such an extremely small polymer droplet is often difficult to produce. Additionally the test is applicable with very soft matrices.

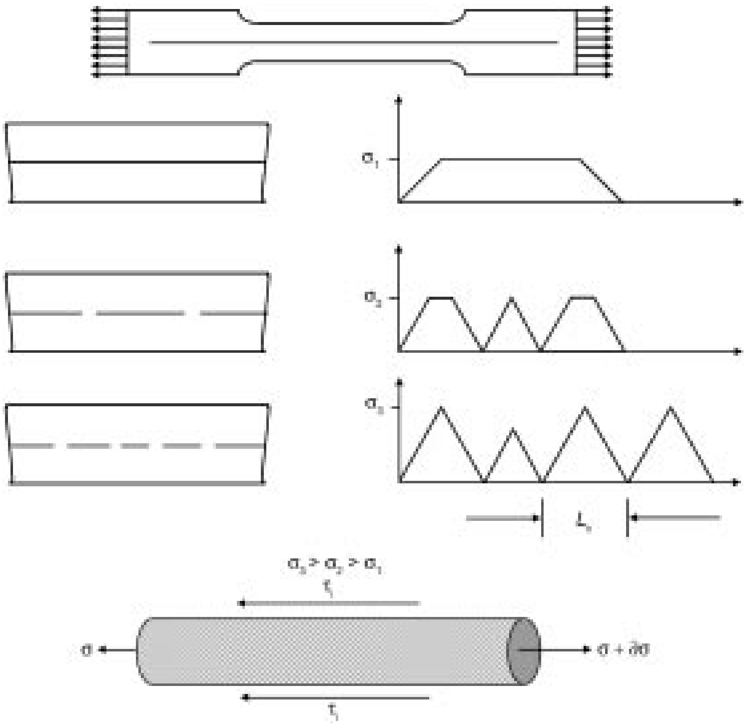
The test has been employed on natural fibre composites, albeit not as much as the single fibre pull-out test (Luo and Netravali, 2001; Eichhorn and Young, 2004; Mottershead and Eichhorn, 2007). An interesting aspect of the test is coupling it with Raman spectroscopy, which is a very powerful method for studying composite interfaces (Eichhorn and Young, 2004; Mottershead and Eichhorn, 2007).

3.5.3 Single fibre fragmentation test

The fibre fragmentation test was originally developed for use with metals containing brittle fibres by Kelly and Tyson (1965) and has been adopted in polymer matrix composites to become one of the most widely used of the



3.9 Schematic representation of the microbond test.



3.10 Schematic representation of the single fibre fragmentation test.

interface tests. Specimens consist of a single fibre encapsulated in a small dog-bone shaped coupon of matrix as shown in Fig. 3.10. The specimen is subjected to an increasing tensile load, which is transferred to the fibre through the fibre–matrix interface. Since the strain to failure of the matrix is greater than that of the fibre, fibre fracture will occur within the matrix coupon without complete failure of the matrix. As the load is increased the fibre will continue to fracture, producing progressively shorter fragments, until the fragments reach such a length that no further fractures can occur. This situation is defined as saturation in the fibre fragmentation process. The shortest fibre length that can break on application of stress is defined as the critical fibre length, L_c. Owing to the statistical nature of fibre strength, a single fibre does not break into fragments of equal size, and a wide variation in fragment lengths is observed. The fragment lengths for transparent matrix composites can be measured using a conventional optical microscope. An average IFSS can then be estimated on the basis of the constant shear model proposed by Kelly and Tyson (1965). In this model it is assumed that at saturation all the fragments are totally debonded so that the IFSS is constant. A simple balance of forces yields an expression for the average interfacial shear strength, τ_i, in terms of the fibre strength, σ_f, and the fibre diameter, d, for the case of a plastic matrix:

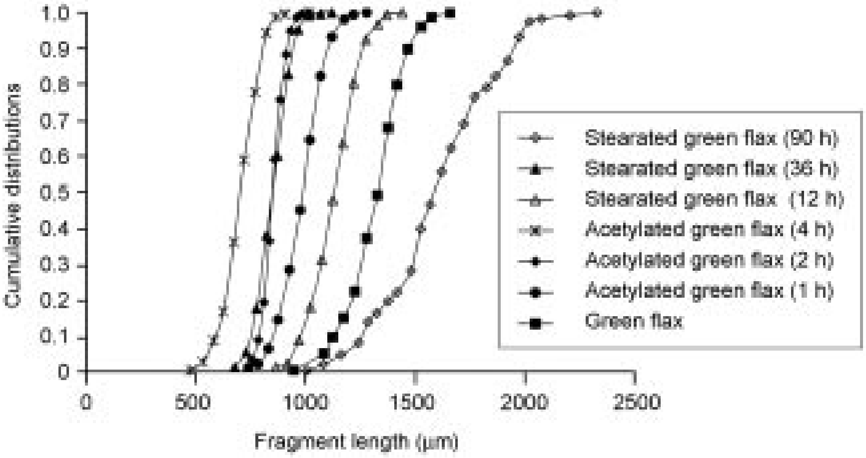
$$\tau_{\mathrm{i}} = \frac{\sigma_{\mathrm{f}}}{2}\left(\frac{d}{L_{\mathrm{c}}}\right) \tag{3.2}$$

A number of shortcomings are apparent in the use of this relationship. Firstly, the value L_c does not take into account the complex distribution of fragment lengths. Secondly, the term σ_f refers to the fibre strength at the critical length and this is not easily measured experimentally. Finally, the entire expression is based on the simplistic model of a linear stress transfer profile. Several more sophisticated methods of data analysis for single fibre fragmentation based on either stress analysis or fracture mechanics have been proposed in the literature and a detailed discussion of these models is provided by Kim and Mai (1998).

Single fibre fragmentation has been employed by several researchers as a tool to investigate the interface in natural fibre composites (Tripathy *et al.*, 2000; Zafeiropoulos, 2001b,c, 2002b; Joffe *et al.*, 2003; Torres and Cubillas, 2005; Herrera-Franco and Valadez-Gonzalez, 2005; Tserki *et al.*, 2005a; Zafeiropoulos, 2007). However, the fibre heterogeneity which is often encountered in natural fibres poses significant difficulties in the interpretation of the data. In particular, natural fibres often have varied diameter across the whole fibre length and this aspect creates significant problems in the application of stress analysis or fracture mechanics approaches for calculating the IFSS or the interfacial critical energy release. This drawback may be tackled through the use of a stochastic approach of data reduction.

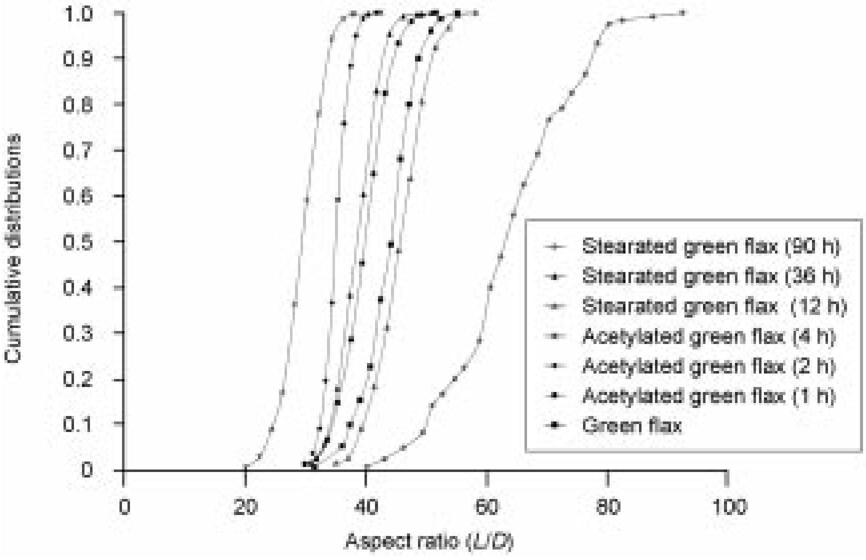
Fraser *et al.* (1983) suggested a different approach for data analysis instead of calculating the IFSS. Through computer simulation of the fragmentation process and assuming random distribution of flaws along the fibre, they were able to demonstrate dependence between the cumulative fragment length distribution and the efficiency of the stress transfer at the interface. Stronger interfaces will allow higher axial stresses to be built on the fibre and they will eventually result in smaller fibre fragment lengths. Once the fibre fragment length cumulative distributions are plotted, systems with stronger interfaces will exhibit shifts of these plots to smaller fragment lengths. In this manner the effect of surface treatments can be indirectly identified without the need of stress analysis or fracture mechanics approaches and variations due to fibre heterogeneity are included within the plots.

A typical example may be seen in Fig. 3.11 for flax/polypropylene composites. The significant fibre diameter variation may be taken into account by plotting the cumulative distributions of the aspect ratio (length/diameter) instead of the fibre fragment lengths as shown in Fig. 3.12. However, this data analysis can only be applied under certain conditions. In particular, the fibre strength must remain unaffected from the application of surface treatments otherwise single fibre fragmentation will also result in smaller fibre fragment lengths. In addition, the fragment length is strongly dependent not only on the interfacial strength and the fibre strength, but also on other properties such as the matrix



3.11 Cumulative distributions of fragment lengths for treated and untreated GR fibres (reprinted with permission from Zafeiropoulos *et al.*, 2002b).

shear yield strength, the difference in Poisson ratios between the fibre and the matrix, and the mode of failure of the fibre (Kim and Mai, 1998). However, if the conditions remain the same between the different samples and the only change is the introduction of specific surface treatments, then the method of Fraser *et al.* is a valuable tool for assessing the effect of these surface treatments.



3.12 Cumulative distributions of fragment aspect ratio (length/diameter) for treated and untreated GR fibres (reprinted with permission from Zafeiropoulos *et al.*, 2002b).

A detailed discussion on the application of the Fraser *et al.* method has been given by Zafeiropoulos *et al.* (2002) and Zafeiropoulos (2007).

The single fibre fragmentation test is a powerful tool for providing information about the interface. From all the available single fibre tests the single fibre fragmentation is the one that represents most closely the actual situation that the fibre will find in the composite. The test can also provide additional information about the modes of interfacial failure that help to further understand the nature of the interface. Finally, this test is the only one where the significant heterogeneity of natural fibres is taken into account.

3.6 Complementary techniques for indirect interfacial assessment

The nature of adhesion cannot be determined only from mechanical testing but supplementary analyses are necessary. Such complementary techniques provide additional information about the chemical composition of the surface, its wetting behaviour, etc., that, coupled with the mechanical assessment of the interface, can shed more light on the structural characteristics of the interface. The most prominent of such techniques are XPS, and ToF-SIMS. Other important techniques such as infrared spectroscopy, SEM fractography and surface energy analysis are not discussed here. The reason for this omission is that IR and SEM are mostly related to bulk rather than surface properties and, hence, provide only indirect information. On the other hand, surface energy analysis is more directly related to adhesion, but a full discussion of the technique requires significant space which is not available here. The interested reader is referred to the comprehensive books of Garbassi *et al.* (1998) and of Mittal (2006) for a full discussion of the topic.

3.6.1 X-ray photoelectron spectroscopy

XPS is a well-established surface analytical technique that relies on the photoelectric effect. The main principle of the technique relies on the fact that an incident X-ray may cause the emission of a core electron of a molecule of the material, provided that it possesses enough energy. This threshold energy value is dependent on the binding energy of the electron, and the intrinsic work function of the spectrometer employed. When the material is irradiated with an X-ray beam of known wavelength, and the kinetic energy of the ejected electron is measured, then the binding energy that the electron experienced in the atom in which it resided may be calculated. The binding energy of a core electron is characteristic of that element and, hence, XPS is a powerful tool for deducing the chemical constituents that are present in a material. Although the incident X-ray photon may penetrate and excite photoelectrons to a depth of several hundred nanometres, only photoelectrons from the outermost layers have a chance of escaping from the material environment and eventually being measured. Most XPS measurements of solids generate useful information from only the outer 2–10 nm of the surface layer. All elements except H and He can be detected using MgKα or AlKα radiation (the most widely used X-ray sources in XPS), with binding energies generally falling between 2 and 1000 eV. For organic systems, such as natural fibres, three elements are of particular interest: C, N and O. Owing to the increase in electronic charge of the nucleus, the binding energy of electrons in the 1s shell is 285, 399 and 532 eV respectively, giving a separation of at least 100 eV between the relevant peaks.

Apart from identifying an element on the surface, XPS also yields useful information about the state of the element present in the spectrum. For organic spectra this is most notably observed in the C 1s envelope. A slight shift in the binding energy of between 0.5 and 6 eV is observed for a carbon atom bonded to a heteroatom. This effect is known as the chemical shift, and it is the electron withdrawal power of the heteroatom that affects the magnitude of the shift. A carbon atom in a $\underline{\mathrm{C}}$–C or $\underline{\mathrm{C}}$–H will appear at ≈285 eV whereas a $\underline{\mathrm{C}}$–OH moiety will be shifted to ≈286.5 eV. A carbon atom that is present as O–$\underline{\mathrm{C}}$–O or $\underline{\mathrm{C}}$=O will be shifted further to the high-energy binding side of the C 1s envelope. This shift arises because the valence electrons are shared somewhat unequally between the carbon and the more electronegative oxygen atom, and this has a slight effect on the core electron orbitals. This effect can show the ratio of carbon atoms in the different environments possible in organic molecules. A full discussion of the principles and instrumentation of XPS may be found in a number of specialised modern textbooks (Briggs and Seah, 1988; Garbassi *et al.*, 1998; Watts, 1990; Woodruff and Delchar, 1994; Briggs, 1998).

XPS has been used in the past by many researchers to study the surface chemistry of mainly wood, paper and regenerated cellulose fibres (Dorris and Gray, 1978; Gray, 1978; Takeyama and Gray, 1982; Zadorecki and Flodin, 1985a; Zadorecki and Rönnhult, 1986; Hua *et al.*, 1987b; Carlsson and Ström, 1991; Felix and Gatenholm, 1991; Felix *et al.*, 1993, 1994; Gellerstedt and Gatenholm, 1999; Wistara *et al.*, 1999; Baiardo *et al.*, 2002; Fardim and Durán, 2003; Fras *et al.*, 2005; Freire *et al.*, 2006) The first published studies date back to 1974 when Soignet *et al.* (1974) showed that free amine and amine hydrosalts were present in diethylaminoethyl cottons. Soignet *et al.* (1976) in a subsequent study used XPS to study the deposition of surface finish and flame-retardant chemicals again on cotton fibres. In a more extensive study Gray and coworkers (Dorris and Gray, 1978; Gray, 1978; Takeyama and Gray, 1982) used XPS on paper and wood fibres of different qualities and they identified that filter paper had an O/C ratio very close to the cellulose value (0.83), while wood fibres exhibited a somewhat lower O/C ratio (between 0.62 and 0.72), indicating the presence of other chemical substances than cellulose on their surface. Dorris and Gray (1978) also studied lignin from two different sources (spruce milled-wood lignin and spruce dioxane lignin) and on two different substrates (on glass and on filter paper) and they showed that the O/C ratios varied from 0.31 to 0.36. Takeyama and Gray (1982) used XPS to study the reaction of stearic acid with filter paper. They observed a reduction of the O/C ratio from 0.79 (untreated paper) to 0.61 (stearic treated paper), which after soxhlet extraction increased to around 0.71. The fact that the O/C ratio of treated fibres remained below the untreated one after the extraction indicates that the stearic acid has reacted with the fibre surface.

Zafeiropoulos and coworkers (Zafeiropoulos *et al.*, 2003; Tserki *et al.*, 2005b) studied the surface chemistry of esterified (acetylated, propionylated and stearated) natural fibres using XPS. The experiments revealed that as-received flax fibres were covered with a layer of hydrocarbon nature, since the fibres presented an O/C ratio of 0.22. The absence of any features linked with aromatic compounds indicated that lignin was very low in these fibres. Subsequent analysis of acetylated and stearated fibres revealed that acetylation led to a slight increase of the O/C ratio, while stearation decreased it. The high-resolution spectra of the C 1s envelope revealed the introduction of ester bonds in the acetylated fibres that were not present in the unmodified fibres. The identification of the 'fatty' in nature layer on top of the flax fibres was significant in understanding the nature of adhesion in flax fibre/iPP composites. In this case, even though the unmodified flax fibres exhibited a higher affinity to the matrix (Zafeiropoulos *et al.*, 2002a) they formed a weaker interface with the matrix (Zafeiropoulos *et al.*, 2002b). The reason for this discrepancy was the fact that the outer layer of the untreated flax fibres was more compatible with the matrix chemically, but acted as a weak boundary layer, thus leading to a weaker interface. However, ester bonds could not be identified for the stearated fibres.

XPS is a powerful technique for surface characterisation that should be employed when the interface is studied. The technique does not only provide information about the effect of surface treatments but may also indirectly help in establishing mechanisms of interfacial behaviour (e.g., by identifying boundary layers).

3.6.2 Time-of-flight secondary ion mass spectrometry

ToF-SIMS uses the particles sputtered as ions from a surface to characterise the chemical nature of the material under analysis. This technique provides highly surface-specific information coupled with very high sensitivity of the material present on the surface. However, the complexity of the spectra from non-trivial systems often requires characterisation by other surface analysis techniques such as XPS in order to aid spectral interpretation.

The SIMS technique requires four separate events to occur for a spectrum to be recorded. These are desorption and ionisation, ion extraction, mass separation and detection. Secondary ions are produced by bombarding the surface of the sample with a finely focused beam of primary ions at keV energies, which is produced by means of an ion gun. Ion extraction is achieved simply by electrostatically attracting the charged particles by means of an electric field, which is pulsed for ToF systems. Negative spectra are routinely available, unlike conventional mass spectra, because the polarity of the electrostatic field may be reversed to attract ions of the opposite charge. This approach is in contrast to fragments produced by electron ionisation in conventional mass spectroscopy, because high-energy electrons are generally too energetic for electron capture, resulting in the production of very few negatively charged particles. Unlike in conventional SIMS, ToF-SIMS offers parallel mass detection and this increases the sensitivity by about 10^2. Furthermore, ToF-SIMS has the advantage of being able to use low ion doses, which makes it more suitable for the analysis of polymers and materials that are easily damaged by a high-energy ion beam.

The electronic configuration and chemical nature of the surface have a strong bearing on the ions produced. Once the primary ion packet has impacted with the target (surface), a range of particles is emitted, of which only 1–5% are thought to be ions. The sample is at positive or negative bias, depending on the mode of spectrometry employed, so ions of only one charge are emitted from the surface because ions of the opposite polarity cannot escape. Other particles known to radiate from the target include photons, secondary and Auger electrons, backscattered primary particles, and neutrals. Electrons constitute the majority of massive particles emanating from the surface. Although the proportion of particles emitted as ions is low, the overall transmission of a ToF-SIMS instrument is very good (~10%) and as a result the required primary ion dose is relatively small, which as mentioned above is beneficial for the analysis of polymers. The technique is more surface sensitive than XPS and the depth from which information can be obtained is less than 2 nm. Another very important feature that makes SIMS of particular value in surface analysis is that hydrogen can be detected in the spectrum, unlike with other techniques (such as XPS). A more detailed description of the instrumentation and a discussion of the principles involved in the technique are beyond the scope of the present study and may be found in the literature (Vickerman *et al.*, 1989; Woodruff and Delchar, 1994; Briggs, 1998; Vickers, 1998).

In contrast to XPS, ToF-SIMS has not been used extensively to study natural fibres mainly due to the complexity of the technique. There exist, however, a few studies that employed the technique on natural fibres (Baiardo *et al.*, 2002; Zafeiropoulos *et al.*, 2003; Fardim and Durán, 2003; Mitchell *et al.*, 2005; Freire *et al.*, 2006). Baiardo and co workers (2002) investigated the extent of surface modification in flax fibres after esterification with three different compounds (acetyl, valeryl and butyryl chlorides). ToF-SIMS experiments were used to prove that esterification did indeed take place. In fact, an examination of the negative spectra revealed that acetylated fibres exhibited a prominent peak at m/z (mass-to-charge ratio) $= 59$ corresponding to the ion $C_2H_3O_2^-$, which is a fingerprint fragment for acetyl esters. Similarly butyrylated and valerylated fibres exhibited prominent peaks at $m/z = 87$ and at $m/z = 101$ in the negative spectra corresponding to ion fragments $C_4H_7O_2^-$ and $C_5H_9O_2^-$, respectively. In a similar study, Zafeiropoulos and coworkers (2003) employed ToF-SIMS in order to investigate acetylation and stearation as efficient methods for surface modification of flax fibres. Like the study of Baiardo *et al.*, acetylated fibres exhibited a prominent peak at $m/z = 59$ in the negative spectrum, denoting that acetylation was successfully carried out and confirming XPS results. However, in the case of stearated fibres, as discussed in the previous section, XPS was not able to prove that the reaction took place. ToF-SIMS negative spectra were also inconclusive since no prominent peaks were found that could be linked to stearic acid. A close examination of the positive spectrum solved the problem in this case. Two prominent peaks at $m/z = 267$ and 285 corresponding to $C_{17}H_{35}CO^+$ and $C_{17}H_{35}CO_2H_2^+$, respectively, were apparent in the spectrum after stearation. These two fragment ions are fingerprints of stearic esters, thus confirming that stearation was successfully carried out.

ToF-SIMS is a more complex method to use but is also far more sensitive than XPS. It can provide information that no other technique can, but the method should never be applied on its own. In addition it is truly a surface analysis technique since information is gathered only from the outer 1–2 nm layers.

3.7 Conclusions and future trends

Natural-fibre composites are envisaged to find more and more applications in the near future, especially in Europe where legislation and public pressure are increasing significantly. The interface will remain the key issue in terms of overall performance since it dictates the final properties of the composites. From the available research on the topic on interfaces in natural-fibre composites, the tendency is in favour of treatments that will not only provide excellent tailoring but will also have minimal impact on economics. Presently maleic anhydride grafted compatibilisers are probably the most popular for interfacial control. Esterification methods will also have potential applications especially if the cost of the chemicals involved continues to decrease. The key perspective for the future of interfacial research on natural-fibre composites will inevitably be in the use of nanofillers rather than fibres. Cellulose nanofibrils and cellulose nanowhiskers will attract significant attention in the near future and the interface will also be of paramount importance in this new class of materials.

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4

Processing techniques for natural- and wood-fibre composites

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4.1 Introduction

Over the past few decades wood and natural-fibre composites have been undergoing a remarkable transformation. The first generation of wood–plastic composites (WPC) and natural-fibre composites (NFC) contained simple composites; their purpose was to get cheap materials with only satisfying properties. One of the first pioneers was Sadao Nishibori. He was a Japanese wood processing engineer, who made one of the first wood/polymer combinations in the early 1970s, which was later called a wood–polymer composite. Even earlier, in 1915, was Henry Ford with his model T Ford that was glued by an adhesive based on wheat. In 1941 another car was built with wood, hemp, sisal and wheat straw, driven by hemp oil. However, owing to the oil prices at that time the 'green technology' was still not economical.

The first oil crisis in 1973 made biocomposites boom significantly. A sleeping giant was awakened. Since that time WPC/NFC have become engineering materials with a very wide range of properties. These materials are continually improving and new compositions and processes are being intensively researched, developed and applied. However, they are constantly under competition and price pressure, just like all materials. The times of simply mixing plastics with natural waste fillers and characterising their main properties are gone.

The R&D sector had led to several innovative solutions focusing on these novel materials with specific properties. The use of new additives, e.g. coupling agents, on maleic anhydride grafted polypropylene basis or new high-quality preparation methods for natural fibres enabled more reproducible properties and allowed better processing control. The understanding of the influence of factors such as moisture, fibre type and content had improved the composites' mechanical properties and their end-product quality. Moreover development of new moulding technologies had increased the process efficiency significantly.

Today NFCs have much improved properties than several years ago. To satisfy the various needs, many companies offer more additives and auxiliary supplies. Different ones are chosen depending on their applications field and compounding methods. In this field, knowledge of chemical interactions (matrix/fibre) and the action mechanisms of additives is necessary. Coupling agents combine fibres and resin, lubricants increase the throughput and improve the surface quality, colorants and UV stabilisers prevent the polymer degradation and increase visual perception. Biocides avoid biological decomposition, especially at a higher fibre content.

The processing methods for natural- and wood-fibre reinforced plastics are applied in the textile as well as in the plastics industry. Textile processing is used mainly in fibre preparation and in semi-finished product production. As a rule these technologies have been known for years and are still used in the processing of natural fibres such as flax or hemp.

Since these fibres are a natural product their textile processing requires much experience and more often much manual labour. The established processing techniques of the plastics industry are characterised by the processing of semi-finished products or easily-dosable granulates. In this area further development of the processing technique has happened quickly in recent years. The application of natural fibres in the plastic technique required an adjustment to the available processing methods. A separation point between textile and plastic techniques is necessary here to allow the processing of natural fibres in the manufacture of fibre compound materials. For example, a new extruder screw design allows better degassing and consequently lower moisture content. A combination of extrusion and injection moulding machines within one unit, the so-called IMC (Injection Moulding Compounder by Krauss-Maffei), improves composite properties and leads to cost reduction in manufacture.

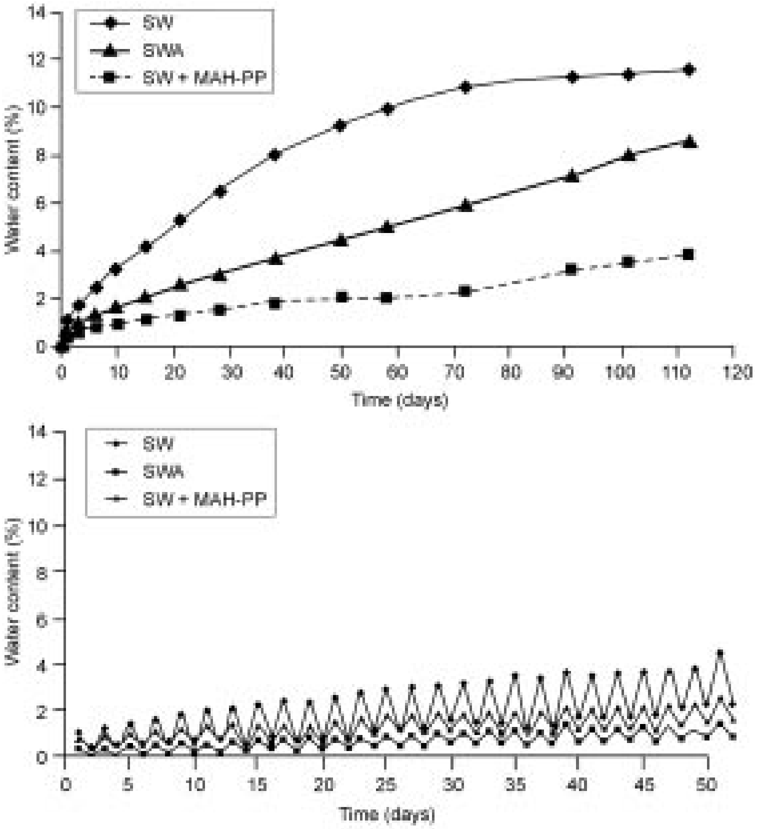
New materials lead to new application fields. The aim is to get a high-strength engineering composite and to reach the level of glass fibre composite (GFC), or even to substitute these ‘conventional composites’ in near future. This can be achieved only by a successful R&D sector. To make it happen, innovative technologies and process solutions need to be intensively researched, in addition to new material combinations. New processing aids are only one possible way. New combined moulding techniques are the trend for the future.

4.2 Factors influencing processing

4.2.1 Moisture

Polymers and their composites are very sensitive to any environmental changes and their properties may be affected considerably by environmental conditions. Variations in moisture are always encountered by these materials in service. Most synthetic polymers absorb moisture within a humid atmosphere and while immersed in water. Natural fibres made of cellulose contain numerous hydroxyl groups that are strongly hydrophilic.[1] The water uptake of NFCs has several adverse effects on their properties and consequently the long-term behaviour can be affected.[2]

Cellulosic fibre reinforced polymers can take up a high amount of water, which generally influences processing,[3,4] causes a reduction in mechanical properties[5] and an increase in swelling,[6] as well as raising heat conductivity and fungal sensitivity. Both the rate of water pick-up and the total amount of moisture absorbed depend on the chemical structure of the fibre and resin, the crosslinking agent, the temperature and the relative humidity,[7] but also on other environmental factors. For example, a much higher amount of moisture can be absorbed via static moisture absorption by immersing samples in water than by cyclic wetting of composites (Fig. 4.1).



4.1 Influence of static and cyclic (wetting–drying cycles) water absorption on moisture content of different WPC on PP basis; SW: 50% by weight softwood, SWA: 50% by weight acetylated softwood, SW+MAH-PP: 50% by weight soft wood and 5% coupling agent (source: IfW).

During the process, the water absorbed by natural fibres (3–12 wt%) acts at the fibre surface like a separating agent, if the fibres are not correctly dehumidified. Additionally, a vaporisation reaction is taking place and micro-voids can occur, owing to the high processing temperature (>>100 °C). As a result of both water vapour and micro-voids, mechanical properties can be affected.[4] In extreme cases the injection moulded part can exceptionally even be foamed causing a high rejection rate. However, this effect can be used in injection moulding of structural foams, where water acts as a foaming agent, if the process is carried out correctly.[8]

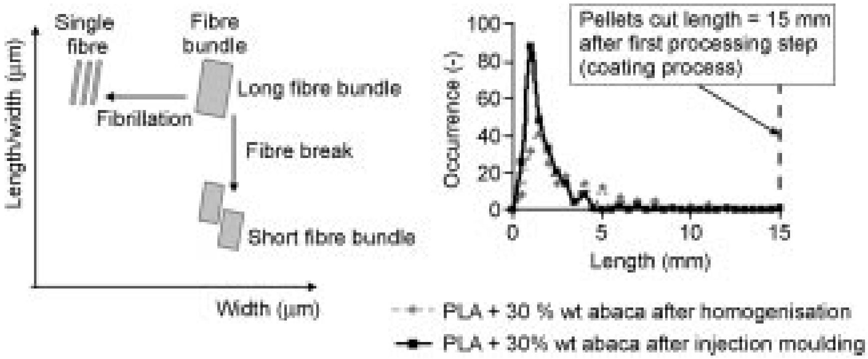
The presence of moistness demands new technical solutions. A new extruder screw design (higher *L/D* ratio) allows better degassing and, consequently, a lower moisture content. Moreover, a machine's barrel must be redesigned. In the direct extrusion process, for example, extruders are characterised by larger degassing sectors that help to remove residual moisture from the fibres. Furthermore, new solutions need to be found in the injection moulding process. Because of very high pressure during the process, water evaporates first at mould venting after the injection phase. Thus small cracks develop, which affect the mechanical properties.[3] In general, water is the reason for the corrosion of metal parts in machines. However, this effect can be avoided by continuous production, or by systematically cleaning all parts.

The enhanced water content can drastically affect some mechanical characteristics, such as compression and flexural/tensile properties,[9–12] but the change is a reversible effect, so that composites, after secondary drying, return to their initial value (before water absorption). Some of the mechanical properties, such as impact strength, decrease in an insignificant way.[1,11] In some cases absorbed water can act as a plasticiser so that the composites show increased ductility and achieve higher strains.[12]

4.2.2 Fibre type and content

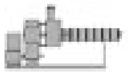
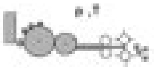
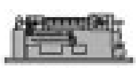
Natural-fibre reinforcement is the most important factor affecting composites' mechanical properties. Therefore the correct choice of fibre type and content is in generally essential for further sustainability of composite and it determines its usefulness as an engineering material. 'Green composites' can be reinforced with wood flour, rice, rye and wheat husk (WPC) or/and with natural fibres (NFC). Wood flour is sometimes also determined as a wood fibre. The main difference between organic fillers, wood flour and natural fibre is their geometrical form and chemical composition. For example, wood flour contains particles that are mostly cubic or spherical, while the natural fibres are longish (fibrous), with high aspect ratio (length/diameter). Organic fillers such as rice, rye and wheat hull contain much more silicates then wood/natural fibres.

The addition of natural fibres or other organic fillers can influence processing; thus some negative effects such as corrosion or abrasion of screw, barrel



4.2 Schematic depiction of fibre fibrillation and shortening during processing[13] (left) and depiction of fibre shortening effect of PLA/abaca composites (right), after homogenisation process on single-screw extruder and injection moulding (source: IfW).

and mould can appear. It is also important to consider that in some cases selected processing parameters need to be changed. Furthermore fibre composite compounding and processing methods determine the fibre length. The compounding process significantly influences the shortening, fibrillation (Fig. 4.2) as well as the thermal deterioration of the fibres in the early stages; the final properties of the product are already being determined at the beginning of the production process.[13] Figure 4.3 shows the different compounding processes for injection moulding of natural fibre reinforced thermoplastics.[14]

Compounding process	Processing principle	Pellet form	Fibre length
Pelletising (with matrix)			< 3 mm
Mixing (cascade mixing)			< 3 mm
Extruder compounding			< 3 mm
Hybrid fibre non-woven pre-consolidation and -cut			< 25 mm
Pultrusion (bast fibres)			10–30 mm
Pull-drill-process (bast fibres)			10–30 mm

4.3 Compounding methods for injection moulding of natural-fibre reinforced thermoplastics, altered and expanded description.[14]

Corrosion and abrasion

For many years the effect of chemical-physical interaction of natural fibres with metal elements of processing unit was underestimated. Because of insignificant hardness and high flexibility, little attention has been paid to both corrosion and abrasion. However, in practice, both the mentioned problems have a significant influence on processing. Abrasion appears mostly if the fillers contain a greater amount of silicates. For example, rice husk contains approximately 18 wt% of silicates, which makes about 9 wt% of quartz crystals at the ratio 50/50 (polymer to filler). Furthermore wood flour (mostly softwood) acts by enhanced temperature corrosion. Softwood begins to pyrolyse below 170 °C. The pyrolyse reaction causes formation of aliphatic organic acids, such as acetic acid and other corrosive products. These substances act on plasticising unit high corrosive. Because of friction between barrel and screw the fibres themselves induce abrasion effects. Moreover, the fibres residual moisture can be the reason for accelerated corrosion. Additionally, fatty acids, aldehydes (integral parts of fibre chemical composition) and several decomposition products produce an intense smell. It is to be expected that all volatiles can react to carboxylic acid, which is also corrosive to machine metal elements.

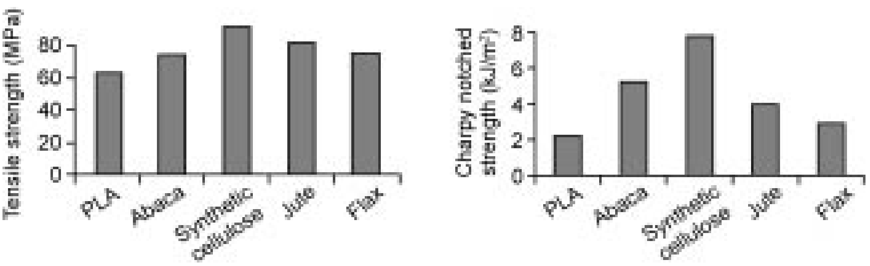
Processing parameters

In general an increasing content of organic fillers or natural fibres decreases mould viscosity drastically. Thus some of the processing parameters need to be changed. Usually, to improve the flow behaviour of polymeric materials, it is sufficient to enhance the processing temperature; however, with regard to natural fibres, a higher temperature accelerates the fibres' thermal degradation and affects the mechanical properties of the composites. Another solution is to enhance injecting pressure or speed. This problem can be avoided by the addition of additives, such as lubricants or foaming agents.

Influence on composites properties

The fibre type is most important determinant of performance in the composite. There are numerous types of natural fibres which differ in chemical structure.[6,15–17] The main component in natural fibres and, consequently, responsible for the mechanical properties of the composite is cellulose. The amount of this structural element can vary from 38 wt% for cereal straw,[16] 40–50 wt% for wood[6] to 90 wt% for cotton.[16] The influence of type of natural fibre on some mechanical parameters of poly(lactic acid) (PLA) biocomposites is presented in Fig. 4.4.

Moreover, the 3D deployment of cellulose molecules in the single fibre is vitally important. For example, fibre cell modulus increases linearly at higher cellulose content, but it decreases as the spiral angle of cellulose increases.[18]



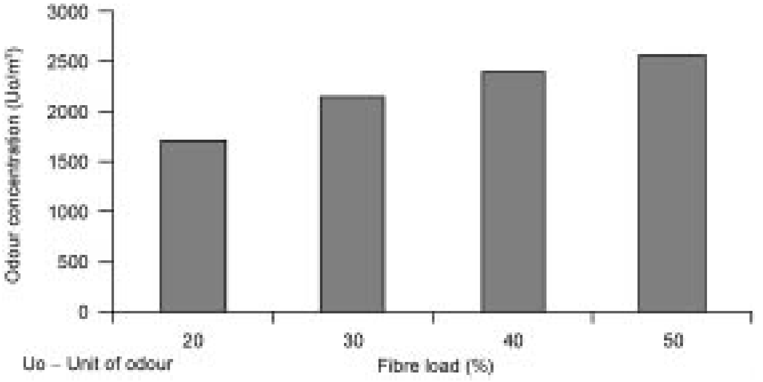
4.4 Influence of different natural fibres on tensile and Charpy notched impact strength (+23 °C) of PLA biocomposites; fibre load 30 wt% (source: IfW).

The next factor that determines mechanical properties is fibre load. In general, increasing the wood flour content increases the composite's stiffness significantly, and additionally its strength is increased through the addition of natural fibres.[6,19] Furthermore, higher fibre load improves impact strength. Unfortunately, increased fibre content increases the composite's odour (Fig. 4.5) as well as water uptake. Moreover, the composite's ductility can be affected.

Besides fibre type and content, the fibre length and its geometry play a dominant role in composites. Usually, most mechanical properties of a fibre can be enhanced with increasing aspect ratio.[20]

4.2.3 Additives

Additives influence the process and improve material characteristics. The use of one appropriate additive in very small quantities (0.5–5%) can significantly improve the throughput and most of the physical, chemical or mechanical properties of the cellulosic material and, consequently, of the composite.[21] Because of the large number of required product properties, the range of different

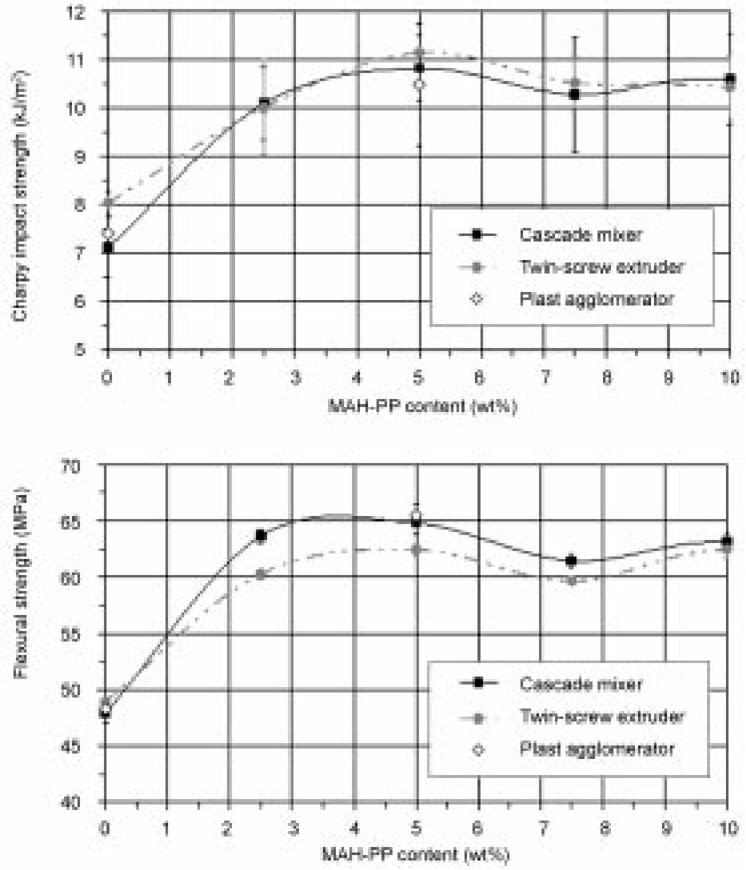


4.5 Influence of abaca fibre content on odour concentration of PP/abaca composites (source: IfW).

additives is also very wide. The following additive groups are usually added to both WPC and NFC.

Coupling agent (CA)

The main purpose of the addition of CA to a composite is to improve its fibre–matrix interaction. It allows better stress transfer from polymer to fibre, and results in much improved mechanical properties[22–24] (Fig. 4.6). In general, strength and impact resistance increase significantly with increasing content of CA, although the stiffness change is only slight.[24–26] With the addition of CA, the composite's moisture uptake increases and melt's viscosity decreases. The influence on melt flow results in easy processing and better impregnation of fibres with polymer matrix.



4.6 Influence of coupling agent content on impact (top) and flexural (bottom) strength of 40 wt% wood flour reinforced PP, manufactured via cascade mixer, twin-screw extruder and plast agglomerator (source: IfW).

Lubricants

Processing aids or lubricants are additives that influence the production process, and as a result a higher output or better product quality can be achieved (Fig. 4.7). Lubricants may be internal, such as waxes or stearates, or external, such as fluoropolymers.[27] Internal lubricants act within the polymer phase and have the following functions:[28]

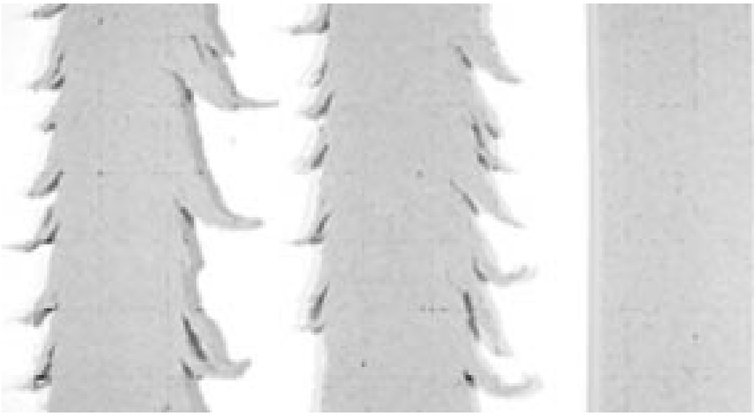
- Viscosity reduction – increases melt flow.
- Heat dissipation – prevents shear burning.
- Resistance to melt fracture – reduces viscosity at high shear rate.

External lubricants act at the interface between resin and other materials and have the following functions:[28]

- Release – reduce adhesion between resin and extruder walls/screw.
- Friction reduction between resin and process equipment.
- Resistance to melt fracture.
- Dispersion – promote incorporation/dispersion of fillers.

Light stabilisers

Besides moisture, UV light and oxidation are the most damaging atmospheric factors that strongly influence the properties of polymer. Not only does optical appearance change, but the mechanical and physical properties can also be influenced. To protect plastics from environmental impact, different light stabilisers are in use. However, the stabilisers need to be chosen very specifically for each polymeric system and in view of end-use application.[28] Depending



4.7 Depiction of melt fracture through use of inappropriate (left) and adequate lubricants (right) (source: Clariant Produkte (Deutschland) GmbH, Pigments & Additives Division).

on the different action mechanisms, the light stabilisers can be classified as follows:[29]

- UV-absorber and decking pigments such as carbon black, TiO_2 – absorb the UV spectrum, in which the polymers undergo photodegradation (280–370 nm).
- Quenchers – substances that deactivate the molecule parts responsible for degradation.
- HALS (= hindered amine light stabilisers) – radical trap, that function as light stabilisers. The HALS stabilisers also improve some of the mechanical properties of WPC/NFC after weathering.[30]

Colorants

In general colorants influence the visual perception of coloured products. In combination with light stabilisers they can also avoid effects of UV degradation. The classifications of colorants include organic and inorganic pigments as well as dyes.[27,31] Dyes are soluble in most polymers. They are available in a wide colour range and they have high temperature resistance. However, dyes can migrate in many polymers and are of relatively high cost.

Flame retardants

The function of flame retardants is to decrease or avoid combustibility of the composites. They begin to work during the start-up phase of the fire.[26,32] Flame retardants can be classified in two main groups: halogen and halogen-free flame-retardant agents. The first group is still the most popular, but it does not fulfil all the current environmental requirements. Flame retardants can act chemically and physically. The chemical reaction takes place in both gaseous and solid forms. The flame retardant acts physically via:

- cooling (endothermic process);
- thinning (by adding of fillers, which thins the flammable materials in solid or gaseous phase);
- formation of a protective film (coating), which isolates the material from the fire centre.

Foaming agent

Most generally, a foaming agent (FA) is a material that, in the vapour phase, expands a polymer melt upon reduction in pressure, and as a result a cellular structure is developed.[6] Foaming agents can be either a physical gas or a chemical that decomposes in a polymer melt during processing and releases a gas. In both cases, the gas has to be homogeneously dispersed and dissolved in the polymer

Table 4.1 Influence of foaming agents on the process and on the end-product properties

Process	End product
Reduced cycle time	Lower density
Decreased mould viscosity	No shrink mark
Reduced injection pressures	Lower warping and interior stress
Reduced clamping force	Better insulation and damping properties
Lower moulding temperatures	

Source: IfW

melt under pressure.[6,33] The influence of FA on NFC and WPC is presented in Table 4.1. The disadvantages of FA in combination with WPC/NFC are decreased absolute mechanical properties (but, in relation to their density, similar or better relative properties)[6,33] and increased water uptake and thickness swelling.

Odour reduction agent

Odour reduction agents act chemically with substances responsible for emissions to non-volatile, or odour neutral molecules. Non-volatile molecules cannot act chemically; thus, adding an odour reduction agent, a corrosion reaction with metal parts of the processing unit is avoided. Odour reduction can also be achieved with physical methods, as aromas are absorbed and non-smell substances are built.[34,35]

Biocide

Like most of the products made of renewable raw materials, composites reinforced with natural fibre, such as WPC and NFC, also demand protection against biological impacts, such as bacteria or fungi. On exposure to sunny and wet environments, for example, some NFCs may show a colour change or even a decline of their mechanical properties.[36] For that reason several biocides are in use. CIBA offers a thiazolyl bentimidazol (Irgaguard F 3000) as a solution against fungi, and another example is dichloro-octyl-isothiazolone (DCOIT) offered by Rohm & Haas.

Some additives (e.g., coupling agents, lubricants or colorants) can act corrosively. For example, most lubricants are made on a stearin or caproic acid ester basis and decompose at processing temperature to form the odorant carboxylic acid, which causes corrosive effects. In such cases a barrel or/and screw coating is required. Sometimes additives have a negative effect on injection moulds, which can result in their corrosion. An appropriate coating sheet, such as chrome-plated parts, can solve the problem. Abrasive effects appear much more rarely than corrosive interaction; however, in this case a corresponding coating can be useful (e.g., via nitration).

4.3 Semi-finished product manufacturing

4.3.1 Production of mats

There are a number of different fleece-making methods used by the textile industry to produce fibre mats (fibre fleece) from natural fibres:

- carding method;
- aerodynamic fleece-making;
- fibre spreading process;
- wet fleece production.

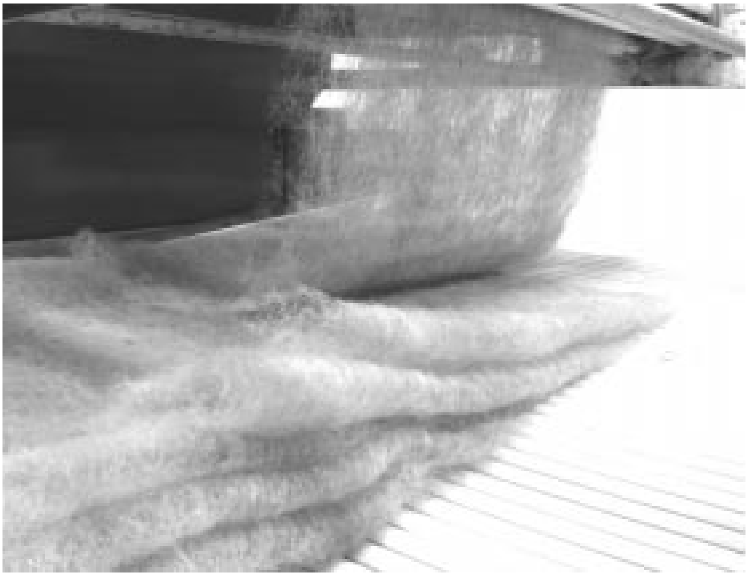
Fleece of 100% natural fibres or of mixtures of natural fibres and thermoplastic high-quality recycled fibres can be made through a carding process. This process is especially suitable for long fibres of 40–80 mm (for instance flax, hemp, jute, kenaf, cotton). The fibres are delivered mostly in bales and coarsely loosened with the help of a special opener. The material is guided through a feeder into a mixer. Then the resulting fibre mixture is delivered via a feeding device to the carder. The carder has the following duties:

- Breaking down the fibre flake to the single fibre;
- Elimination of dust, shive and short fibres;
- Orientation of the fibres in the fibre web.

In carding, the fibre material is guided over rotating rollers that are covered with little hooks; they separate the fibres and produce a fibre web. From this fibre web a needled fleece is produced through laying and needling (Figs 4.8 and 4.9).

Fleeces may be parallel layered fleece (lengthways fibre orientation) or cross-layered (right-angled fibre position). When using thermoplastic binding fibres the stabilisation of the fleece is realised through thermo-bonding. The carding method is often used in the processing of natural fibres such a flax or hemp; it is well suited for the production of semi-finished products since high mass per unit area, 1000–2000 g/m^2, can be achieved.

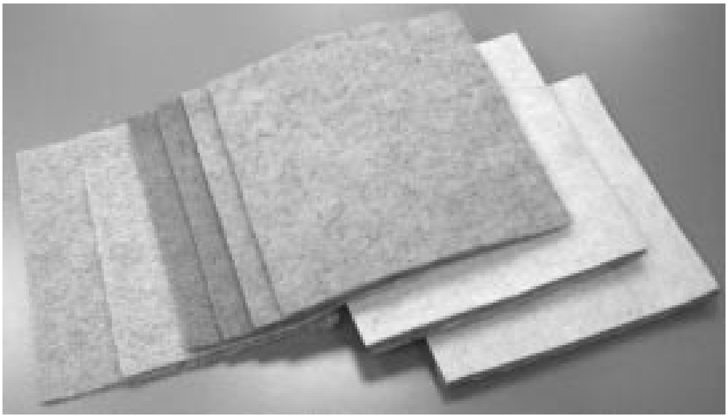
When long fibres are used with the aerodynamic method, the fibre dispersal happens similar to the carding process via one or more hook-covered rollers. Short fibres can be directly whirled with air. After opening, the fibre material enters an airstream. The mixture of air and fibres is condensed through suction on a continuously moving sieve and deposited. The airflow condenses the settled fibres and thus forms the fleece. The fibres in the fleece are statistically distributed and oriented in length and cross direction, as well as perpendicular to the surface by the airflow, resulting in almost even properties in all directions. It is possible to process very short fibres under 10 mm in length (e.g., cellulose) as



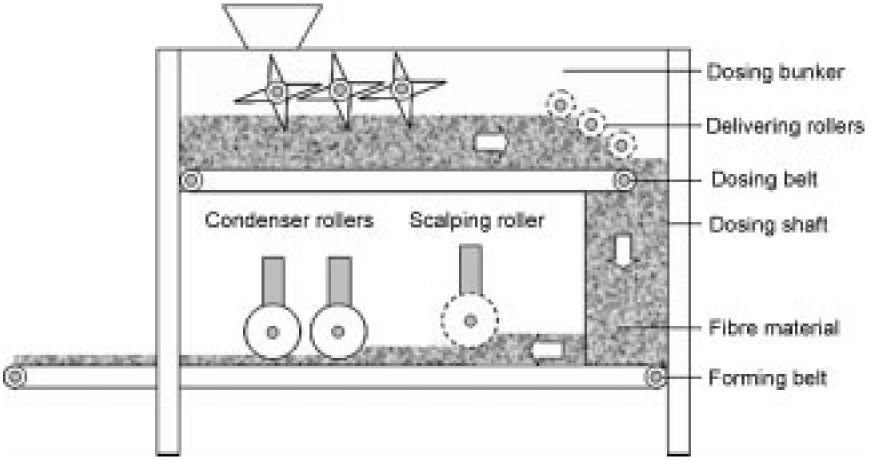
4.8 Laying of the fibre web (source: TITK).

well as long fibres of 40–80 m (e.g., coconut fibres) with this process. The stabilisation of the fleece is usually achieved through needling, thermo-bonding or also through spraying with binding agents.

The fibre spreading method makes possible a dry fleece with short strengthening fibres, e.g. wood fibres. The technology is known from the manufacture of particle board and allows the production of fleeces with large surfaces. To produce wood fibre mats, mostly fibres of evergreen trees (fir) are mixed with short thermo-plastic fibres and deposited on a conveyer belt with a fibre form machine (Fig. 4.10).



4.9 Natural fibre fleece (source: TITK).



4.10 Processing principle of wood fibre dosing.[37]

The wood fibres are placed in a dosing bunker and are raked to a defined height with specialised rakes. The dosing conveyer transports the fibre material in the direction of the delivering rollers. The amount of dosed fibre can be adjusted by varying the speed of the conveyer and the number of revolutions of the scatter rollers. The fibre material then falls through the dosing shaft on to the forming conveyer. The speed of the forming conveyer can also be varied. It is possible to change the height of the strewn fleeces through adjustment of the conveyers. The fibre material is then combed with the help of a scalping roller, which allows for an adjustment to achieve a smooth surface and a defined surface mass of the fleece. To reduce the volume, the fibre fleece can be compressed with condenser rollers. The stabilisation of the fleece happens as a rule through needling or thermo-bonding. In the wet process almost all fibres that can disperse sufficiently in water can be processed. The forming of the fleece is similar to paper production. The important processing steps are:

- dispersion of the fibres in water;
- continuous fleece forming on a drain belt;
- stabilisation, drying and rolling up of the formed fleece sheet.

In this process the fibre material is distributed in the watery medium and, if needed, mixed with other components (other types of fibres, binders). After dispersion and laying the fibres on a sieve, the liquid is extracted and the fleece is dried. The surface weight of the fleece can be varied by the relation of fibre to water in the suspension, the guidance of the amount of suspension as well as the draining speed of the drain belt. It is possible to produce very even and light fibre fleeces with low mass per unit area with the wet process. For that reason this process is used mainly in the paper industry.

4.3.2 The production of slivers and fibre yarns

Through the use of the classic textile spinning mill technique it is possible to produce slivers and fibre yarns. The fibre preparation (opening, mixing, carding) is similar to fleece production. After carding, the fibre web is gathered into a sliver with the help of a can coiler (Fig. 4.11).

The slivers can be used in the plastics industry as semi-finished products for further processing. Alternatively, in another textile step it is possible to make fibre yarns (Fig. 4.12) out of slivers. Slivers are doubled and stretched to increase fibre orientation and evenness. After that, spinning into preliminary yarns and fine fibre yarns can take place.

4.11 Sliver production (source: TITK).

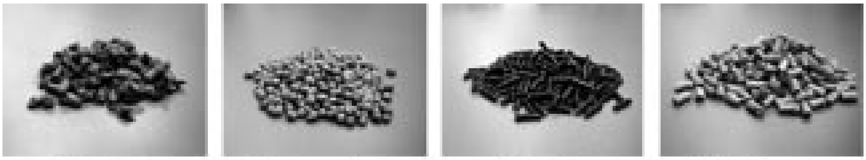
4.3.3 Granulate production

In a number of processes in the plastics industry, e.g. extrusion and injection moulding, the production of easily dosable granulates is required when using natural fibres. Natural-fibre granulates can be produced with different methods. Different results are obtained with regard to the homogeneity of the granulate and the achievable fibre lengths (Fig. 4.13).

The simplest way to produce free-flowing granulates is through pelletising with a heating/cooling mixer or pellet mills.[38,39] Together, the natural fibres and the matrix material are condensed and agglomerated in this technique. The fibre content is adjustable within a wide range. It is also possible to produce concentrates with a high fibre content. The resulting pellets contain short fibres of approximately 1 mm fibre length and have an irregular structure. The fibres are not homogeneously distributed in the matrix and are highly condensed as a rule.

4.12 Natural-fibre yarns (source: TITK).

Another way to produce granulates is by compounding the matrix material and reinforcement fibres with the help of an extruder. Because of their influence on the mixing process, twin-screw extruders are used by the plastics industry. The reinforcement fibres are added either as free-flowing short fibres or as roving, and mixed in an extruder with the matrix material. A definite shortening of the fibres occurs through the shearing effect of the extruder screws. The medium fibre length that can be achieved in the granulate is mostly under 1 mm. Primary problems in the processing of natural fibres are the dosage and the homogeneous distribution of the fibres. Natural fibres are usually delivered in pressed bales and have available length distribution. In fibre materials such as flax or hemp, cut fibres can be made only via the intermediate step of band creation. Because of the low fibre density the fibres are hard to pour. A solution to the dosing problem can be achieved through the use of carding slivers.[40] Here the handling of the voluminous carding slivers should be considered. Pre-condensed pellets (fibre concentrates) could be used as dosing help in the extrusion process.



Pelleting
Fibre length < 1 mm

Compounding
Fibre length < 1 mm

Pultrusion
Fibre length > 10 mm

Pull-drill process
Fibre length > 10 mm

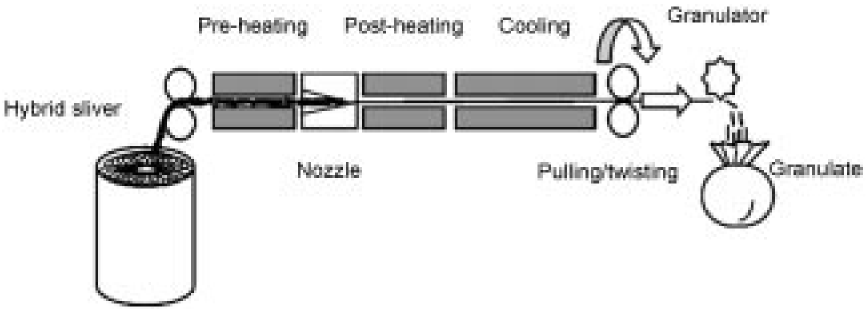
4.13 Different natural-fibre granulates (source: TITK).

Long-fibre reinforced thermoplastic granulates are usually produced with the pultrusion process. In this process the rovings are continuously impregnated with a polymer melt in a pultruder. At the exit of this appliance the cross-section of the strand is calibrated by a nozzle, then cooled and granulated. The fibre length of the reinforcement fibres is equal to the granulate cut length in the pultruded granulates and is between 10 mm (injection moulded material) and 25 mm (extrusion compression materials). A prerequisite for the pultrusion process is always a strand-like semi-processed fibre product that can transfer a stronger pull. Natural fibres have to be spun into yarns; since they are a natural product they can only be processed with a limited fibre length. These natural-fibre yarns have a relatively low tensile strength that limits their application in the pultrusion process.

An interesting alternative to granulate production with natural fibres is the pull-drill method (Fig. 4.14). This specific process is based on textile techniques and makes the production of long-fibre granulates with a defined fibre length and fibre orientation possible.[41]

Base materials for the process are carded slivers consisting of mixtures of natural fibres and thermo-plastic matrix fibres (hybrid slivers). The fibre slivers are heated in a pre-heating zone, pulled through a nozzle and twisted at the same time. Through the twisting of the sliver and the compressing within the nozzle, natural and matrix fibres make contact and stick together. This results in a compact material strand that can flow continuously. Following the nozzle passage the strand passes through a second heating zone for further strengthening, followed by cooling, consolidation and granulation of the strand.

A very homogeneous distribution of the strengthening fibres is guaranteed by the textile mixture of the components. The thermal strain on the fibres is also reduced since in the production of the granulate only the mantle of the material strand is melted. Cylindrical granulates with a defined grain structure and cut length are the result; their length can be adjusted to between 5 and 30 mm. In this process the fibre content can be varied widely. It is possible to manufacture granulates with a fibre content of 30–40 wt% for injection moulding as well as concentrates with 70–80 wt% for use in compounding.



4.14 Production of granulates with the pull-drill method.

4.4 Processing technologies

4.4.1 Thermoplastics

Compression method

The pressure method is very popular in the manufacturing of natural-fibre composites because of its high reproducibility and a low cycle time. The two methods in use are compression and flow compression moulding. The processes differ in the kind of semi-finished product used and its cutting, and also in the tool structure and the processing. In the compression moulding process, flat semi-finished products or hybrid fleeces are usually used that are either larger than the form or are cut exactly to the size of the desired part.

The semi-finished product (natural fibre/PP-mat) is put into the pre-heating station and heated to the melting temperature of the matrix material. It is subsequently guided into the pressure tool unit, condensed and reshaped. The compression moulding method is especially well suited for the production of large-scale (mainly automotive) construction components with even wall thicknesses. It is often used in the manufacture of natural-fibre reinforced components since the use of hybrid fleece eliminates problems of wetting. A special method of compression moulding is the one-step-method (production of components with decorations in on step). In this process the decorative material and the base material are pressed together and through bonding adheres to the matrix material.

The impact extrusion method is known from the processing of GMT (glass mat reinforced thermoplastic). In this process sheets or fleeces can be used as semi-finished products. The cuts are smaller than the form. The weight of the semi-finished product is the same as the finished part. Because of the flow of the cut material the areas of the form not covered get filled completely when the press is closed. This process is used in the manufacture of complex components with different wall thicknesses, small division bars or embedded metal parts. This process has not gained any importance so far for the production of natural-fibre composites since there are no natural-fibre composite semi-finished products on the market.

Compression moulding materials are mainly used in the automobile industry to produce car interior lining parts. The main reason for this application is the great strength and stiffness and the low composite density of the natural-fibre composites. The properties of the reinforcement fibres (strength, stiffness and fibre length) and the adhesion between fibre and matrix are also greatly influential on the interconnection properties of the composite.

In connection with the use of honeycombed structures, the compression moulding process offers the possibility of ‘sandwiching’. That makes very high flexural stiffness possible by low weight of components. Paper or cardboard structures in honeycomb form, but also those made of PP, can be used as core material. Varying the structure of the outer mantle and the honeycomb core optimises the mechanical properties of the 'sandwich composites'.

Extrusion

The extrusion process is used by the plastics industry in the production of granulates and also in the continuous production of semi-finished products or components. Single-screw as well as twin-screw extruders that run either co- or counter-rotating may be used for this process. Single-screw extruders are used when the mixing effect does not have to be very high. As a rule, co-rotating double-screw extruders are used in the production of granulates (compounding) (Fig. 4.15) or in the processing of natural-fibre reinforced plastics. Because of the excellent mixing effect of the twin-screw extruder the natural-fibre material can be homogeneously distributed and wetted in the thermo-plastic melt.

Counter-rotating twin-screw extruders are mainly used in the processing of wood fibre reinforced thermoplastics (WPC). Because the screws run in opposite directions, a secure material feed and a defined compacting of the material can be achieved. Typical examples of application for this technology are the production of extruded profiles for decking and wall coverings.

4.15 Extrusion of natural-fibre reinforced PP sheets (source: TITK).

Injection moulding

In injection moulding it is possible to produce complex geometric components with function elements fast and in great numbers. It offers a number of advantages over compression moulding.[42]

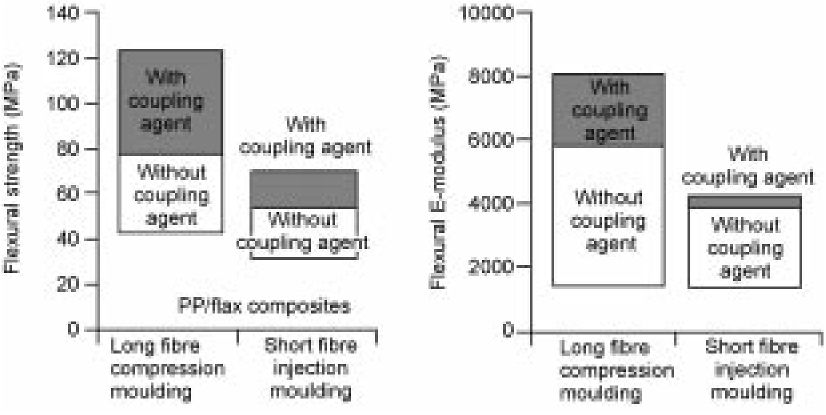
- economies of scale;
- minimal warping and shrinkage;
- high function integration possible;
- use of recycling material possible;
- hardly any finishing needed.

In injection moulding the raw material is usually added as a granulate to the injection moulding machine and melted into a fluid mass. The plasticised thermo-plastic material is then injected under high pressure into the form. The reinforcing fibres influence the injection moulding process when fibre reinforced granulates are used. That requires a specific adjustment of the tools and the process requirements. There is also the possibility of adding a decoration material directly for injection in-mould lamination with the fibre/plastic mixture (back-injection technology).

The decorative material is introduced into the tool and fixed in the parting plane, followed by the injection of the plasticised materials behind the decoration material. After cooling and removal from the form, the base material adheres tightly to the decoration material, thus avoiding the extra step of finishing touches. Special demands are made of the decoration material (strength, expansion, temperature resistance) in the back-injection technology. Those can be addressed by an appropriate of the build-up textile surface.

Injection embossing is a special method of the back-injection technology. With this method the tool is not completely closed when the form is filled; an embossing slit of a few millimetres remains open. Once the material is injected the tool closes completely, which results in lower injection- and inner-form pressure than the back-injection into the closed form. Thus a decoration-friendly injection of the material in use is possible.

Comparison of the properties of injected natural fibre composites with the characteristic value of form-pressed materials shows that pressed parts show better mechanical properties because of the longer reinforcement fibres and the higher fibre content (Fig. 4.16). The injection moulding process leads to a shortening of fibres. Also, the fibre content that can be realised, 20–40 wt%, is lower than that with compression moulding. A much higher fibre content is not possible since an increase of fibre clearly lowers the flow ability of the melt. The compression moulding method has disadvantages with regard to the component complexity. Only relatively simple, flat components can be produced. Besides that, break-throughs/bursts and edge trimming chad of 10–20% cause a loss of the component weight of 10–20%. That can be avoided with injection moulding of natural-fibre reinforced thermoplastics.



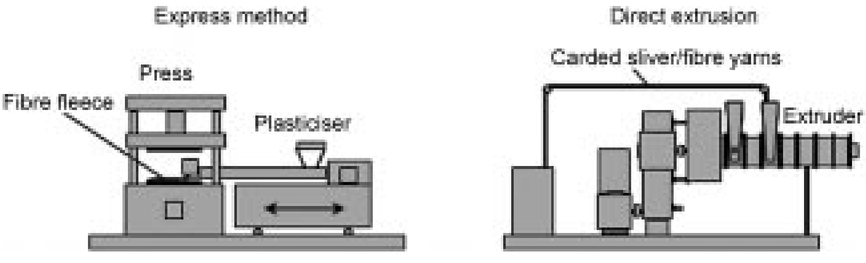
4.16 Property comparison of injected and pressed natural-fibre composites.

LFT-D method

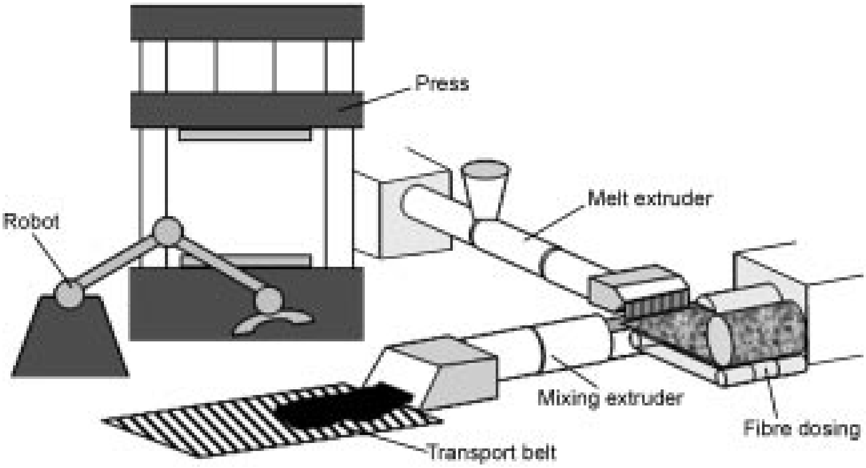
Different approaches are possible to directly process natural fibres with the LFT-D process (Fig. 4.17). One variation of direct processing is the 'express-method'.[43] The basic thought of the combined extrusion and press method is to saturate the natural fibre mats with the melt directly in the pressing tool. In a first step a film of molten mass is placed into the pressing tool with the help of an adjustable extruder, and subsequently a natural-fibre fleece is added to the molten mass and the layers are pressed together.

The advantage of the express method is the short thermal exposure of the natural-fibre materials. The complete wetting of the fibre mats is, however, problematic: they are relatively dense because of the structure of the natural fibres. The processing method has been tested in a laboratory setting but, so far, there has been no industrial-scale production.

Another possibility to process natural fibres with the LFT-D method is the direct feeding of fibre yarns or slivers into a twin-screw extruder[44] or directly into an injection moulding machine. Research has shown that it is possible to retain the long-fibre structure through an optimal configuration of the screws;



4.17 Express method and direct extrusion of fibre yarns.



4.18 Dosing of fibre fleece in the LFT-D process.

however, the handling of slivers is rather problematic in an industrial application (extrusion with high throughput).

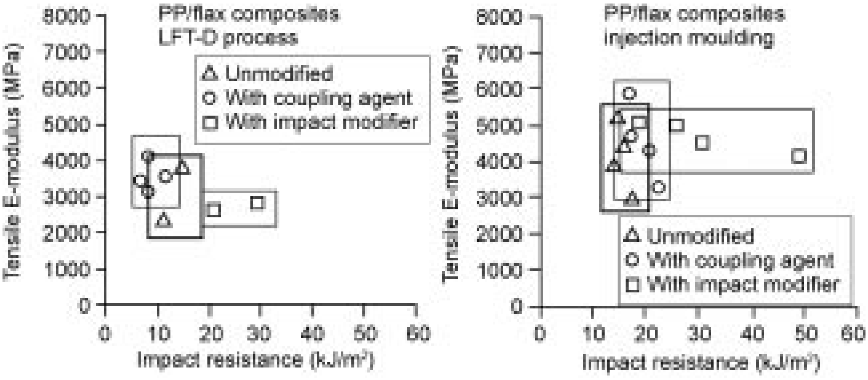
The fibre yarns have found industrial use.[42] In the Daimler Chrysler (2006) LFT-D process, abaca was used as reinforcement fibre. The abaca fibres are added to the twin-screw mix-extruder in the form of fibre yarns. At the same time molten PP is dosed via a second extruder (melting extruder) into the intake zone of the mix-extruder. The fibre material is wetted with the PP matrix and then in a continuous action through a slot die as plastic strand is ejected. The plastic strand can then be cut to the required metered volume and formed into a component by a press.

Besides these two processes, another solution for the dosing of natural fibres in the LFT-D process has been developed.[45] This technology is based on the use of minimally strengthened fibre fleece (Fig. 4.18). With this process, costly yarn manufacture can be avoided. The fibre fleece can be produced on conventional fleece-producing machines that have a high productivity, cut to the width of the metering zone and wound. The fibre material can be fed continuously into the extruder via an appropriate dosing conveyer belt at the factory. The mechanical properties of natural-fibre composites that can be achieved with this technology lie at a fibre content between 20 and 30 wt% and are almost comparable to the properties of injected natural-fibre composites (Fig. 4.19).

4.4.2 Thermosets

Resin transfer moulding

Resin transfer moulding (RTM) is a method for the production of component parts made of fibre–plastic composites. During the RTM procedure, dry semi-



4.19 Properties of PP/flax composites made with LFT-D and injection processing.

finished fibre parts are streamed and consequently soaked with reaction resin within a closed vessel by a pressure gradient. The component hardens within the vessel.

Besides rigid and soft forms there are also hybrids, as shown in Fig. 4.20. The method is employed for producing a canoe by using solid external and soft internal vessels, applying an autoclave. The racing car body panels of the Ford Mustang (Fig. 4.20) are produced the same way.

The pressure gradient can be produced by evacuation of the vessel or by admission of the resin with high pressure. Hybrids are possible as well. RTM is often combined with pressing during serial production.[48] The following methods can be distinguished with regard to admission by pressure gradient: high-pressure injection, twin-wall injection, vacuum injection, differential pressure injection.[49]

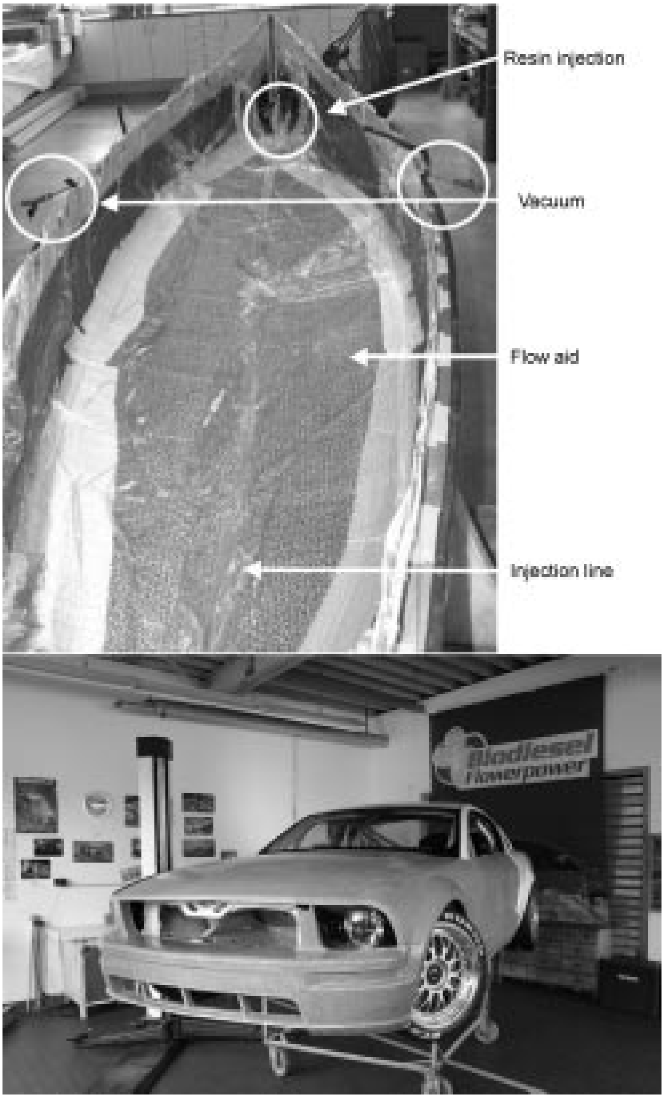
The number and composition of the injection points are further differentiating factors. As an example, Fig. 4.20 shows a form of injection with a flow aid and a injection line under the film. The resin is injected through a wide conduit, which is placed over or under the semi-finished fibre part.[48,50]

Process characteristics

Owing to comparatively low productivity, the costs of the parts are moderate to high, although the tool costs are relatively low. The advantages are excellent component strength and good varnishability.[51]

Sheet moulding compound

The sheet moulding compound (SMC) material made of natural fibres and a special resin based on vegetable oil and carbohydrates represents an effective



4.20 Illustration of tooling,[46] Bioconcept car Ford Mustang with car body made of natural fibres.[47]

alternative to the established systems within the technically specialised sector. This material could in particular be employed for external car body panels, which are exposed to humidity, cold, heat, road salt and impact loading. As a result, eco-plastics made of renewable primary products could more and more compete with traditional components made of steel or fibre reinforced plastics. Procedural modifications are not necessary, unlike conventional SMC production of component parts.[52]

Table 4.2 Comparison of glass fibre and natural-fibre characteristics[54]

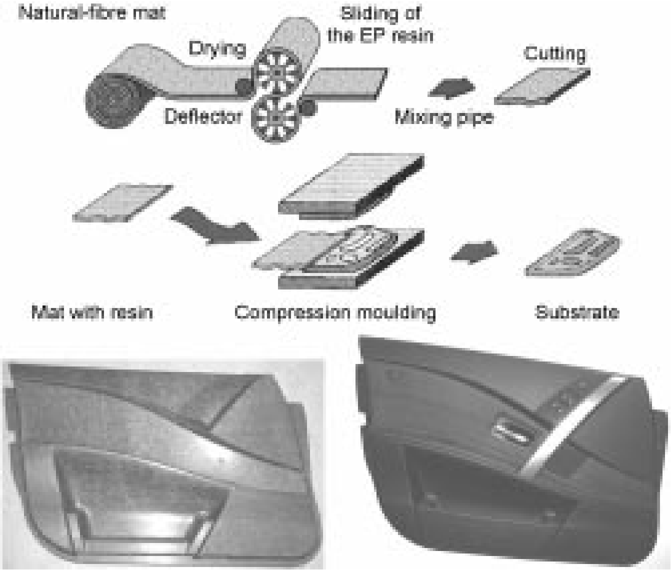
	NF-Part	GF-Part	Part-standard
Density (g/cm^2)	1.2–1.35	1.8	2
Tensile strength (MPa)	45–65	120	65
Tensile modulus (MPa)	4000–7000	13 000	5500
Bending strength (MPa)	80–150	200	150
Impact strength (kJ/m^2)	8–25	70	50
Burning rate (mm/min)	2.5–27	6	100
Water absorption unpainted (%)	4.88 ± 0.19	4.57 ± 0.12	

The middle bumper part for a city bus was manufactured with standard tools. The risk potential for the fabricator was lower, both during production and treatment of the prepregs which were made of natural fibres and vegetable oil. As aromatic emissions would not occur; in particular, there was no need for breathing protection.[53] Table 4.2 shows some material properties of the natural fibre–SMC components in comparison with fibreglass parts.

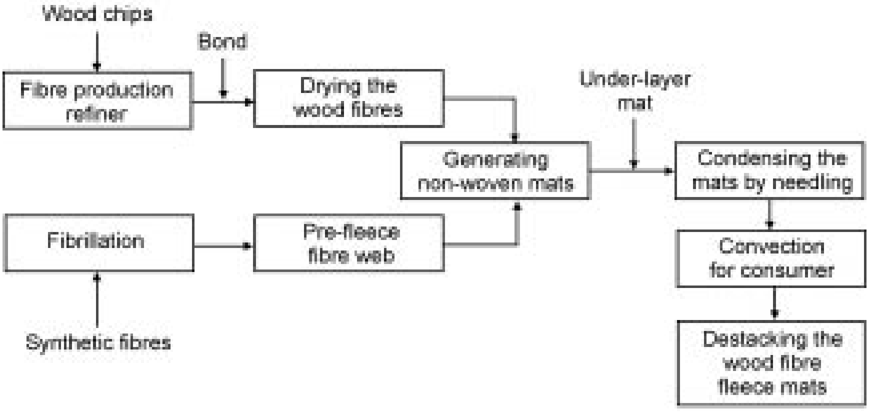
4.5 Other processes

4.5.1 Thermoset mat compression moulding

The mat compression process uses a mat which is made of natural fibres. As shown in Fig. 4.21 the mat is just sprayed, not moistened, with resin and



4.21 Mat compression process and ready component part; raw and covered by all functional and decorative details.[55]



4.22 Production of wood fibre mats.[56]

compressed into its final contour in a hot tool; by using the air permeability the parts can be covered easily in a vacuum covering process.[55] The production of the employed mats is illustrated as an example in Fig. 4.22 which shows the manufacturing of mats from wood fibre at Bo-Systems GmbH Natural Fiber Systems, Sontra.

Process characteristics

Despite high tool costs, a moderate price level is achieved due to moderate production rates. The thermoset materials are very strong and heat resistant at moderate costs.[51]

4.5.2 Production of compression moulded thermoset semi-products

Bakelite has produced wood filled moulding material from phenolic resin used for mass components such as switches and connectors. During the manufacturing process of the wood-filled phenoplast a mould pressure of about 150 bar is built up at a temperature of 160–179 ºC. The hardening time of about 50 seconds leads to shrinkage of 0.4–0.8%; in addition the post-shrinkage is about 0.15–0.30%.

A composition of cellulose or textiles increases the parameter of the final product and accordingly the procedure regarding pressure and temperature also changes as both of them increase. Temperature stability at high stiffness and stability is characteristic for this material. However, this common technology more and more competes with thermoset injection moulding which includes the production of moulding mass in the process.

4.5.3 Thermoset injection moulding

Injection moulding of thermosets is basically identical to that of thermoplastics, with the exception that the thermoset material is injected cool into a heated mould. The heated mould causes a crosslinking reaction in the material and a hard part is removed from the tool.

Process characteristics

Owing to high tool costs, the part costs are relatively low because of the high production. Thermoset materials are very stable.[51]

4.6 Future trends

Significant advances in the processing of natural-fibre reinforced plastics are expected, especially in the foaming and the injection moulding processes. The future looks very promising for both technologies. Appropriate extraction and measuring processes for fibre composites will become increasingly more important for their assessment and will become part of the standardising process.

The differing fibre geometrics and distributions achieved in the fibre processing are reflected in the properties of the composites, but they can be smoothed out with the injection moulding process. Access for industrial use is determined by the marketplace. An important consideration is that the automobile industry is especially cost-conscious. Any time new processes or materials are used, the production costs are the foremost judgement criterion, consisting of process, tools, material and labour costs. The ecological properties are also an important factor for the application of new technologies. This applies especially to bio-based materials.

According to an analysis of automobile parts (for instance door panels) based on the use of compounds and on the appropriate production processes as well as the time of their introduction, the trend and the positive development for the use of NFCs becomes very clear.

4.7 Conclusions

Natural fibres are renewable resources. Their positive effect on the ecology has been proven through many environmental-performance evaluations and life-cycle assessments. Among other criteria, production, processing, usage and methods for recycling were studied.

Applications of natural-fibre reinforced products have been developed for years by the supply companies for the automobile industry; they develop and offer together with the automobile companies – especially in Europe – new technical solutions. Inventive ways for the creation of new products and composites will be added to the constantly improving standard processes. Ever stronger growing international competition and the cost-consciousness of the consumer will be the driving forces for the acceptance of the offered solutions.

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5

Development of non-wood natural-fibre composites

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5.1 Introduction

Crystalline cellulose performs as well as glass or Kevlar fibres in tensile tests (Table 5.1). Cellulose is a major component of plant fibres, which are plentiful, so it might be possible for cellulose to compete on price as well as performance. Unfortunately, the development of cellulose-reinforced composites has not proved a simple task. A few products have approached or exceeded some of the mechanical properties of glass-reinforced composites, but none has approached the properties of Kevlar-reinforced composites.

This chapter outlines a scientific basis for development of natural-fibre composites, starting with a simple model for the structure of a plant fibre and working through the implications for the properties of composite materials: tensile modulus and strength, water uptake, etc. The discussion then turns to practical considerations, showing how fabrication methods have been developed to conserve or improve the desirable properties of natural fibres.

One approach to selecting an appropriate plant fibre is to consider the role of the fibre in the living plant. Bast fibres stiffen the stems of plants, so they might be ideal for stiffening composites. Leaf fibres must withstand repetitive flexing motions as a leaf moves in the wind, so they might be ideal for toughening composites. Seed hairs do not need to be stiff or tough, but they usually expand

Table 5.1 Experimental tensile properties of cellulose compared with synthetic reinforcing fibres

Fibre	Tensile modulus (GPa)	Tensile strength (GPa)	Reference
Cellulose I	138	>2	Nishino *et al.* (1995), Yano *et al.* (2005)
E-glass	73	2.3	Van de Velde and Kiekens (2001)
Kevlar-49	97	2.3	Wang and Xia (1998)

to a low bulk density, so they might be considered ideal for insulating material rather than reinforcing composites. The discussion that follows is illustrated by data for fibres taken from each of these three categories: flax and ramie represent the bast fibres, sisal and harakeke the leaf fibres, cotton and coir the seed hairs.

Natural-fibre composites include products from animal fibres. Composites have been made from thermoplastic or thermosetting resins reinforced with waste silk (Han *et al*., 2006), or keratin fibres from poultry feathers (Barone and Schmidt, 2005; Hong and Wool, 2005). The use of feathers is of particular interest, since the fibres are hollow and the composites are of low density relative to products made with plant fibres. The overwhelming majority of natural-fibre composites are made from plant fibres, so animal fibres will not be mentioned in the remainder of this chapter.

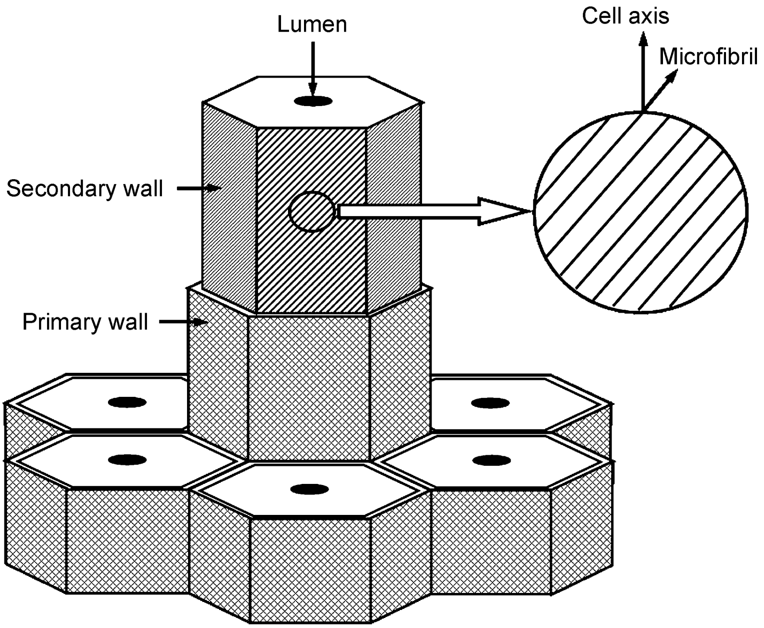
5.2 Matching properties to end uses

5.2.1 Structure of a plant fibre

Some of the obstacles to development are illustrated in Fig. 5.1. Non-wood plant fibres are usually bundles of cells, each with a polygonal cross-section so that they pack together efficiently. Each cell starts as a thin-walled tube. A secondary wall is later deposited inside the primary wall, so that the cavity within the tube shrinks in diameter. This cavity is known as the lumen. Cellulose molecules are long chains of glucosyl monomer units, wound around the cell wall as it thickens. Bundles of tens of molecules aggregate to form crystalline structures known as microfibrils. The angle θ between microfibril and cell axes is known as the microfibril angle. The microfibrils are embedded in a matrix of hemicelluloses. Cell-to-cell adhesion is dependent on pectins through the early stages of growth, and is later enhanced by the formation of lignin in some types of fibres.

The cheapest reinforcing fibres are the raw bundles of cells, sometimes known as technical fibre. The mechanical properties of the composite are complicated by the presence of two kinds of interface: one between the technical fibre and the matrix, the other between adjacent cells within each bundle (Stocchi *et al*., 2007). The latter interface might be unacceptably weak. Cell-to-cell weaknesses can be removed by separating the cells, but this introduces a new problem: each liberated cell contains helically wound cellulose which can stretch like a spring. Other problems can include smooth primary walls that allow the cell to be pulled out of the matrix, or open lumens that conduct water into the interior of a composite.

These problems should not be seen as obstacles that must all be overcome. A more realistic approach is to identify simple treatments that can modify some of the fibre properties, then match the properties to end uses. Five key properties



5.1 Representation of a bundle of fibre cells, with the primary wall of one cell cut away to expose the secondary wall. The inset defines the microfibril angle θ.

are discussed here: tensile modulus, tensile strength, impact resistance, water resistance and fire resistance.

5.2.2 Tensile modulus

The theoretical relationship between the tensile modulus (E_f) of a reinforcing fibre and the microfibril angle θ within that fibre is (McLaughlin and Tait, 1980):

$$E_f = v_x E_x \cos^2\theta + (1 - v_x) E_{nx} \qquad 5.1$$

Here v_x is the volume fraction of cellulose within the fibre and E_x and E_{nx} are the tensile moduli of cellulose and non-cellulosic matter, respectively. Moharir *et al.* (1982) confirmed a relationship between tensile modulus and microfibril angle, using cotton fibres from 24 different varieties.

The factor of $\cos^2\theta$ in Eq. [5.1] suggests that it might be advantageous to select fibres with a low microfibril angle, but this consideration should not be overrated. Mukherjee and Satyanarayana (1986) tabulated typical values of θ for 15 different types of plant fibres. In general, bast fibres show the lowest values: $\theta < 10°$, so the factor $\cos^2\theta$ is approximately unity. Most leaf fibres show $15° < \theta < 25°$, so $\cos^2\theta$ is in the range 0.8 to 0.9 and the influence on performance might not be detectable. For coir, i.e. the hairs on a coconut, $\theta = 45^\circ$ and $\cos^2\theta = 0.5$. Clearly coir cannot be expected to stiffen a composite as effectively as bast or leaf fibres.

Differences in v_x seem likely to be as important as the microfibril angle, or even more important. Values of v_x are rarely published, but the densities of cellulose and non-cellulosic substances are similar, so we can use the weight fraction of cellulose instead of the volume fraction. Values of $v_x = 0.4$ to 0.8 are typical for bast and leaf fibres (Mukherjee and Satyanarayana, 1986; Ndazi *et al.*, 2006), except for the bast fibre ramie with $v_x = 0.8$ to 0.9. Coir has a particularly low cellulose content ($v_x = 0.4$).

Some publications provide analytical data for alpha-cellulose, i.e. the sum of cellulose and associated hemicelluloses. This information can be misleading, since hemicelluloses contribute little to the tensile modulus of a fibre. It is important to confine the use of v_x to mean the fraction of true cellulose in the fibre.

The advantages of a promising natural fibre can be lost if the composite fabrication process is unsuitable. The tensile modulus (E_c) of a fibre-reinforced material can be calculated using Cox–Krenchel theory (Garkhail *et al.*, 2000):

$$E_c = \eta_o \eta_L V_f E_f + (1 - V_f) E_m \qquad 5.2$$

Here V_f is the volume fraction of fibre in the composite and E_m is the tensile modulus of the matrix. The orientation factor η_o takes values of 1 for a perfectly aligned unidirectional structure, 3/8 for randomly oriented fibres in mats, or 1/5 for random orientation in three dimensions. The length factor η_L is unity for long fibres, but can take values of $\eta_L < 1$ when fibres are shortened below a critical value, e.g. chopped and blended with resin. Values of $\eta_L \ll 1$ are typical for fibres shortened by attrition during injection moulding. Weak regions in plant fibres can make them susceptible to attrition, relative to glass fibres, leading to median lengths of <0.4 mm for some plant fibres in injection-moulded composites (Karmaker and Youngquist, 1996).

Tensile strengths for flax-reinforced composites are shown in Table 5.2, in order to illustrate the influence of the fabrication method on the tensile modulus. Data were selected from the literature so that the volume fraction was $V_f = 0.40$ in all cases. Let us suppose that $\eta_L = 1$, and that E_{nx} and E_m are negligible relative to $E_x = 138$ GPa (Table 5.1). If we use a value of $\cos^2\theta = 1.0$ typical of a bast fibre, as discussed above, and $v_x = 0.64$ (Baley, 2002), then Eq. [5.1] gives $E_f = 88$ GPa and Eq. [5.2] gives theoretical values $E_c = 35$ and 13 GPa for unidirectional and random-mat reinforcement, respectively. Table 5.2 shows experimental values of 28 and 9 GPa, respectively. The experimental values are close to the theoretical potential for both types of composites. If we assume that injection moulding left the fibre orientation fully randomised, then $\eta_o = 1/5$ and the theoretical modulus is $E_c = 7$ GPa. The relatively low experimental modulus of $E_c = 2.3$ GPa is attributed to fibre damage during injection moulding, so that the mean length was less than the critical value and $\eta_L \ll 1$.

Table 5.2 Experimental tensile properties of composites reinforced with flax fibres at $V_f = 0.40$

Fibre	Matrix	Tensile modulus (GPa)	Tensile strength (MPa)	Reference
Unidirectional	Epoxy	28	133	Van de Weyenberg *et al.* (2003)
Unidirectional	Polypropylene	29	320	Madsen and Lilholt (2003)
Random mat	Polypropylene	8.6	43	Garkhail *et al.* (2000)
Random mat	Polypropylene	8.8	52	Van den Oever *et al.* (2000)
IM short fibre	Polypropylene	2.3	24	Arbelaiz *et al.* (2005)

IM = injection moulded.

For comparison, an experimental tensile modulus of $E_c = 31$ GPa has been reported for unidirectional glass fibre in epoxy, achieved at $V_f = 0.48$ (Oksman *et al.*, 2002). The experimental value of 28 GPa for unidirectional flax in epoxy (Table 5.2) achieved a lower volume fraction of $V_f = 0.40$. This shows that flax can compete with glass as a reinforcing fibre in situations where stiffness is the primary requirement.

5.2.3 Tensile strength

McLaughlin and Tait (1980) discussed a theoretical basis for tensile strength in biocomposites, suggesting a dependence on microfibril angle similar to that observed for tensile modulus. Mukherjee and Satyanarayana (1986) confirmed a dependence on $\cos^2\theta$, with a correlation coefficient $r = 0.93$ for fibres from 15 plant species:

$$\sigma_f = v_x \sigma_x \cos^2\theta \qquad 5.3$$

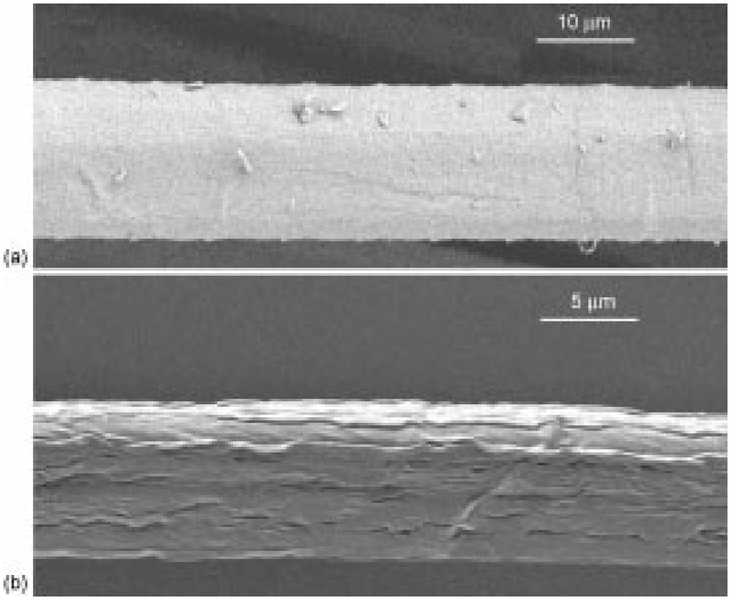
For example, if we use $v_x = 0.64$ and $\cos^2\theta = 1.0$ for cellulose in flax fibre, as above, and $\sigma_x > 2$ GPa (Table 5.1), then Eq. [5.3] suggests $\sigma_f > 1.3$ GPa. Baley (2002) reported a mean value of $\sigma_f = 1.3$ GPa for numerous tests on single flax fibres.

The rule of mixtures does not give useful predictions of tensile strength for biocomposites. For example, suppose that flax fibres, with $\sigma_f > 1.3$ GPa as above, are used to reinforce a composite at $V_f = 0.40$. The rule of mixtures suggests $\sigma_c > 500$ MPa. Experimental values of 133 MPa and 320 MPa (Table 5.2) are far below the theoretical potential. The problem of low tensile strength is even worse for random mats. Experimental values (Table 5.2) for flax–polypropylene show little improvement over a value of $\sigma = 33$ MPa for pure polypropylene. An experimental value for an injection-moulded composite (Table 5.2) shows a decrease in strength relative to pure polypropylene.

The low tensile strengths of natural-fibre composites might, in part, result from defects known as kink bands or nodes. These defects can be detected by electron microscopy (Baley, 2002) or polarised light (Hughes *et al.*, 2007). They appear to be regions of relatively low stiffness, since they extend in the early stages of tensile testing (Baley, 2002). This leads to stress concentrations in the matrix in the vicinity of a defect (Eichhorn and Young, 2003; Hughes *et al.*, 2007), presenting an initiation point for a crack. Hand isolated fibres are virtually free of kink bands (Bos *et al.*, 2002), so the strength of a composite might be influenced by the method of fibre isolation.

Poor matrix adhesion might also contribute to the problem of low tensile strength. Considerable effort has been expended in attempts to improve fibre–matrix interfaces.

- Some technical fibres, e.g. coir (Brahmakumar *et al.*, 2005), are surrounded by a natural waxy layer that is compatible with hydrophobic polymers such as polyethylene. Removal of the waxy layer has a negative influence on the tensile strength of a composite (Brahmakumar *et al.*, 2005).
- Some plant fibres have smooth surfaces, others have rough or corrugated surfaces. Smooth surfaces seem more likely so pull out of the matrix. The difference is illustrated in Fig. 5.2 for a bast fibre (flax) and a leaf fibre from harakeke (*Phormium tenax*). In the latter case, the roughened surface arose from treatment with aqueous NaOH at 170 °C (Duchemin *et al.*, 2003).



5.2 Scanning electron microscope images of single plant fibres: (a) commercial flax sliver, (b) harakeke (*Phormium tenax*) leaf fibre pulped with aqueous NaOH at 170 °C.

- Chemical treatments have included soaking in alkali and reactions with organosilanes or acrylonitrile (Mehta *et al.*, 2006). In some cases, these treatments have doubled the tensile strength of composites.
- Compatibilisers strengthen fibre–matrix interfaces. For example, Arbelaiz *et al.* (2005) increased the tensile strength of injection-moulded flax–polypropylene composites by approximately 40% through addition of maleic anhydride–polypropylene copolymer as a compatibiliser.

5.2.4 Impact resistance

While low microfibril angles are ideal for stiffness, the fibres can be subject to brittle fracture. Increasing the microfibril angle improves toughness. Pavithran *et al.* (1987) discussed a theoretical basis for an optimal microfibril angle of 20º. Their experimental values of Charpy impact strength seemed to support the theory, with maximum impact strength observed for polyester reinforced with sisal ($\theta = 20º$). Wambua *et al.* (2003) likewise found higher impact strengths for composites reinforced with sisal, relative to composites reinforced with bast fibres or coir. Rodríguez *et al.* (2005) found no detectable advantage in using sisal, relative to bast fibres. While there are inconsistencies among reports, it seems that there is no disadvantage in using leaf fibres such as sisal in situations where toughness is important.

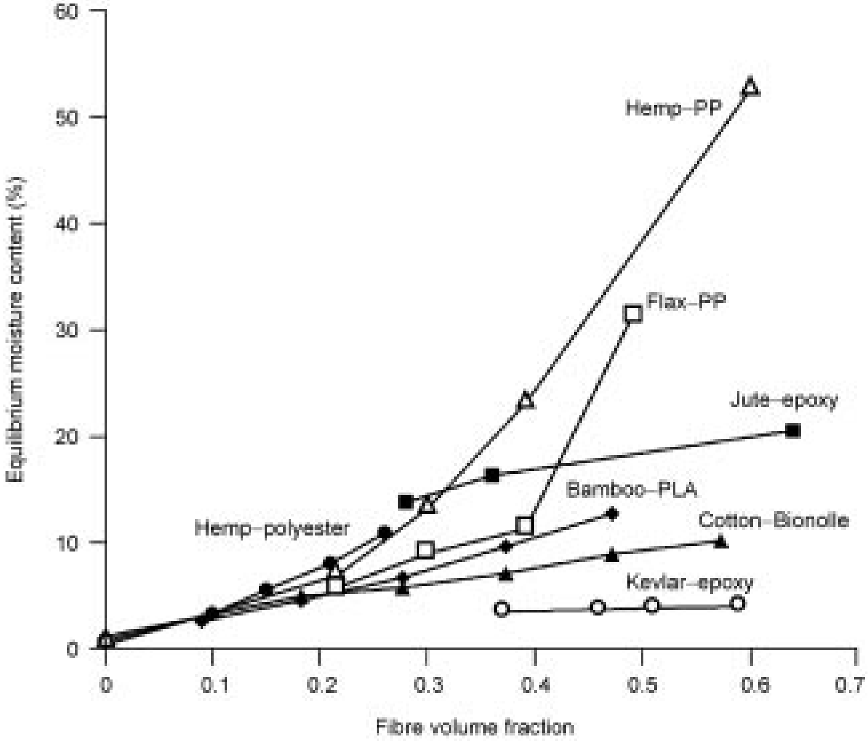
The impact strength of a natural-fibre composite is usually just a fraction of the value observed for the corresponding glass reinforced composite, at the same volume fraction (Pavithran *et al.*, 1987; Rodríguez *et al.*, 2005). Impact strength clearly remains one of the weaknesses of natural-fibre composites. The source of this weakness might be the presence of kink bands in natural fibres, providing crack initiation points as discussed above in the context of tensile strength (Eichhorn and Young, 2003).

5.2.5 Water resistance

One of the obstacles to widespread acceptance of natural-fibre composites is the relatively rapid water uptake, which can lead to dimensional instability and rotting. Plant fibres develop around a living cell which dies to leave a cavity or 'lumen' (Fig. 5.1). The fibre cell is therefore tubular in shape, and can transport water into a composite. If the fibres are formed into random mats, which are then laminated to form a composite, lumen transport will move water from the edges to the centre. Movement of water from the faces to the centre will be slower, since it involves diffusion of the water molecules through the matrix and across the fibres. Rouison *et al.* (2005) confirmed rapid uptake through edges, using magnetic resonance imaging to monitor changes in hemp–polyester composites immersed in water. In some technical fibres, e.g. coir (Brahmakumar *et al.*, 2005), a bundle of fibre cells surrounds a central cavity or 'lacuna'. The existence of a lacuna can enhance movement of water into the composite.

When a natural-fibre composite is immersed in water long enough for equilibrium to be established, the moisture content is not always a linear function of the fibre content (Fig. 5.3). At low fibre contents, the matrix restrains expansion of the fibres. At high fibre contents, there is insufficient matrix to maintain this restraint and the fibres can soak up more than their own weight in water (Hargitai *et al.*, 2006). For comparison, Kevlar-reinforced composites reach equilibrium moisture contents of just a few per cent (open circles in Fig. 5.3). Glass- and carbon-reinforced composites reach equilibrium moisture contents that are typically <1% (Chateauminois *et al.*, 1994; Wan *et al.*, 2005).

The primary concern, regarding water uptake, is the associated swelling. This might cause components to buckle or separate from other components. In some cases the water uptake can also cause cumulative damage. Kim and Seo (2006)



5.3 Water uptake in composites: jute–epoxy (solid squares, Rao *et al.* 1981), Kevlar–epoxy (open circles, Aronhime *et al.*, 1987), cotton–Bionolle (solid triangles, Tserki *et al.*, 2003), flax–polypropylene (open squares, Arbelaiz *et al.*, 2005), bamboo–poly(lactic acid) (solid diamonds, Lee and Wang, 2006), hemp–polypropylene (open triangles, Hargitai *et al.*, 2006), hemp–polyester (solid circles, Dhakal *et al.*, 2007).

compared composites made from woven sisal mats. After five wet–dry cycles, the strengths of vinyl–ester and epoxy composites had decreased to 80% and <20% of the original values, respectively. Loss of strength in the epoxy composite can be attributed to hydrolysis reactions.

There have been numerous attempts at improving water resistance by treating plant fibres. Bisanda and Ansell (1991) treated sisal with an organosilane to decrease the influence of water on the mechanical properties of sisal–epoxy composites. Stamboulis *et al.* (2000) showed that the water uptake of flax–polypropylene composites could be decreased by approximately 30% through heat treatment of the flax prior to fabrication of the composite. Lee and Wang (2006) treated bamboo fibres with lysine diisocyanate to decrease water uptake in poly(lactic acid) and poly(butyl succinate) composites. Unfortunately, fibre treatment processes are usually too expensive to be considered worthwhile in commercial production.

5.2.6 Fire resistance

The combustibility of natural fibres is a cause for concern, in terms of the heat generated when natural-fibre composites burn (Manfredi *et al.*, 2006). Heat output is, however, just one of the properties to be considered in evaluating fire resistance. The time to ignition and flame velocity are also important, and results from those tests are promising.

A low lignin content is considered desirable in designing composites for fire resistance (Manfredi *et al.*, 2006). Thus for acrylic composites, those reinforced with flax (containing 2% lignin) took twice as long to ignite relative to those reinforced with sisal (containing 10% lignin). Flax–acrylic and jute–acrylic composites both took longer to ignite than the glass–acrylic composite.

Müssig *et al.* (2006) measured flame velocities for hemp–epoxy composites, and found velocities typically twice as fast as for a glass–polyester standard. When aluminium hydroxide was added as a flame retardant, the flame velocity dropped to less than half of that for the glass–polyester standard.

5.3 Development of fabrication methods

5.3.1 Laminated composites

The first modern natural-fibre composites emerged from a search for a cheap substitute for mica, to be used as insulating material in the electrical appliance industry. The chemist Leo Baekeland and the electrical engineer Sir James Swinburne, working independently, made thermosetting resins from mixtures of phenol and formaldehyde. Baekeland filed his patent first (Baekeland, 1909), so the resin became known as Bakelite. Researchers at Westinghouse Electrical and Manufacturing Company reinforced Bakelite with paper or cloth to make composite panels for use in switchboards, radios, etc. (O'Conor, 1918). The inventors left Westinghouse to establish the Formica Insulating Company in 1913. They later experimented with different combinations of resins and reinforcing fibres to expand the range of Formica products from insulators to machinable composites and decorative surfaces (www.formica.com).

In the original Westinghouse manufacturing process (O'Conor, 1918), reinforcing fabric was coated with resin on one side. The fabric was then dried, cut into sheets, stacked between steel plates, and pressed between the heated platens of a hydraulic press. Suitable fabrics included plain-weave cotton cloth. Similar cotton–phenolic composites are still manufactured, almost a century later, for use in gears, pulleys, rollers, guides and bearings (www.norplex-micarta.com).

5.3.2 Unidirectional fibre reinforcement

During the 1940s, natural-fibre composites were considered as possible substitutes for metals. For example, unidirectional flax fibres were embedded in phenolic resin to make Gordon Aerolite (Gordon, 1964; Bishopp, 1997). This composite material had a tensile modulus less than that of aluminium ($E = 48$ and 70 GPa respectively), but the fact that its density was roughly half that of aluminium made it attractive for use in aircraft. Gordon Aerolite was used to make 30 tailplanes for Miles Magister trainer aircraft (Bishopp, 1997). It was never manufactured on a large scale because composites with unidirectional reinforcement have limited application in engineering (Gordon, 1964). Glass–polyester composites were developed at the same time as Gordon Aerolite, and found more widespread uses.

In fabrication of a unidirectional composite, it is important to ensure that the fibre content is kept as high as possible. This can be achieved, at least on a laboratory scale, by using a 'leaky mould' (Bisanda and Ansell, 1991). A mixture of fibre and resin is compressed in a mould that is designed to allow excess resin to flow from the fibres. Pultrusion is another approach. Yarns or fabrics are pulled through a resin bath and compressed by rollers (Angelov *et al.*, 2007), or a commingled yarn of natural fibre and thermoplastic is drawn through hot rollers (Van de Velde and Kiekens, 2001).

Plant fibres can sometimes be more than a metre long, but even that length is too short for fabrication methods to be modelled on the methods used for continuous glass filament. New fabrication methods include microbraiding (Khondker *et al.*, 2006), in which yarn is made by winding a thermoplastic polymer around a unidirectional bundle of plant fibres. The yarn can be made into unidirectional preforms, and the thermoplastic melted in a heated mould. Conventional twisted yarns can also be used, and the composites can even show superior strength if the twist is optimised (Goutianos *et al.*, 2006).

5.3.3 Random fibre reinforcement

The Ford Motor Company made an experimental automobile body from plant fibres and resin compressed in moulds (Anonymous, 1941). The composite was said to have an impact strength greater than steel, but the vehicle never went into commercial production. Ecological concerns motivated fresh funding for development of natural-fibre composites during the 1980s. During the 1990s, natural fibres began to displace glass fibres as reinforcing for automobile interiors. Impact strength was considered more important than stiffness in this application, so it was important that the fabrication methods should retain the long fibre lengths characteristic of non-wood sources. The earliest long-fibre automobile components were made by two processes (Magurno, 1999; Brosius, 2006):

1. Natural fibres were mixed with thermoplastic fibres and formed into non-woven mats. The mats were stacked to give the desired thickness, then moulded at a temperature sufficient to melt the thermoplastic fibres. Examples included Flexform, a 50 : 50 blend of flax and polypropylene fibres.
2. Natural fibres were formed into needle-punched mats, a thermoset resin was applied and the mats were moulded at a temperature sufficient to cure the resin. Examples included the flax/sisal-epoxy door panels used in the Mercedes E-class.

More recent developments have included (Brosius, 2006):

- Long-fibre thermoplastics (LFTs) produced by melt compounding in an extruder, followed by moulding under pressure. The fibres are not as severely degraded as those in injection moulded composites. Examples include the spare wheel pan cover of the 2005 Mercedes A class, made from abaca–polypropylene LFT.
- Sheet moulding compounding (SMC) in which two layers of release film enclose a resin–fibre–resin sandwich. Examples include experimental combinations of hemp with polyester and vinyl ester resins at Ford Motor Company.

5.3.4 Novel resins

Current development projects include biofibre–bioresin composites, i.e. natural fibres embedded in resins made from natural polymers. O'Donnell *et al.* (2004) described composite panels made from plant fibres and a resin made by chemical modification of soybean oil. Müssig *et al.* (2006) described a bus component made from hemp fibres in an epoxy resin made from vegetable oils. Toyota Motor Company made an electric vehicle in which the entire body was reinforced by kenaf fibre embedded in resin made from lignin extracted from kenaf plants (Nishino *et al.*, 2006).

5.4 Future trends

While natural-fibre composites are now common in the automobile industry, they are expected to be excluded from most aircraft, rail and subway markets until the issues of flame, smoke and toxicity are dealt with (Brosius, 2006). Future improvements in fire resistance might prove difficult, given that one of the incentives for using plant fibres is the possibility of disposal in the form of pelletised solid fuels.

Improving toughness is perhaps the second priority for future work. The impact strength of natural-fibre composites is usually just a fraction of that of glass fibre composites, at the same volume fraction of fibre (Pavithran *et al.*, 1987; Rodríguez *et al.*, 2005). This is of concern in designing automobile components that will absorb energy during a collision, or designing sports equipment such as surfboards that are currently reinforced with glass fibre.

End-of-life options require further development before natural-fibre composites will become accepted as truly sustainable. Composting and burning are frequently discussed as likely disposal methods, but neither is currently used on a large scale. If natural-fibre composites end up in landfills, along with fibreglass and conventional plastics, then the advantages will be less obvious to consumers.

5.5 Sources of further information and advice

Further discussion on this topic can be found in several review articles, e.g.

- General reviews: Saheb and Jog (1999), Peijs (2000), Ndazi *et al.* (2006), Yu *et al.* (2006).
- Fibre treatments: Mohanty *et al.* (2001, 2002), George *et al.* (2001), Jacob *et al.* (2005), Li *et al.* (2007).
- Research projects in key laboratories: Riedel and Nickel (1999), Eichhorn *et al.* (2001).

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6

Cellulose nanocomposites

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6.1 Introduction

Nanotechnology can be defined as the understanding and control of matter at dimensions of roughly 1–100 nm, where unique phenomena enable novel applications. That definition was used by the US National Nanotechnology Initiative, launched by President Clinton in 2001 (www.nano.gov). Cellulose can be prepared in the form of crystalline whiskers with cross-sectional dimensions typically in the range 2–20 nm. These were described as crystallites until recently, when the popularity of the prefix 'nano' led to introduction of the word 'nanocrystal'. There are numerous theoretical advantages in using cellulose nanocrystals, rather than conventional cellulosic fibres, to reinforce composite materials.

Cellulose can also be prepared in fibrous structures or tangled masses, with a nanoscale porosity that justifies the use of the word nanocomposite when the particles are used as reinforcement. Clearly it is important to distinguish between nanocomposites reinforced with whiskers or nanoporous particles, so this chapter begins with a discussion of sources of cellulose and the nature of the nanoparticles that can be produced.

The choice of a polymeric matrix also influences the performance of nanocomposites, and is discussed here. Cellulose nanocomposites rarely show the theoretical improvements in performance, but there are now such a large number of published studies that a pattern of successes and failures is emerging. The chapter ends with projections to future research topics that might lead to commercial products.

6.2 Nanofibrous and nanocrystalline cellulose

While different sources yield different types of cellulose nanoparticles, the procedures for isolating cellulose usually follow a three-step scheme:

1. Chemical or enzyme treatment to remove non-cellulosic matter.
2. Partial hydrolysis, by acid or enzymes, to break fibres at crystal defects.

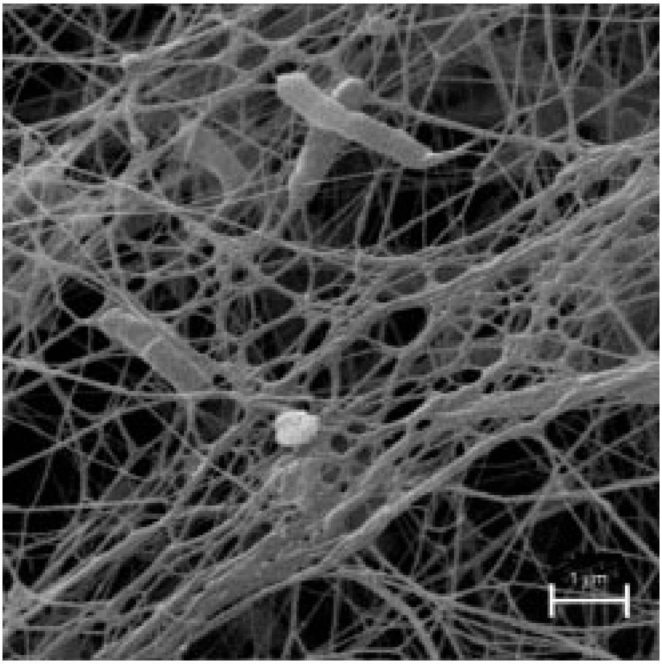
3. Mechanical disintegration, e.g. by use of shear forces, to separate nanoparticles.

These steps usually yield a colloidal suspension in water, stabilised by the negative charges of anionic groups introduced during partial hydrolysis. Details of treatments, and the order of steps (2) and (3), depend on the source of the cellulose: animal, algal, bacterial or plant.

6.2.1 Cellulose from bacteria

Bacteria such as *Gluconacetobacter xylinus* extrude cellulose from their cell walls into the surrounding medium. The cellulose chains crystallise into structures with cross-sectional dimensions typically 6 nm by 2 nm, and these crystalline structures aggregate into ribbons up to 50 nm wide (Gindl and Keckes, 2004). An electron microscope image is shown in Fig. 6.1.

Gel-like hydrated masses of bacterial cellulose are eaten as a desert in Japan, the Philippines and Indonesia (Yano *et al*., 2005). Non-cellulosic matter can be removed by boiling a hydrated mass in 1% (by weight) aqueous NaOH, washing and drying under vacuum (Nakagaito *et al*., 2005). The nanofibrous product can be further processed, by acid hydrolysis and disintegration, to yield nanocrystals (Grunert and Winter, 2002).



6.1 Electron microscope image of nanofibrous bacterial cellulose.

6.2.2 Cellulose from animals

Some of the largest of all known cellulose nanocrystals are obtained from animals of the subphylum Urochordata, commonly known as tunicates or sea squirts. The cellulose reinforces proteins in a protective tunic. Nanocrystals can be obtained by bleaching and dissolving the protein, disintegrating the cellulosic mass in a homogeniser, and hydrolysing the particles in sulphuric acid (Favier *et al.*, 1995). The nanocrystals are parallelepiped rods, typically >1 μm long and 10–20 nm wide (Favier *et al.*, 1995; Ljunberg *et al.*, 2006).

6.2.3 Cellulose from algae

Some green algae reinforce their cell walls with crystalline cellulose. Particularly large nanocrystals have been found in algae of the class Chlorophyceae. Nanocrystals can be obtained, e.g. by treating cell walls in 0.1 M aqueous NaOH at 100 °C for 2 h, then in 0.05 M HCl at room temperature overnight, washing, homogenising, freeze-drying, then partly hydrolysing in 66% (by weight) aqueous H_2SO_4 for 3 h, washing, and partly hydrolysing with either cellulase or 2.5 M HCl at 100 °C for several hours (Hayashi *et al.*, 2005). Typical nanocrystals are 10 nm wide and 350 nm long.

6.2.4 Cellulose from vascular plants

Plant cells start as thin-walled structures, reinforced by cellulose nanofibrils that form a random network. Fibre cells do not stop growing on completion of this primary wall, but construct a thicker layer known as the secondary wall. Cellulose nanofibrils reinforce the secondary wall also, but the nanofibrils tend to run parallel to their neighbours. In some cases, the secondary walls become encrusted with lignin. The isolation of nanofibrous masses from secondary walls can therefore be challenging.

Parenchymal cell cellulose (PCC) was developed in the 1980s (Weibel, 1989). Parenchymal cells do not have specialised functions, but are produced to provide bulk and fill gaps in a growing plant. They stop developing when the primary wall is completed, so the nanofibrous networks are readily isolated. PCC can be obtained from food processing wastes, e.g. sugar beet pulp (Dinand *et al.*, 1996) or potato pulp (Dufresne *et al.*, 2000).

Microfibrillated cellulose (MFC) was also developed in the 1980s (Turbak *et al.*, 1983). This was obtained from plant celluloses through a high-energy homogenisation process, and was originally intended for use in food, cosmetics, etc. MFC is typically obtained from wood pulp, e.g. softwood sulphite pulp (Zimmermann *et al.*, 2004). The pulping process removes most of the encrusting lignin from the secondary cell walls, so that nanofibrous cellulose can be liberated by treatment in an ultra-turrax, followed by homogenisation with a microfluidiser (Zimmermann *et al.*, 2004). MFC is a tangled mass of fibres with diameters typically in the range 20–100 nm and lengths of tens of micrometres.

The success of the mechanical treatment depends on generation of high shear forces. Chakraborty *et al.* (2005) treated wood pulp in a laboratory refiner for up to 125 000 revolutions, then generated high shear forces by immersing the fibres in liquid nitrogen and grinding them in a cast iron mortar and pestle.

The finest cellulose nanocrystals have been obtained from plants, e.g. from sugar beet (Samir *et al.*, 2004), sisal leaf fibres (de Rodriguez *et al.*, 2006). The presence of lignin in the cell walls of some plant fibres requires an additional bleaching step, e.g., using aqueous $NaClO_2$ (de Rodriguez *et al.*, 2006). As for most other nanocrystal sources, the key step is partial hydrolysis in aqueous H_2SO_4. Bondeson *et al.* (2006) optimised this step for releasing nanocrystals from microcrystalline cellulose. They found best results for 2 h of treatment in aqueous H_2SO_4 at 63% by weight. The nanocrystals were <10 nm wide and 200–400 nm long.

6.3 Nanocomposite fabrication

6.3.1 Nanofibrous reinforcement

If the cellulose is nanofibrous, the resin must be capable of penetrating the nanoscale pores. One strategy is to dilute the resin with a solvent that is later removed by evaporation.

Nakagaito *et al.* (2005) diluted phenol-formaldehyde resin with methanol in order to impregnate sheets of nanofibrous bacterial cellulose. The methanol was removed by evaporation, and the sheets hot-pressed to form composites. MFC has likewise been impregnated with phenol-formaldehyde resin and hot-pressed to make composites (Nakagaito and Yano, 2005). Gindl and Keckes (2004) dissolved cellulose acetate butyrate in acetone to impregnate sheets of freeze-dried bacterial cellulose.

Dufresne *et al.* (2000) mixed a solution of gelatinised starch with a suspension of potato PCC, then homogenised the mixture in an ultra-turrax to ensure impregnation of the nanofibrous structures. Hepworth and Bruce (2000) used 10% (by weight) aqueous poly(vinyl alcohol) to impregnate nanofibrous cellulose from swede roots. Wang and Sain (2007) mixed aqueous poly(vinyl alcohol) with a suspension of nanofibrous cellulose isolated from soybean pods. Bruce *et al.* (2005) mixed suspensions of poly(vinyl acetate) or acrylic polymers with suspension of swede-root cellulose. Chakraborty *et al.* (2006) mixed aqueous poly(vinyl alcohol) with a suspension of wood-pulp MFC to form films. In all of these examples, the water was removed by evaporation to form nanocomposite films.

6.3.2 Nanocrystalline reinforcement

Nanocrystals of cellulose are usually prepared in the form of a colloidal suspension. The use of H_2SO_4 in the hydrolysis step helps stabilise the suspension, since it introduces sulphate groups on the surfaces of the nanocrystals. The negatively charged nanocrystals repel each other. The suspension must be transformed into a composite without allowing the nanocrystals aggregate in clumps.

One way of achieving the transformation is to mix the suspension of nanocrystals with a polymer emulsion, then remove the water by evaporation or freeze-drying. Hajji *et al.* (1996) used an emulsion obtained by copolymerisation of styrene with butyl acrylate to make composites from tunicate cellulose nanocrystals. They extruded the composite to make specimens for mechanical testing. Helbert *et al.* (1996) obtained cellulose nanocrystals from wheat straw and mixed them with a similar latex to make nanocomposites. Ruiz *et al.* (2001) mixed tunicate nanocrystals with an epoxy prepolymer in the form of an aqueous emulsion, and added a water-soluble hardener (polyoxypropylene triamine). Nonyl phenol polyethylene oxide was added to stabilise the emulsion at an average droplet size of $< 2\,\mu$m. Films were cast, retaining a good dispersion of nanocrystals in the epoxy matrix.

Sometimes it is possible to freeze-dry the suspension of nanocrystals, then resuspend them in an organic solvent, e.g. chloroform (Petersson *et al.*, 2007) or toluene (Ljundberg *et al.*, 2006). In the latter case, a phosphoric acid ester of polyoxyethylene-9-nonylphenyl ether was added to the suspension of nanocrystals to inhibit aggregation during freeze-drying. The resuspended nanocrystals were mixed with a solution of polypropylene in toluene and cast to form films.

6.3.3 All-cellulose composites

Nishino *et al.* (2004) made an ‘all-cellulose’ composite by embedding unidirectional cellulose fibres in a matrix of regenerated cellulose. Gindl and Keckes (2005) extended the ‘all-cellulose’ concept down to dimensions of nanometres by partly dissolving microcrystalline cellulose in a mixture of LiCl and *N*,*N*-dimethylacetamide. Evaporation of some of the water left gels, which were washed to remove the LiCl and *N*,*N*-diacetamide. The gels dried to films.

6.4 Advantages of nanocomposites over natural-fibre composites

The primary advantage of cellulose nanocomposites might be transparency, rather than mechanical performance. When the reinforcing fibre have diameters less than one-tenth of the wavelength, they do not scatter light (Yano *et al.*, 2005). Transparent nanocomposites have been made from epoxy and acrylic resins, reinforced with bacterial cellulose at weight fractions of 60–70% (Yano *et al.*, 2005).

Cellophane is useful as a benchmark in discussing the mechanical properties of cellulose nanocomposites. Cellophane is produced by introducing an aqueous solution of cellulose into a bath of a coagulating salt (Brandenberger, 1909). It is a semi-crystalline, transparent, biodegradable film that was commonly used in packaging until synthetic polymer films were developed. The tensile modulus of cellophane is in the range 3.7–5.4 GPa, and the tensile strength is in the range 75–125 MPa (Fink *et al.*, 2001).

Flexural and tensile properties of several cellulose-reinforced nanocomposites are listed in Tables 6.1 and 6.2, respectively. The tables are not comprehensive, but the entries are intended as representative of the different classes of nanocomposites. In most cases, the mechanical properties are similar to those reported for cellophane. Two classes show promise, in terms of mechanical performance:

- nanocomposites reinforced with bacterial cellulose;
- all-cellulose composites.

In particular, the achievement of Nakagaito *et al.* (2005) in fabricating a nanocomposite from nanofibrous bacterial cellulose and phenol-formaldehyde resin, with a flexural modulus 28 GPa, and a flexural strength of 400 MPa, cannot be matched in published results for conventional natural-fibre composites.

It is frequently claimed that adding nanofibrous cellulose to a polymer can increase the tensile modulus by orders of magnitude. While that statement is correct, it is important to remember that it does not necessarily present an advantage over conventional plant-fibre composites. In fabricating a nanocomposite, it is necessary to select a polymeric matrix that is compatible with the fabrication process. Some of the most suitable polymers show poor mechanical performance in the absence of reinforcement. For example, a copolymer of styrene and butyl acrylate has a tensile modulus of just 0.2 MPa, increasing to 114 MPa with addition of nanofibrous sugar beet cellulose at a weight fraction of 0.06 (Samir *et al.*, 2004). In other words, the modulus

Table 6.1 Flexural properties of nanocomposites

Nanofibre	Fibre fraction	Matrix	Modulus (GPa)	Strength (MPa)	Reference
Bacterial	0.12	PF[a]	28	400	Nakagaito *et al.* (2005)
Wood MFC[b]	0.15	PF[a]	19	370	Nakagaito and Yano (2005)

[a] PF = phenol-formaldehyde; [b] MFC = microfibrillated cellulose.

Table 6.2 Tensile properties of nanocomposites

Nanofibre	Fibre fraction	Matrix	Modulus (GPa)	Strength (MPa)	Reference
Bacterial	0.32	CAB[a]	6	129	Gindl and Keckes (2004)
Wood MFC[b]	0.05	PVAc[c]	5.4	102	Chakraborty *et al.* (2006)
Swede root	0.22	PVA[d]	5.4	70	Hepworth and Bruce (2000)
Soybean pod	0.10	PVA[d]	6.6	108	Wang and Sain (2007)
Swede root	0.50	PVAc[c]	8.5	145	Bruce *et al.* (2005)
Swede root	0.50	Acrylic	4.2	125	Bruce *et al.* (2005)
Sugar beet	0.06	PS-co-BA[e]	6.3	114	Samir *et al.* (2004)
Tunicate	0.06	PS-co-BA[e]	5.0	32	Hajji *et al.* (1996)
MCC[f]	–	Cellulose	13.1	243	Gindl and Keckes (2005)

[a] CAB = cellulose acetate butyrate; [b] MFC = microfibrillated cellulose; [c] PVAc = poly(vinyl acetate); [d] PVA = poly(vinyl alcohol); [e] PS-co-BA = poly(styrene-co-butyl acrylate); [f] MCC = microcrystalline cellulose.

increased by a factor of 570. For comparison, a typical epoxy vinyl ester resin has a tensile modulus of 3.1 GPa, increasing to 8.0 GPa when reinforced by kraft pulp at a weight fraction of 0.33 (Neagu *et al.*, 2006). While the improvement was modest, the end result was far superior to that reported for the nanocomposite.

Nanofibrous cellulose can be effective at much lower fibre fractions than those required in conventional natural-fibre composites. For example, Chakraborty *et al.* (2006) compared composites made from poly(vinyl alcohol) reinforced with bleached kraft pulp or with MFC made from that pulp, both at fibre weight fractions of 0.05. The tensile modulus increased from 4.0 to 5.4 GPa and the tensile strength increased from 58 to 102 MPa. The weight fraction of 0.05 was optimal for MFC, with a steady decline in mechanical performance at higher loadings. Conventional fibre-reinforced composites usually show a steady improvement in mechanical properties as the weight fraction is raised, so it might have been possible to match the performance of the nanocomposite, without the expensive fibre treatment, simply by adding more kraft pulp to the composite.

6.5 Future trends

The greatest obstacle to commercial fabrication of cellulose nanocomposites is the cost of the processing steps, including the costs involved in using large volumes of processing water. In the case of bacterial cellulose, there are costs involved in freeze-drying the gels. In the case of MFC, there are additional costs in generating high shear forces to separate the nanofibres. Cheaper fabrication seems likely to be a focus of future research efforts.

Modulus and strength are commonly cited as relevant properties for cellulose nanocomposites, yet the experimental results, discussed above, do not show a competitive advantage over existing materials such as cellophane. Future projects might shift the focus to improving other mechanical properties such as toughness. Fiedler *et al.* (2006) drew attention to the toughening effect of nanoparticles, showing that adding just 0.3% of amine-functionalised carbon nanotubes to an epoxy matrix can improve the fracture toughness by 45%. The improvement was attributed to fibre pull-out mechanisms, along with an enormous surface area per unit weight of nanoparticles. Little is known about the toughening effects of cellulose nanocrystals.

6.6 Sources of further information and advice

Research into cellulose nanocomposites is so new that there are few review articles available. A review by Samir *et al.* (2005) covers some of the general principles involved in isolating and using cellulose nanocrystals.

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Part II

Case studies and opportunities

7

Natural-fiber composites in the automotive sector

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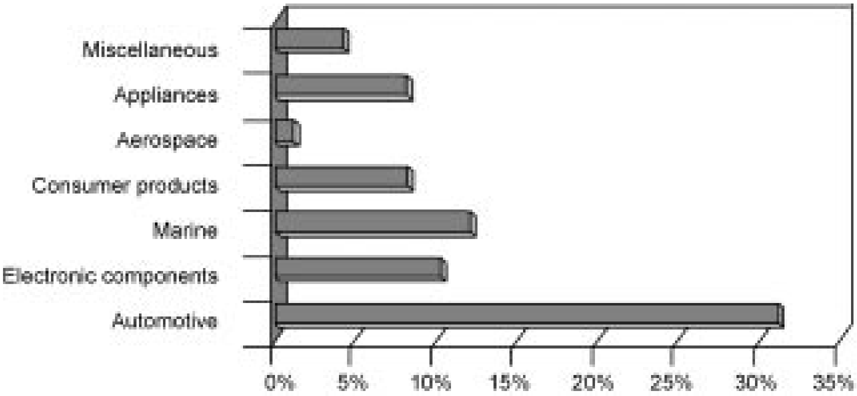
7.1 Introduction

The use of natural fibers in composite materials is increasing due to legislation forcing automotive manufacturers to reuse and recycle materials, which is leading to an increase in the biobased material content in automotive applications.[1,2] Natural fibers (cost: US$200–1000/tonne and energy to produce: 4 GJ/ton) have cost and energy advantages over traditional reinforcing fibers such as glass (cost: US$1200–1800/tonne and energy to produce: 30 GJ/ton) and carbon (cost: US$12500/tonne and energy to produce: 130 GJ/ton). In addition, plant-based biofibers: are widely available, are low in density, have acceptable specific strength properties, are relatively non-abrasive, and have potential for energy recovery, carbon dioxide sequesterization, and biodegradability.[3–6]

Natural fibers being eco-friendly, lightweight, strong, and low cost have already started to replace glass and mineral fillers in numerous engineering applications in automobiles, furniture, packaging, and construction. Natural fibers can be embedded in the polymeric matrices to reinforce and achieve desired properties such as impact strength, stiffness, low density, sound damping, and texture together with eco-friendly characteristics in the composites. The automobile industry has discovered the advantages to be gained from natural fibers and the natural-fiber composites (NFC) made through the combination of natural fibers (such as flax, sisal, hemp, kenaf, or jute) with different polymers such as: polypropylene (PP), polyethylene (PE), and poly(vinylchloride) (PVC). A potentially large area of usage of these composites is the automotive industry because the need is greatest.[1–3] Fiber reinforced composites have gained importance in the automotive sector where high mechanical properties and dimensional stability must be coupled with low weight. Natural fibers such as flax and sisal have already shown that they can be used successfully in composite components in order to realize reduction of weight and cost.[4,5] The trends towards utilization of natural fibers in the automotive sector started in the 1990s in Europe and reached North America some years later. The demand for reinforced



7.1 The use of natural fibers in automotive and other sectors.[8,9]

plastics in the United States is projected to grow 2.5% annually to over four billion (1.81 billion kg) pounds in 2007, valued at US$6.5 billion.[1,6,7] This will create a market for 2.8 billion (1.27 billion kg) pounds of resin and 1.3 billion (0.59 billion kg) pounds of reinforcements. The automotive and construction industries will remain the leading markets for reinforced plastics, together accounting for 63% of the total in 2007.[6,7]

Demand for natural fiber-based materials originated from the automotive industry as seen in Fig. 7.1.[8,9] In order to remain competitive in the market, automotive industries throughout the world are continually optimizing the cost versus quality. The increased importance of renewable resources for raw materials and recyclability or biodegradability is driving the movement from petroleum-based synthetics to agro-based natural fibers in automotive applications.[9,10] Concurrently, these fiber-based composites can contribute to an automotive cost reduction of 20% and weight reduction of 30%.[11] Recently, natural-fiber reinforced biocomposites have been used as automotive parts because of their good mechanical properties and light weight that improves fuel efficiency and reduces emissions during the use-phase of the component.[9,11] A market study by Kline & Company (Little Falls, NJ) forecasts North American demand for both natural fibers and wood, used as plastic additives to range from 15% to 20% per year in automotive applications. Hence, there is growing interest in the use of natural fibers as reinforcements for polymers because natural fibers have the functional capability to substitute glass fibers that are currently being used in the industry.[1–5] Furthermore, rising oil prices and increased activity with regards to environmental pollution prevention have also catalyzed the research and development of biodegradable polymers. Car makers have targeted applications such as door panels, headliners, package trays, dashboards, and trunk-liners, based on natural fiber composites with a thermoplastic or thermosetting polymer matrix. The main drivers for use of natural-fiber-based composites in automotive applications are:

- demands for lightweight parts, which leads to a lowering in fuel consumption; and
- good recycling possibilities of the components made with thermoplastic polymers, reducing the waste disposal problem.

Other factors that are promoting their applications in automotive sector are as follows:

- *Reduction of greenhouse emissions.* The pressure to curb the greenhouse effect causing gases such as CO_2 and an increasing awareness of the finiteness of fossil energy resources are leading to the development of new materials that are entirely based on renewable resources.
- *Competitive pricing.* Automotive industries have already developed using composites with non-wood fibers such as flax and hemp, as well as cellulosics, as an alternative to fiber glass. The resultant composites are lighter, and the natural fibers and cellulosics used by the German car industry (VW/Audi, BMW, and Daimler Chrysler) to produce interior door panels, parcel shelves, dashboards, etc., are competitively priced compared with fiberglass 'chopped strand mat'.[5,8,12]
- *Technical advantages.* Technical benefits such as lower energy loss, better wear protection, longer lifetime of tools, etc. (depending on the application) can be converted into cost saving potential that more than offsets the higher price of the bio-based materials.
- *Growth opportunity for agriculture.* Large consumption of NFC in the automotive sector will create new jobs in agriculture, to improve the efficiency of crop production and adapt plant products to meet the industry needs.
- *Societal benefits.* Improvement in the health of many industrial workers through reduced contact with harmful substances.

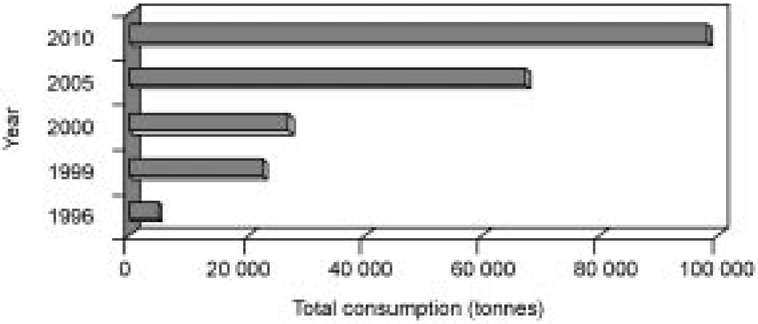
The use of natural fibers, however, also has some limitations. They are moisture sensitive and their bonding with polymer matrices is weak. Moreover, there are some concerns over natural-fiber quality, consistency, and processing temperature limits (200 °C). The first two of the above-mentioned problems can be partly overcome by suitable fiber surface treatment. The application of natural-fiber-based composite parts in automobiles is currently limited to car interiors. The use of natural-fiber composite parts for exterior applications are occasional and limited.[13,14]

7.2 The use of natural-fiber composites (NFC) in the automotive sector

The design concept is a major factor with regard to material selection whereas the sustainability argument is usually a minor factor with regard to material selection. Natural-fiber reinforced composite materials have a definite advantage in this respect. Any future success of natural-fiber reinforced composite matrials in the automotive industry depends largely on the expenses associated with the raw materials and components, the weight of the components, and the workability and machinability using established technologies such as compression molding and lamination. Natural fibers are moisture and UV-sensitive, they have low impact properties, and can have large variations in mechanical properties. The variation in quality is one of the limitations of natural fiber due to the natural processes affecting growth, with harvests varying from year to year. Natural fibers do tend to produce an odor during processing, though it is not hazardous. However, some problems have to be solved for successful application of natural fibers in composites. In order to achieve the goal for an economical, technical, and environmental advancement in the production of automotive parts, more research will be needed to investigate the applicability of diverse natural fibers in terms of processability, strength, thermal, and acoustic performance, and weather sustainability.

7.2.1 Market estimates and forecasts

During the 1990s, automobile manufacturers made significant advancements in the development of natural-fiber composites. The European Commission implemented ‘European Guideline 2000/53/EG’ that set a goal of improving automotive recyclability to 85% of a vehicle (by weight) being recyclable by 2005. This percentage will be increased to 95% by 2015.[15,16] Japan is similarly strict, requiring 88% of a vehicle to be recovered in 2005 (recovery allows for incineration of some components), rising to 95% by 2015.[17,18] In the United States, according to the national energy policy of the 2002 farm bill,[19] biomass research and development is a national priority. Therefore, legislation in the United States and Europe have formulated specific directives for the end-of-life of vehicles[18] that promotes the use of environmentally safe products. The US agricultural, forestry, life sciences, and chemical communities have developed a strategic vision[17] for using crops, trees, and agricultural residues to manufacture industrial products and have identified major barriers[20] to its implementation. The number of automobiles produced in the United States, Europe, and Asia surpassed 50 million in the year 2000, and on an average each automobile utilizes fibers or fabrics, woven or non-woven-based composites to a level equivalent to 20 m^2 of cloth. As many as 40 automotive components such as trunk and hood-liners, floor mats, carpets and padding, speakers, package trays, door panels, and oil/air filters contain fabrics made of synthetic fibers.[5,21–23] According to the market research report ‘Opportunities in Continuous Fiber Reinforced Thermoplastic Composites 2003–2008’, published by E-Composites (Grandville, MI), ‘the market for continuous fiber reinforced thermoplastic composites has experienced a global growth rate of 105 percent in the last 5 years. The growth rate in 2002 was 93 percent.’ The European and North



7.2 Total consumption of natural fibers in Europe.[29]

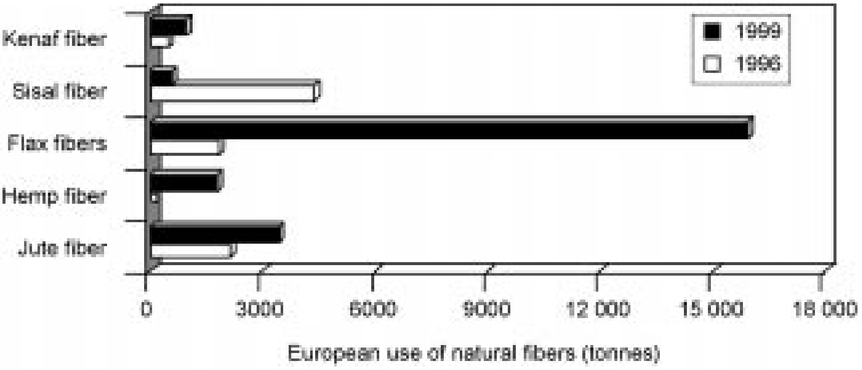
American market for natural fiber reinforced plastic composites reached 685 000 tonnes, valued at US$775 million in 2002.[24] In Europe, projections for 2005 and 2010 suggest that the total application of natural fibers in the European automotive sector could rise to between 50 000 and 70 000 tonnes in 2005 and to more than 100 000 tonnes by 2010 as shown in Fig. 7.2. Principia Partners (Exton, PA) estimated that the 2002 market for natural-fiber composites in North America and Western Europe was almost 1.3 billion (0.59 billion kg) pounds valued at US$900 million. At that time, natural-fiber composites were mostly used for decking and building products in the United States, while over half the 300 million (136.07 billion kg) pounds used in Western Europe went into automotive applications. The directive, which came into effect at the turn of this century, predetermines the deposition fraction of a vehicle to 15% for the year 2005, then gradually reduced to 5% for the year 2015.[9,12,15,22,25–28]

7.2.2 Issues to address

The remainder of this chapter deals with the various aspects of natural-fiber reinforced polymeric composites (NFC) used for automotive applications. Different types of polymers, starting from thermoplastic to thermosetting to biodegradable polymers used as the matrix for making NFC will be discussed in brief, highlighting their salient features. Several fabrication and processing technologies will be illustrated. The characterization techniques applied for NFC will also be mentioned. The key developments that have occurred in this area are summarized in brief.

7.2.3 Plant fibers used in NFC

Practicality demands that reinforcing fibers should be locally grown to minimize costs: for instance, the European automotive industry mainly uses flax and hemp, whereas the Brazilian automotive industry mostly consumes locally grown sisal. The principal fibers now being used in the automotive industry are



7.3 Use of natural fibers in the German automotive industry.[7]

flax and hemp, grown in Western Europe, and sub-tropical fibers such as: jute and kenaf mainly imported from Bangladesh and India; banana from the Philippines; and sisal from South Africa, the United States and Brazil. Kenaf also grows well in the United States. Flax fiber has been the most relevant natural fiber for the German automotive industry (Fig. 7.3). The mechanical properties of natural fibers are very good and can successfully compete with glass fiber on the bases of specific strength and modulus (Table 7.1).

7.3 Resins for fiber reinforced composites

The primary functions of the resin are to transfer stress between the reinforcing fibers, act as a glue to hold the fibers together, and protect the fibers from mechanical and environmental damage. Resins are divided into two major groups known as thermosets and thermoplastics. Thermoplastic resins soften when heated, and may be shaped or molded while in a heated semi-fluid state and become rigid when cooled. Thermoset resins, on the other hand, are usually liquids or low melting point solids in their initial form. When used to produce finished goods, these thermosetting resins are ‘cured’ by the use of a catalyst, heat or a combination of the two. Once cured, solid thermoset resins cannot be converted back to their original liquid form. Unlike thermoplastic resins, cured thermosets will not melt and flow but soften when heated and, once formed, cannot be reshaped.

7.3.1 Thermosets

The worldwide thermoset resin industry is thriving and producing lightweight, high-performance, high-quality products for an ever-expanding range of markets. Thermosetting resins include a wide range of materials: unsaturated polyesters, epoxies, vinyl esters, acrylics, phenolic resins, polyurethanes, etc.

Table 7.1 Mechanical properties of natural fibers compared with glass fiber[3,6,29,30]

Fiber	Density (g/cm^3)	Tensile strength (MPa)	Tensile modulus (GPa)	Specific modulus	Elongation to break (%)	Moisture absorption (%)	World production (10^3 t)
Sisal	1.33	600–700	38	29	2–3	11	378
Hemp	1.48	550–900	70	47	1.6	8	214
Flax	1.4	800–1500	60–80	26–46	1.2–1.6	7	830
Jute	1.46	400–800	10–30	4–21	1.8	12	2300
Kenaf	1.4	292	22	15	2.0	–	970
Banana		54–754	7–20	–	–	–	–
Coir	1.25	220	6	5	15–25	10	100
Bamboo	0.8	391–1000	48–89	–	–	–	10 000
Pineapple leaf fiber		413–1627	34.5–82.5	–	–	–	–
Abaca	1.5	980	–	–	–	–	70
Ramie	1.5	500	44	29	2.0	12–17	100
E-glass	2.55	2400	73	29	3.0	–	

The applications of thermosets are many and varied. One of the primary uses is as the matrix in composite materials. Composites are now accepted as high-performance engineering materials in many fields such as automotive, aerospace, and marine. They are using a wide range of fabrication techniques from autoclave molding to resin transfer molding. Key developments and trends are indicated here. Recycling is another environmental issue that is being tackled by manufacturers. Thermoset materials are designed for a long lifetime and are therefore difficult to break down. However, methods of reuse and recycling are available. Innovations in materials include the use of natural-fiber reinforcement in composites and the application of biopolymers as the matrix materials.

Any resin system used in a composite material should have sufficient adhesion with the reinforcing material to effectively transfer loads from the matrix to the reinforcing fiber and will prevent cracking or fiber/resin debonding at the interface when stressed. The matrix/reinforcing material combination should give good mechanical properties, including good toughness and good resistance to environmental degradation. Toughness is a measure of a material's resistance to crack propagation; but in a composite this can be hard to measure accurately. Generally the more deformation the resin can accommodate, the greater will be its crack resistance and toughness. In contrast, a resin system with a low strain to failure will tend to result in a brittle composite that cracks easily. Environmental resistance, resistance to water and other aggressive substances with an ability to withstand constant stress cycling are properties essential for any resin system.[31] Thermosetting resins are formed by the chemical reaction between the resin and a curing agent/hardener at specified temperature, undergoing a non-reversible chemical reaction to form a hard, infusible product. In some thermosets that undergo 'condensation' reactions, such as phenolic resins, volatile substances are produced as by-products. Other thermosetting resins such as polyester and epoxy cure by 'addition' reaction mechanisms that do not produce any volatile by-products and thus are much easier to process.

Upon addition of the catalyst or hardener, a resin begins to become more viscous until it reaches a state when it is no longer a liquid and has lost its ability to flow. This is the 'gel point'. The resin continues to harden after it has gelled and, some time later, it reaches its full hardness and properties. This reaction itself is accompanied by the generation of heat (exotherm), which in turn speeds the reaction. The whole process is known as the 'curing' of the resin. The speed of cure is controlled by the amount of accelerator in a polyester or vinyl ester resin or by varying the type of hardener in an epoxy resin. Generally, polyester resins undergo a greater exotherm and a faster development of initial mechanical properties than epoxies of a similar working time. The resins can be cured at different temperatures depending on the choice of the curing agent used, ranging from room temperature to elevated temperature. However, curing at elevated temperatures has an added advantage. It enhances the final mechanical properties of the material. Many resin systems do not reach their ultimate mechanical properties unless the resin is subjected to 'post-cure'. The post-cure involves increasing the laminate temperature after the initial room temperature cure, which increases the amount of crosslinking of the molecules that can take place. To some degree this post-cure occurs naturally at warm room temperatures, but higher properties and shorter post-cure times will be obtained if elevated temperatures are used. Although there are many different types of resin used in the composite industry, the majority of structural parts are made with three main types, namely: polyester, vinyl ester, and epoxy.

7.3.2 Thermoplastics

Although natural-fiber reinforced commodity thermoplastics have a wide range of applications in the automotive industry, there have been few reports of cellulosic natural-fiber reinforced engineering thermoplastics. One of the main limitations is the need to process the thermoplastic composites at a temperature below the decomposition temperature of cellulose, the limit being ~180 °C. The only commodity thermoplastics amenable to natural-fiber reinforcement are PE and PP. Of all the thermoplastics, PP shows the most potential benefits when combined with natural fibers for making biocomposites of industrial value. Most work on natural-fiber reinforced PP composites is based on melt mixing of short natural fibers and PP granules with subsequent compression/injection molding.

7.3.3 Biodegradable polymers

According to the ASTM,[32] 'biodegradable' can be defined as '... capable of undergoing decomposition into CO_2, methane, water, inorganic compounds or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standardized tests, in a specified period of time, reflecting available disposal conditions.' There are several types of environmentally degradable plastics such as (i) biodegradable polyesters, (ii) biodegradable starch-based polymers, (iii) water-soluble polymers, (vi) photodegradable polymers, and (v) controlled degradation master batches. Biodegradable polymers come from classes of materials such as: polyhydroalkanoates (PHA), polylactides (PLA), polylactide aliphatic copolymer (CPLA), polycaprolactone (PCL), poly(glycolic acid) (PGA), and poly(vinyl alcohol) (PVA).

Polyhydroalkanoate homopolymers and copolymers such as poly(beta-hydroxybutyrate) (PHB) and poly(hydroxybutyrate-co-valerate) (PHBV) are produced by the bacterial fermentation of sugar or lipids; the resulting polymers have melting points that range from 40 to 180 °C.[6,33] PHB has properties similar to those of PP; however, it is more brittle and stiffer. PHBV is tougher and less stiff.

Polylactide is produced from lactic acid that can be generated by the biological fermentation of renewable resources such as starch and sugars.[6,33] The polymer resembles clear polystyrene, provides good aesthetics (gloss and clarity), but the inherent physical properties of PLA such as its brittleness, high rate of water permeation, and moisture sensitivity make the PLA polymer unsuited for many applications, and needs modifications for most practical applications (e.g., plasticizers to increase its flexibility).

Polylactide aliphatic copolymer is a biodegradable mixture of lactide and aliphatic polyesters.[6,33] It can be either a hard plastic similar to PS or a soft flexible one similar to PP depending upon the amount of aliphatic polyester present in the mixture. It is easy to process, with stability up to 200 °C.

Polycaprolactone is made by polymerizing ϵ-caprolactone derived from the chemical synthesis of crude oil.[6,33] It has a low melting point (58 to 60 °C), low viscosity, as well as good water, oil, solvent, and chlorine resistance, and is easy to process. PCL is compatible with most thermosetting and thermoplastic resins and elastomers. It increases impact resistance and aids in the mould release of thermosets. It is used as an additive for other resins to improve their processing characteristics and acts as a polymeric plasticizer in PVC.

Poly(glycolic acid) is a synthetic homopolymer of glycolic acid.[6,33] It can be polymerized via a condensation reaction to obtain a polyester as the monomer is terminated by a hydroxyl group at one end and a carboxyl group at the other.

Since petroleum-based plastic products generally do not degrade in a landfill or composting environments, they pose a serious environmental problem. For this reason, biodegradable polymers such as PLA have been the subject of many studies during the past decade.[6,34–40] PLA is gaining a reputation as a very useful bioengineering tool because it has the advantages of being completely biodegradable and being synthesized from corn, a renewable plant feedstock.[38] The Nebraska facility of Cargill Dow is capable of producing up to 300 million pounds (140 000 tonnes) of PLA per year, using 40 000 bushels of corn per day (1 088 640 kg)[41] and production is expected to more than triple to one billion (0.45 billion kg) pounds by 2007.[42] The adoption of PLA for automotive parts has also been studied since PLA-based automotive parts emit less CO_2 than petroleum-based thermoplastics.[39] However, major improvements in the heat and impact resistance of PLA are needed to match the properties of petroleum-based thermoplastics.[29,39] Pure PLA has a tensile strength of 62 MPa and a modulus of 2.7 GPa in contrast to 36 MPa and 1.2 GPa for pure PP.[35] Moreover, PLA can be processed by injection molding, blow molding, and film forming; because the glass transition temperature (T_g) of PLA is 59 °C and the melting temperature (T_m) is 172 °C.[35] Oksman *et al.* showed that PLA–flax composites had better mechanical properties than PP–flax composites.[34,43] Although PLA has mechanical properties suitable for automotive applications[34,41] it is considered too brittle for many commercial applications. Nevertheless, it is possible to overcome brittleness and poor processability of stiff and hard polymers by combining them with other materials. Most research on PLA composite ultimately seeks to improve the mechanical properties to a level that satisfies a particular application.[34,41] Indeed some researchers consider the enhanced toughness the main advantage of natural fibers in composites.[6,34,35,44–48] One way to improve the mechanical and thermal properties of PLA-based biopolymers is to modify them by adding fillers or reinforcements.[6,43–46] An additional benefit of natural fiber as the filler is the reduction in the overall cost of the composite. PLA can be melt-processed with standard processing equipment at temperatures below those at which natural fibers begin to degrade, and at a relatively low cost. Hence, PLA is a versatile material with applications in the automotive industries.[45,49–54]

The mechanical properties of a composite material depend primarily on the strength and modulus of the fibers, the strength and the chemical stability of the matrix, and the effectiveness of the bonding between matrix and fibers to transfer stress across in the interface. Generally, the utilization of natural fibers as reinforcing materials in thermoplastics requires strong adhesion between the fiber and the polymer matrix. Cellulose has a strong hydrophilic character due to three hydroxyl groups per monomeric unit, but biopolymers such as PLA and PHB are generally hydrophobic. Since both components of the composite, biopolymer (e.g. PLA) and natural fiber, are biodegradable, the composite as an integral part is also expected to be biodegradable.[6,43] Hence, since PLA can open many new opportunities in auto industrial bioplastic applications, there is a need to better understand and describe its properties as the matrix material for biocomposite materials. Recently, Toyota Bio Indonesia has begun producing PLA (Toyota Eco Plastic), which is used for automotive applications.[54–58] Toyota Auto Body chose kenaf, because it is a fast-growing annual grass and absorbs seven times more carbon dioxide than cedar. Bioplastics and biofabric are ‘carbon neutral’. The carbon dioxide released by burning the plants used to make the parts is offset by the carbon dioxide the plants absorb as they grow.[54]

7.4 Processing of natural-fiber composites for the automotive sector

Many automotive companies are experimenting with natural fibers as a way to substitute for non-degradable and non-recyclable glass fiber. Although glass fibers are widely used commercially in the automotive composite industry, they have several disadvantages compared with natural fibers (Table 7.2).[6,35,56,59,60] Natural fibers have the potential to reduce vehicle weight by up to 40% net vehicle weight compared with glass fiber, which currently accounts for the majority of automotive composites. Much less energy is used in growing, harvesting, and preparing natural fibers than in producing glass fibers. The energy to produce plant fibers has been estimated as some 4 GJ/tonne, compared with around 30 GJ/tonne for glass fiber, which has to be drawn from a melt at several hundred degrees Celsius, using raw materials obtained through energy-intensive mining. Vollenberg and Hinkens reported that the specific moduli (the ratio of

Table 7.2 Comparison between glass fibers and natural fibers

	Glass fibers	Natural fibers
Health risk when inhaled	Yes	No
Cost[56,59]	~US$1.20–1.50/kg	~US$0.30–0.55/kg
Recyclability	No	Yes
Energy consumption	High	Low
Renewability	No	Yes
Disposal	Not biodegradable	Biodegradable
Distribution	Wide	Wide
Fiber emissions[60]	Glass fiber (/kg): Energy 48.3 MJ	China reed fiber (/kg): Energy 3.4 MJ
Separation	Difficult	Easy
Shatter resistance	Low	High
Weight reduction[60]	2.5–2.8 g/cm^3	1.2–1.5 g/cm^3
Sound-absorbing properties	Low	High

the composite modulus to the composite specific gravity) of high fiber volume fraction bast fibers/PP composites are in the same range as glass fiber/PP composites.[61] For example, the specific tensile and flexural moduli of 50% (w/w) kenaf coupled [2% (w/w) maleic anhydride grafted polypropylene] composites were marginally higher than typical values reported for 40% (w/w) coupled glass/PP injection-molded composites (Table 7.3).[61] Table 7.4 shows the natural fibers used in the US automotive market.

Recently Toyota developed Eco Plastic, made from PLA with composites from kenaf, which is being used in the spare tire cover and floor mats of the RAUM.[62,63] Currently in Japan a pilot plant is producing 1000 tonnes of Eco Plastic per year and this is hoped to increase to 20 million tonnes by 2020.[51] Toyota is already using kenaf fibers instead of glass as reinforcement in some plastic interior components and is dedicated to producing 15% of its resin-based parts from renewable or recyclable materials by 2010.[63] According to a report of

Table 7.3 Properties of fiber reinforced PP composites[53]

Reinforcement in PP	None	Glass fiber	Kenaf fiber
Fiber by volume (%)	0	40	50
Fiber by weight (%)	0	19	39
Specific gravity	0.9	1.23	1.07
Flexural modulus (GPa)	1.4	6.2	7.3
Specific flexural modulus (GPa)	1.6	5.0	6.8
Tensile modulus (GPa)	1.7	9.0	8.3
Specific flexural modulus (GPa)	1.9	7.3	7.8
Notched Izod impact (J/m)	24	107	32
Elongation at break (%)	$\gg$10	2.5	2.2

Table 7.4 Natural fibers used in the US automotive market (as reinforcement in polypropylene)[29]

Fibers	Application
Flax	Seatbacks
Wood	Inserts
Flax	Spare tyre covers
Wood	Spare tyre covers
Hemp/kenaf, 50:50	Door panel
Kenaf	Rear parcel shelves
Flax	Rear parcel shelves
Kenaf	Other interior trim
Flax	Other interior trim

the Toyota Motor Corporation,[63] the reasons that have driven Toyota's research into bio-based materials are: (i) reduction of the use of materials toxic to humans or the environment, (ii) environment-friendly technologies, (iii) reduction in the use of PVC, and (iv) increasing the dismantling speed at the end of life of the vehicle. Ford also discovered the soy-based foam for seating, replacing 40% of the standard petroleum-based polyol raw material.[51] Ford also is working to develop PLA-based materials and in 2003 the Ford Model U hybrid-electric car made extensive use of recyclable composites.[64] Corn-based PLA polymer materials are used in the interior roof fabric and floor matting, while soy and corn-derived resins replace carbon black in the tires. Such materials are now used in Ford Mondeo door inserts and flax-based floor trays, pillar panels and central consoles in Volvos.[51]

7.4.1 Composite fabrication techniques

In the automotive industry each manufacturing technology has its own possibilities and restrictions, and the cost of fabrication of a composite material part generally represents a major portion of the total cost. Many applications are centered on time-tested manufacturing techniques such as: compression molding, sheet molding compound (SMC), pultrusion, reaction injection molding (RIM), vacuum-assisted resin transfer molding (VARTM), etc.[65,66] An overview of the different processing possibilities in the automotive industry is given in Table 7.5. There are several manufacturing processes used for natural fiber-based automotive parts:[66–69] (i) FIBRIT process, (ii) Polywood process, (iii) Lignotock process, and (iv) natural fiber/PP (LoPreFin, Fibroflax). Maguro has presented an overview of the technologies used to produce such parts (injection molding, low pressure injection molding and co-injection molding), with emphasis on the research studies performed on several kinds of natural fibers to be applied to semi-finished products, e.g. granules containing short natural fibers

Table 7.5 Different processing techniques for automotive components[68,69]

Process	Fibers (%)	Polymer (%)
Hot pressing	Coir fiber (50%)	Latex (50%)
Long-fiber injection molding	Sisal fiber, Carden band (20–40%)	Thermoset; polyurethane resin (60–75%)
Long-fiber injection molding	Sisal mat (20–40%)	Thermoset; polyurethane resin (60–75%)
Granules, injection molding, extrusion	Hemp, flax, kenaf (20–40%)	Thermoplastics; PP or Co-PES, cellulose acetate, natural resin, polylactide (60–80%)
Fiber mat, heating, cold pressing	Hemp, flax, kenaf (45–55%)	Thermoplastics; PP or Co-PES, cellulose acetate, synthetic fiber, natural resin, lactate (45–55%)
Fiber mat, gluing, hot press	Jute, sisal, hemp, flax, kenaf (45–55%)	Thermosets; epoxy or polyurethane resins (35–50%)
Fiber mat, gluing, hot press, extrudate glued profile	Jute, sisal, hemp, flax, kenaf (40–50%)	Thermosets; phenolic or polyester resins (50–60%)
Casting, hot press	Natural fiber (partly synthetic fiber)/wood (85–90%)	Thermosets; acrylate or melamine resins (5%)

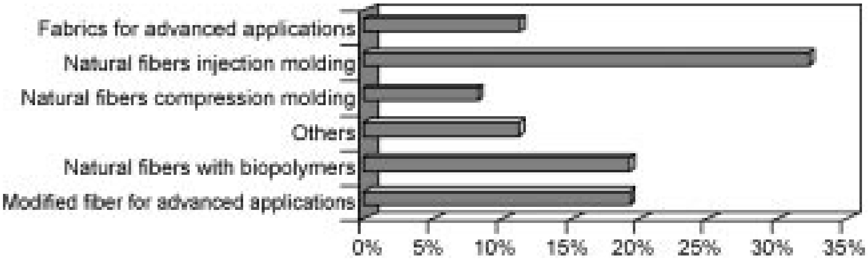
for injection molding processing.[66] BASF AG, Germany has developed compression molding techniques for resinated natural fiber mats, natural-fiber/PP hybrid mats, and NMT (natural-fiber mat reinforced thermoplastics).[67]

Owing to their unique properties – good fracture toughness, thermal stability, etc. – considerable interest has been generated in the manufacture of thermoplastic composites.[70,71] Thermoplastic polymers are substituting thermosetting polymers as matrix materials for high volume consumer-driven composites, due to more stringent recycling standards.[6,44,70] Shorter processing time, no chemical reactions involved and reprocessibility are certain advantages from the processing point of view. Bruijn[72] highlighted the advantages and disadvantages of natural-fiber mat thermoplastics in automotive applications. The various common forms of preparing a fiber with thermoplastics are: (i) film stacking,[70] (ii) powder impregnation/pultrusion,[73] and (iii) solution impregnation.[71] The necessary low-cost nature of composite products (especially in the case of composites that are fabricated using PLA biopolymer) requires both a cost-efficient processing system and inexpensive raw materials. In order to contribute to suppressing the increase in CO_2 emissions, the adoption of PLA for automotive parts has also been studied since the PLA system emits less CO_2 compared to petroleum-based thermoplastics.[74] However, major improvements in heat and impact resistance are needed for this application.[44,74] The structure of fibers can be modified using physical and/or chemical treatments since the physical properties of the fibers are determined by the structure, angle of fibrils, cellulose content, and degree of polymerization.[75]

Many of the problems in the manufacturing process can be traced to a lack of fundamental scientific knowledge of the interactions between the natural fibers and matrix materials. The hydrophilic nature of natural cellulosic fibers/fillers affects adhesion to a hydrophobic matrix, which may result in a loss of strength. In order to overcome this, the natural cellulosic fiber/filler surface has to be modified in order to promote adhesion.[76–78] Generally, coupling agents improve the degree of crosslinking in the interface region and offer a suitable bonding result, as well as the creation of high fiber surface area required for the optimization of fiber–resin reinforcement.[78,79] Coupling agents are molecules that possess two functionalities, one that reacts with the hydroxyl groups of cellulose in the fiber and the other that reacts with functional groups of the matrix.[80] These changes will effectively result in improved surface tension, interfacial strength, wetting ability, adhesion, and compatibility with polymeric materials.[78–80]

In order to enhance the behavior of these composites, natural fibers have been treated with sodium hydroxide and a silane coupling agent.[75,77,78,80,81] 3-Aminopropyl triethoxysilane (APS) was used as the natural-fiber surface-modifying coupling agent because Dupraz *et al.*[81] suggested that APS has the ability to bond to both polylactide and bioceramic particles. Besides, the interaction can be understood in terms of the chemistry of silane, the fiber surface, and PLA.[82] During surface treatment, APS hydrolyses and the resultant silanol groups can bond with the natural fiber surface. Amine groups from APS can form hydrogen bonds to COO sites on the hydrolyzed PLA backbone.[81,82] Figure 7.4 shows that in 2005, natural-fiber composite materials were most frequently used in injection molded products, followed by those with a bioplastic matrix and those modified for use in advanced applications.[44]

In February 2006 Mitsubishi Motor Corp. announced the formulation of interior automotive components from plant-based polybutylene succinate (PBS) incorporating bamboo fibers.[44] These components, called ‘green plastics’, made from the biocomposite used in a new concept minicar that was launched in Japan in 2007. The PBS resin is made from succinic acid and 1,4-butanediol, with the acid derived from the fermentation of sugars. PBS proved to be capable of reducing carbon dioxide emissions by more than 50% over the life cycle of the automobile interior when compared with conventional petroleum-derived plastics such as PP.



7.4 Natural fibers for different processing techniques.[44]

7.4.2 Extrusion

There is recognition of the importance of the effect of processing methods on the properties of automotive composites, where extreme care and precise knowledge are needed to develop a viable commercial scale manufacturing process. A common high-speed processing method for thermoplastic composites is extrusion. A recent publication highlights the process for NFC. A twin-screw extruder, WP (Werner and Pflider), was used to combine polypropylene (ProFax 6523, Basell Polyolefins, Elkton, MD, melt flow index of 4.0 g/10 min, M_w = 470 kDa with a polydispersity index of 5) and poly(lactic acid) (Biomer L9000, Biomer, Krailling, Germany, M_w = 220 kDa; M_n: 101 kDa) with recycled newspaper cellulose fibers (RNCF) (CreaMix TC 1004, CreaFill Fibers Corp., Chestertown, MD). The RNCF are reclaimed from newspaper/magazine or kraft paper stock. TC 1004 fibers are sold at less than US$0.20/lb ($0.44 kg), a substantial cost savings over traditional reinforcements such as glass. The average length of the recycled cellulose fibers was 850 μm and the average width of fibers was 20 μm. Bamboo fiber (length: 500 μm and diameter: 20 to 70 μm) was obtained from Japan. APS was used for the surface treatment of the fiber that was purchased from Gelest Inc. Morrisville, PA. The glass fibers (Chopped Stand 735: Johns Manville, Toledo, OH, fiber glass chopped stands for polypropylene) were found to have average lengths of 413 μm and 387 μm after injection molding as PLA/glass (70/30 wt%) and PP/glass (70/30 wt%) composites, respectively, decreased from their original length of 3170 μm, which agrees with the fact that the injection process affects the fiber length.[83] Usually, if it is to be effective in the composite, a fiber of 3–50 mm in length and 9–18 mm in diameter should maintain a critical length.[27] The fibers and polymer matrix resin, mixed at a ratio of 30:70 wt%, were fed into a ZSK-30 WP twin-screw extruder with an *L/D* ratio of 30.[76] A uniform temperature of 183 °C was maintained in all six zones of the extruder. The PLA matrix resin was fed at 46.5 g/min, while the fibers are fed through a side feeder at a rate of 20 g/min. The screw speed was set at 100 rpm. The product extruded was chopped to form pellets having lengths of 11 mm. The pelletized composites were then injection-molded into tensile coupons for testing.

7.4.3 Injection molding

Since injection molding provides products with high dimensional tolerances at short cycle-times and resulting lower costs, it is an important manufacturing process for polymers. Determining the correct setting for injection molding is a major concern in the plastics industry because the processing parameters have crucial effects on the quality of products.[83–85] The filling time, melting temperature, molding temperature, and packing pressure are the parameters that govern the injection molding process. After extrusion, the pelletized PLA-based composites are dried in a convection oven at 80 ºC for 2 hours prior to injection molding. The injection molding was carried out using a Cincinnati-Millacron injection molding machine (85 tonne (85 000 kg) capacity) with four temperature zones.[86] The nozzle temperature was 185 ºC and the barrel zones were kept at 183 ºC. The cooling time was 50 seconds and the hold, pack, and fill pressures were maintained at 6.89, 8.96, and 6.89 MPa, respectively. The glass fiber reinforced PP pelletized composite was also formed into test specimens using the Cincinnati-Milacron injection molder, where the cylinder heating zones were set to: 178 ºC (rear), 185 ºC (front) and 195 ºC (center), and the nozzle temperature was set at 185 ºC and the mould temperature was set at 65 ºC. Samples were molded for flexural and tensile tests according to ASTM D 790 and ASTM D 638 standards, respectively.[44] For PLA automotive interior parts, key developments include a new nucleating agent for crystallization and a compatibilizer.

7.4.4 Thermoforming

Thermoforming is a manufacturing process for thermoplastic sheet or film. The process follows a path from extrusion to molding. In this process, extruders are used to produce sheet or film which is then pulled into an oven and heated until it reaches a certain temperature. Then it is stretched over or into a temperature-controlled, single-surface mold. Cast or machined aluminum is the most common mold material, although epoxy and wood tooling are sometimes used for low-volume production. The sheet is held against the mold surface using vacuum or pressure until cooled. The formed part is then trimmed from the sheet. The trimmed material is usually reground, mixed with virgin plastic, and reprocessed into usable sheet.[87,88] There are several categories of thermoforming, including vacuum forming, pressure forming, twin-sheet forming, drape forming. Finally, the plastic is moved to a cutting zone where the shapes are cut out of the plastic. Thermoforming has the following advantages and disadvantages.

Advantages:

- Extremely adaptive to customer design needs and wider design scope.
- Rapid prototype development.
- Material and process are optimized for cost effectiveness.
- Flexible tooling design offers a competitive advantage.

- Weight savings for consumer and manufacturer.
- No anticorrosion spray necessary.
- Paintable and colored plastic availability.
- Fully integrated process with limitless flexibility for small to large product designs.

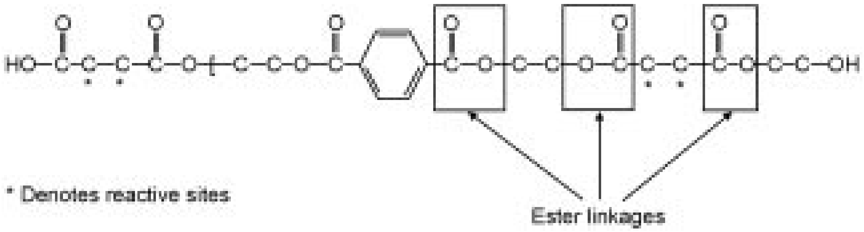
Disadvantages:

- High initial equipment investment.
- High startup and running costs possible.
- Part must be designed for effective molding.

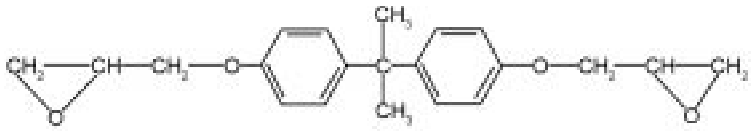
Leao *et al.*[89] used several natural fibers such as curaua, coir, jute, ramie, and sisal in preparing automotive components by thermoforming process.

7.4.5 Hand lay-up

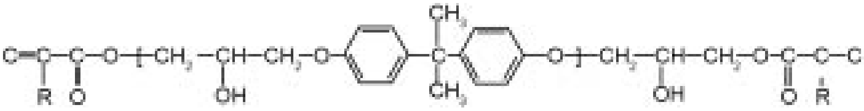
In this process, the resins are impregnated by hand into fibers, which are in the form of woven, knitted, stitched, or bonded fabrics. This is usually accomplished by rollers or brushes, with an increasing use of nip-roller type impregnators for forcing resin into the fabrics by means of rotating rollers and a bath of resin.[90] Laminates are left to cure under standard atmospheric conditions. Thermosetting resins such as polyester (Fig. 7.5), epoxy (Fig. 7.6), vinyl ester (Fig. 7.7) or phenolics are normally used.



7.5 An idealized chemical structure of a typical unsaturated polyester resin.



7.6 An idealized chemical structure of a typical epoxy.



7.7 An idealized chemical structure of a vinyl ester resin.

Advantages:

- Widely used for many years.
- Simple operation.
- Low cost tooling, if room-temperature cure resins are used.
- Wide choice of suppliers and material types.
- Higher fiber contents, and longer fibers than with spray lay-up.

Disadvantages:

- Resin mixing, laminate resin contents, and laminate quality are very dependent on the skills of laminators. Low resin content laminates cannot usually be achieved without the incorporation of excessive quantities of voids.
- Health and safety considerations of resins. The lower molecular weights of hand lay-up resins generally means that they have the potential to be more harmful than higher molecular weight products. The lower viscosity of the resins also means that they have an increased tendency to penetrate clothing, etc.
- Resins need to be low in viscosity to be workable by hand. This generally compromises their mechanical/thermal properties due to the need for high diluent/styrene levels.

7.4.6 Resin transfer molding

Resin transfer molding (RTM) consists of filling a mold cavity, rigid and closed, by injecting a resin through one or several ports, depending on the size of the component. The reinforcements are placed in the interior of the mold before closing and locking it. Usually, polyesters, epoxies, phenolics or acrylics are used, and they can be filled if needed. Different kinds of mold materials can be used, depending on the expected production rate. Heat can be applied to the mold to shorten the cure-time, in which case the use of steel molds may be necessary. The reinforcements may be continuous strands, cloth, woven roving, long fiber, and chopped strand, but generally it is continuous filament mats, which are used. The use of preforms made from continuous strand mats permits a considerable increase in production rates to be achieved. It is also known as 'resin injection process'.[91,92]

Advantages:

- Accurate fiber pacing can be achieved.
- Uses only low-pressure injection.
- Much uniformity in thickness and fiber loading can be maintained, resulting in uniform shrinkage.
- Moldings can be manufactured to close dimensional tolerances.
- Ability to mould complex structural and hollow shapes.
- Ability to produce laminates of 0.5–90 mm in thickness.

- Process can be automated, resulting in higher production rates with less scrap.
- Components will have good surface finish on both sides.

7.4.7 Vacuum-assisted resin transfer molding

In VARTM, the reinforcing fabrics are laid up as a dry stack of materials as in RTM. The fiber stack is then covered with peel ply and a knitted type of non-structural fabric. Then the resin is drawn into the dry reinforcement on a vacuum bagged tool, using only partial vacuum to drive the resin.[90] The fiber content can be maximized here, by reducing the voids percentage compared to other large-part manufacturing processes, like hand lay-up.[93] Thus these products can attain high mechanical property. Resins used are generally epoxy, polyester, or vinyl ester.

Advantages:

- Only one side of the component has a molded finish.
- Much lower tooling cost due to one half of the tool being a vacuum bag, and less strength being required in the main tool.
- Large components can be fabricated.
- This process reduces worker contact with the liquid resin and also reduces volatile content.
- Standard wet lay-up tools can be modified for this process.
- Cored structures can be produced in one operation.

Disadvantages:

- Relatively complex process to perform.
- Resins must be very low in viscosity, thus comprising mechanical properties.
- Unimpregnated areas can occur, resulting in very expensive scrap parts.

7.4.8 Pultrusion

In this process, fibers are pulled from a creel through a resin bath and then on through a heated die.[90,94] The die completes the impregnation of the fiber, controls the resin content, and cures the material into its final shape as it passes through. This cured profile is then cut to length. Fabrics may also be introduced into the die to provide fiber direction other than 0°. Although pultrusion is a continuous process, producing a profile of constant cross-section, a variant known as ‘pulforming’ allows for some variation to be introduced into the cross-section. The process pulls the materials through the die for impregnation, and then clamps them in a mold for curing. This makes the process non-continuous, but accommodating of small changes in cross-section. The resins commonly used are epoxy, polyester, vinyl ester, and phenolic.

Advantages:

- This can be a very fast, and therefore economic, way of impregnating and curing materials.
- Resin content can be accurately controlled.
- Fiber cost is minimized since the majority is taken from a creel.
- Structural properties of laminates can be very good since the profiles have very well-aligned fibers.
- High fiber volume fractions can be obtained.

Disadvantages:

- Limited to constant or near constant cross-section components.
- Heated die costs can be high.

7.4.9 Bulk molding compounds

Bulk molding compounds (BMC) are polyester-based thermosets. These are also called dough molding compounds (DMC). They are prepared by blending resin (mostly polyester resin), mineral fillers, reinforcing fibers, additives and peroxide catalysts in a dough mixer, usually of the Z-blade type. Organic peroxides such as benzoyl peroxide or tertiary butyl perbenzoate are used as the catalysts.[95] The heat and pressure created during the molding process result in decomposition of catalyst. This leads to crosslinking of the resin to form a network. This crosslinking results in a rigid structure in which the molecules are held by chemical bonds. BMC or DMC are state-of-the-art composite materials for a wide range of applications in the building and construction sector as well as in other sectors such as automotive, mass transport, electrical, sanitary, and household industry. BMC/DMC has excellent environmental and recycling properties.

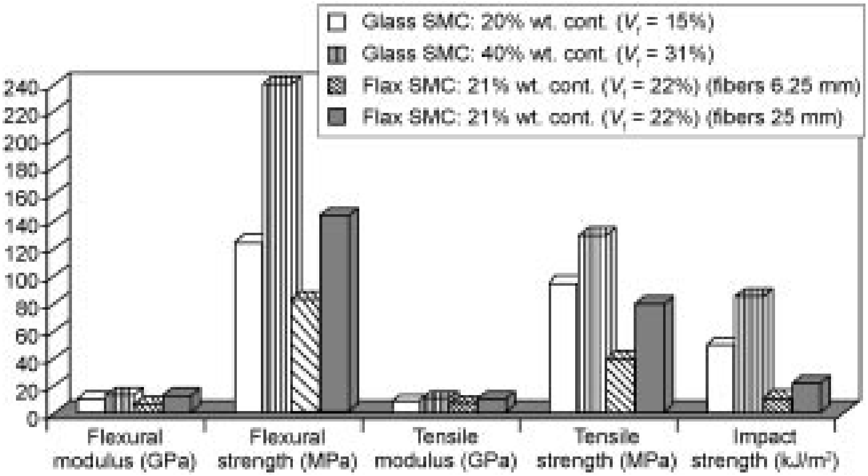
An important difference with glass SMC (sheet molding compound) is the production of the prepreg. Normally prepregs are made by chopping the glass strands and dropping them on a film of resin-filler compound. This preparation does not work for natural fibers since the chopping is very difficult. Other techniques are being developed. An appropriate method needs to result in a layer of fibers with an anisotropic orientation that is loose enough to provide sufficient fiber flow during the molding process.

Bulk molding compounds are extensively used in the transportation industry. Headlamp reflectors, car body panels and under-bonnet parts are extremely demanding, technical applications. When compared with other materials and presently used technologies like steel stamping, thermoplastic injection, aluminium die casting, etc., BMC offers many benefits that allow the car makers to optimize their design to develop cost-effective processes. Nearly 100% of the car makers use headlamp reflectors made of BMC. The ‘zero shrink’ of BMC makes possible the computer-aided design (CAD) of the shape and profile of the reflector. Such complex shapes are not possible in steel stamping. BMC has a coefficient of linear expansion similar to steel. Since the car makers are continuously looking for weight reduction the low specific gravity of the BMC parts is an added advantage. The key advantages of BMC in car body panel are as follows:

- Very low coefficient of thermal expansion (very close to steel), which means a close and constant fit between the steel and composite panels.
- Several components and functions can be integrated within a single complex part, reducing secondary assembly operations.
- Weight reduction: a BMC panel is nearly 30% lighter than an equivalent steel panel.
- Creep resistance of BMC, specially at working temperature, is an important advantage over thermoplastics.
- The corrosion and chemical resistance of BMC enables it to withstand the demanding tests of the car industry (exposure to diesel, petrol, etc.).
- Excellent noise absorption of BMC contributes towards the environmental and comfort requirements of the car industry.

7.4.10 Sheet molding compound

SMC is a fiber reinforced composite material that is a composite of fibers, usually a polyester resin, pigments, fillers, and other additives that have been compounded and processed into sheet form to facilitate compression molding.[96] It is suited for large pan volumes using automated equipment. High mechanical properties and excellent surface appearance make SMC ideal for automotive applications; in the US automotive industry much SMC is used in automated equipment for side panels and trim. Natural fiber is well suited for this molding technique and fiber dust or short fibers could be used to fill and thicken the SMC. The potential to use natural fibers such as hemp or kenaf exists in any area SMC is found, including radiator supports and grill opening reinforcements, with several applications already commercialized.[97,98] The Ford Freestyle uses natural-fiber reinforcements in its third-row seatback, and the Expedition and Lincoln Navigator have natural fibers in their door-trim panels. The Centre of Lightweight Structures at the Technische Universiteit, Delft, has sought to adapt glass fiber reinforced plastic processing techniques for use with natural fibers.[99,100] One consideration is how to subdue ‘springy’ natural fibers when constructing the preforms for subsequent use in fabrication by RTM, vacuum infusion, vacuum pressing, and similar processes. New binders have been developed for this purpose. Because of their tendency to stick together, natural fibers are harder to chop and scatter on to resin film than glass fibers when preparing prepreg materials, so, once again, existing methods have to be modified. Researchers at the Centre of Lightweight Structures at the Technische Universiteit Delft have compared properties of natural-fiber SMC with glass-



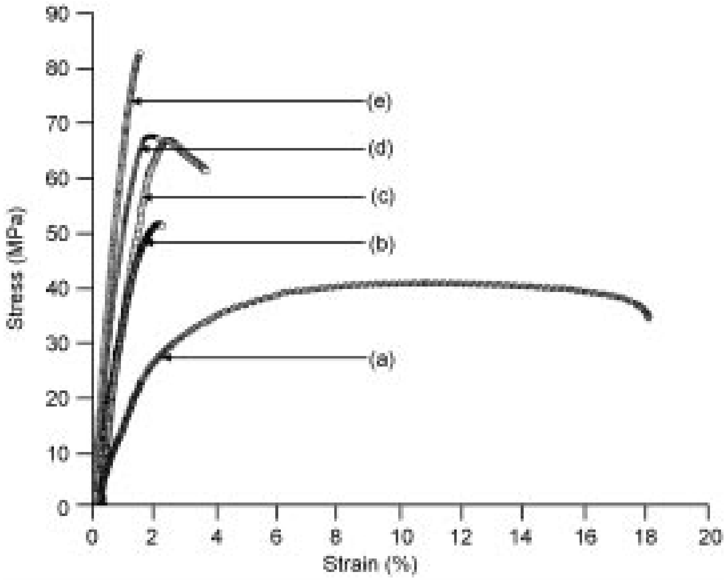
7.8 Comparison of properties of sheet molding compounds produced from natural fiber (two different fiber diameters) and glass (two different volume fractions) (source: Centre of Lightweight Structures at the Technische Universiteit Delft).

based SMCs (Fig. 7.8). Results are encouraging when long fibers are used, but impact strength remains a point of vulnerability.

7.5 Mechanical characterization of natural-fiber composites

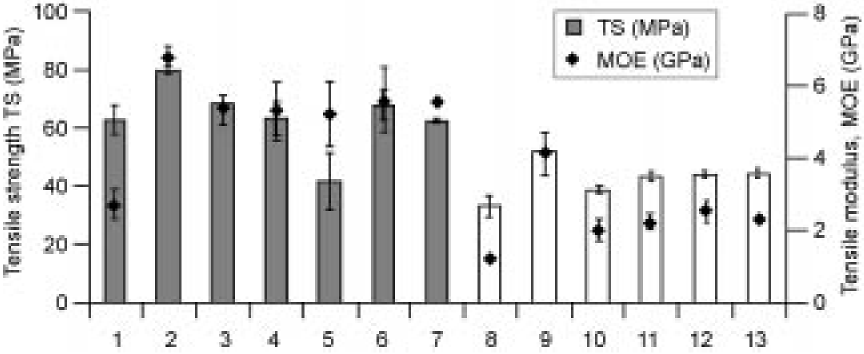
7.5.1 Tensile properties of the composites

A thorough study of the mechanical behavior of natural-fiber composites that were processed by twin-screw extrusion followed by injection molding (as described in Sections 7.4.2 and 7.4.3) is presented here. A tension test reflects the average property through the thickness, whereas a flexural test is strongly influenced by the properties of the specimen closest to the top and bottom surfaces. The stresses in a tensile test are uniform throughout the specimen cross-section, whereas the stresses in flexure vary from zero in the middle to maximum in the top and bottom surfaces. The stress–strain curves of extruded and injection molded PLA- and PP-based composites are given in Fig. 7.9, which shows the effect of chopped glass fibers and RNCF on the tensile strengths of virgin and reinforced PLA. The tensile properties of PLA/fiber composites were compared with PP/fiber composites. The results of the tensile tests performed with the composites and the pure PLA and PP are shown in Fig. 7.10. PLA has better mechanical properties than PP. Pure PLA has a tensile strength of 62 MPa and a modulus of 2.7 GPa in contrast to 36 MPa and 1.2 GPa for pure PP. It can be seen in Fig. 7.10 that the addition of 30 wt% RNCF



7.9 Stress–strain curves: (a) PP (100%) (☆), (b) PP/glass (70/30) (○), (c) PLA (100%) (□), (d) PLA/RNCF (70/30) (▽), and (e) PLA/glass (70/30) (◇).

increased the tensile strength of virgin PLA from 62.9 MPa to 67.9 MPa, which indicates that the stress is transferred from the PLA matrix to the stronger fibers.[101] Further improvement (up to 80.2 MPa) was achieved by adding 30 wt% glass fibers. Both tensile strength and modulus of the PP based com-



7.10 Tensile properties of the neat polymers and the natural-fiber composites: (1) neat PLA, (2) PLA/glass (70/30), (3) PLA/RNCF (70/30), (4) PLA/wood (70/30), (5) PLA/bamboo (70/30), (6) PLA/NaOH treated bamboo (70/30), (7) PLA/silane treated bamboo (70/30), (8) neat PP, (9) PP/glass (70/30), (10) PP/RNCF (70/30), (11) PP/bamboo (70/30), (12) PP/NaOH treated bamboo (70/30), and (13) PP/silane treated bamboo (70/30) (MOE = modulus of elasticity).

posites also increased, which indicates improved adhesion between the glass fibers and the PP matrix.

Osswald suggested[102] that at a critical fiber length, stress is transferred from the matrix to the fiber, resulting in a stronger composite. Stress is efficiently transferred only if the bond between the matrix and fiber is good.[102] Generally, stress is assumed to be transferred from the matrix to the fiber by a shear transfer mechanism when the fibers are of finite length. There is a minimum fiber length required in the case of a specific fiber-type to build up the shear stress between fiber and resin to the value of tensile fracture stress of the fiber.[34,103] The matrix cannot effectively grip the fiber to take the strain, and the fibers will slip and be pulled out, instead of being broken under tension, if the fiber length is less than this critical length. This shortest fiber length (pull-out length) is called the critical fiber length (or the maximum value of load transfer length).[102] Oksman *et al.*[34] reported that the tensile strength and modulus of PLA/flax composites were 53 MPa and 8.3 GPa, respectively, at a 30 wt% flax fiber content. Usually, the quality of a fiber reinforced composite depends considerably on the fiber–matrix interface because only a well-formed interface allows stress transfer from the matrix to the fiber. Therefore, good interfacial adhesion between the matrix and fibers is essential to improve the mechanical strength of composites. Our results indicated that that the RNCF contributes more to tensile strength and modulus, whereas the PLA matrix plays the important role in improving these properties.

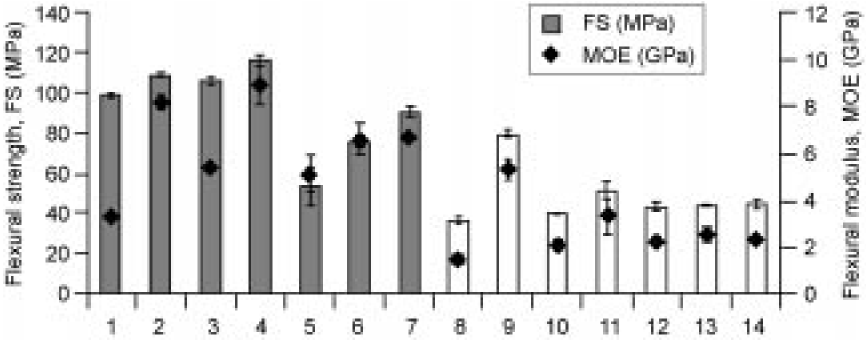
Glass fiber reinforced PLA composites (30 wt% glass fiber content) had a tensile strength of about 80 MPa[104] (in Fig. 7.10), though higher values (88 MPa) at 22 vol.% of reinforcement fibers have been reported for glass fiber mat/PP composites.[60] Cyras *et al.*[105] reported a tensile modulus of 0.7 GPa and a maximum strength of 14.4 MPa with a 30 wt% sisal fiber content in the case of starch/poly(ϵ-caprolactone)/sisal fiber composites. These values are low compared to our PLA/RNCF composite modulus of 5.3 GPa and the strength of 68 MPa. Most of the products used in the automotive industry have a blending ratio of 50:50 wt% for natural fibers and 30:70 wt% for glass fibers; these ratios generate the optimal tensile strengths.[106,107] Rowell *et al.* reported that recycled newspaper fibers have high aspect ratios and contribute to an increase in the moduli of the composites and can also improve the strength of the composite when suitable additives are used to improve stress transfer between the matrix and the fibers.[108]

As shown in Fig. 7.10, in the cases of both NaOH-treated bamboo fiber and silane-treated bamboo fiber reinforced PLA composites, both tensile strength and modulus increased with the presence of surface-treated fibers. The tensile properties of these PLA-based composites were clearly influenced by the chemical modification of bamboo fibers that effectively resulted in improved adhesion between the fiber and the matrix. Usually, the orientation of fibers in the composites influences the tensile strength of fiber reinforced composite. The better the fibers are aligned, the higher strength values that can be obtained. Furthermore, a silane coupling agent helps to promote adhesion between the bamboo fibers and PLA and has also shown that the adhesion between the fiber and the matrix played an important role on the final mechanical properties of the composite.

7.5.2 Flexural properties of the composites

Flexural stiffness is a measure of deformability. The flexural stiffness of a structure is a function of two properties: the elastic modulus (stress per unit strain) of the material that composes it; and the second moment of inertia, a function of the cross-sectional geometry. The flexural strength and modulus of PLA- and PP-based composites are summarized in Fig. 7.11. The flexural modulus results were comparatively higher than the corresponding tensile modulus ones. The flexural modulus and strength of both PLA- and PP-based composites increased significantly with the addition of the glass fibers as well as with the addition of the RNCF. It should be mentioned that the PLA composite with the fiber content of 30 wt% has a flexural strength and modulus of 106.2 MPa and 5.4 GPa, respectively, which are much higher than that of neat PLA. Although the strengths of the composites are lower than typical glass composites, the moduli of the highly loaded RNCF composites might be comparable to those of glass fiber composites.

The RNCF composites also have the added advantage of being reprocessed without significant loss in properties, which is unlikely in the case of glass composites.[109] The insufficient wetting of reinforcing material by the matrix



7.11 Flexural properties of the neat polymers and the natural-fiber composites: (1) neat PLA, (2) PLA/glass (70/30), (3) PLA/RNCF (70/30), (4) PLA/wood (70/30), (5) PLA/bamboo (70/30), (6) PLA/NaOH treated bamboo (70/30), (7) PLA/silane treated bamboo (70/30), (8) neat PP, (9) PP/glass (70/30), (10) PP/RNCF (70/30), (11) PP/wood (70/30), (12) PP/bamboo (70/30), (13) PP/NaOH treated bamboo (70/30), and (14) PP/silane treated bamboo (70/30).

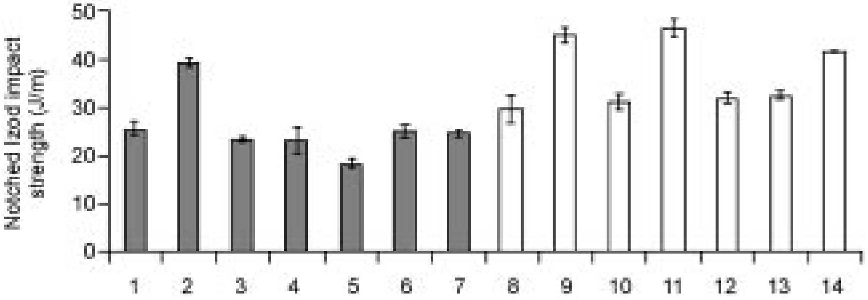
resin could be one cause for the decrease in the flexural properties in the case of high fiber content.[34,35] Figure 7.11 shows that the glass fiber reinforced PLA composite has a flexural strength of 106.2 MPa (17.4 vol.%) in contrast to 79.7 MPa (13.3 vol.%) for the glass fiber reinforced PP composite. Here, fiber volume fraction (v_f) was calculated using:

$$v_f = \frac{100(w_f/\rho_f)}{(w_m/\rho_m) + (w_f + \rho_f)} \qquad 7.1$$

where w_m = weight fraction of matrix in composite, ρ_m = density of matrix, w_f = weight fraction of fiber in composite, and ρ_f = density of fiber. The densities of PLA, PP, and glass fibers are 1.25, 0.91, and 2.54 g/cm^3, respectively. Wambua *et al.*[110] described that hemp reinforced PP composites showed the high flexural strength properties (54 MPa) compared well with glass mat composites (60 MPa). It seems that the mechanical properties of the RNCF-reinforced PLA composites compared favorably with the corresponding properties of glass fiber reinforced PLA composites. Figure 7.11 also shows the flexural properties of the bamboo fiber reinforced PLA composites. It is evident from Fig. 7.11 that there is an appreciable rise in flexural modulus at 30 wt% when compared with neat PLA, but the flexural strength decreased in the case of bamboo fibers. There is an increasing trend of flexural strength for all composites after adding wood fibers. Flexural modulus increased significantly with the addition of 30 wt% surface-treated fibers. This reveals that the incorporation of the fibers into the matrix provides effective reinforcement. When fibers were treated with NaOH or a silane coupling agent, the strength of the composites became higher than that of untreated versions due to the intrinsically increased strength of the fibers, manifesting a better wetting of the fibers by the matrix. In the cases of silane-treated bamboo fiber reinforced PLA composites, the flexural modulus increased significantly with the addition of the bamboo fibers. The large increase in modulus suggests an efficient stress transfer between the polymer and fiber.[3,6] These results indicate the stiffness of these new materials is very high. The quality of a fiber reinforced composite depends considerably on the fiber–matrix interface because a well-formed interface allows stress transfer from the matrix to the fiber.

7.5.3 Notched Izod impact strength of the composite

Generally speaking, impact strength is the ability of a material to resist fracture under stress applied at high speed. Figure 7.12 represents the results of the notched Izod impact strength measurements of PLA- and PP-based composites. Pure PLA has impact strength of 25 J/m and after addition of RNCF, the impact strength of the composite decreased slightly (Fig. 7.12). The RNCF composite showed low impact strength compared with glass fiber reinforced composites. Pure PP has an impact strength of 29.7 J/m (or 7.5 kJ/m^2) (Fig. 7.12). The



7.12 Notched Izod impact properties of the neat polymers and the natural-fiber composites: (1) neat PLA, (2) PLA/glass (70/30), (3) PLA/RNCF (70/30), (4) PLA/wood (70/30), (5) PLA/bamboo (70/30), (6) PLA/NaOH treated bamboo (70/30), (7) PLA/silane treated bamboo (70/30), (8) neat PP, (9) PP/glass (70/30), (10) PP/RNCF (70/30), (11) PP/wood (70/30), (12) PP/bamboo (70/30), (13) PP/NaOH treated bamboo (70/30), and (14) PP/silane treated bamboo (70/30).

standard deviation obtained for the impact strength results was not considered high for this type of test, as discussed by Fejeskozma and Kargerkocsis.[111] According to the Herrmann *et al.*,[112] natural-fiber composites appear to compare well with glass mat composites in terms of specific impact strength properties (impact strength divided by density). In this study, it is obvious that the low value of impact strength at fiber content might be due to the presence of too many fiber ends within the body of cellulose fiber reinforced composites, which may cause crack initiation and potential composite failure.[113] Moreover, the addition of cellulose fiber content also increases the probability of fiber agglomeration, which creates regions of stress concentrations that require less energy to elongate the crack propagation.[53,114,115] A recent study looking at how interfacial adhesion may be a problem for cellulose fibers and polymer matrix composites, pointed out that adhesion needs to be further improved to optimize the mechanical properties of this RNCF reinforced composite.[116] Riedle and Nickel[117] have shown that the mechanical properties of natural-fiber mat reinforced PLA composites reached mechanical properties near those of glass fiber mat reinforced plastics. Mueller and Krobjilowski suggested that based on an optimized manufacture (referring to thermal processing conditions) even the impact strength of natural-fiber composites can reach values comparable to those of glass fiber composites.[118]

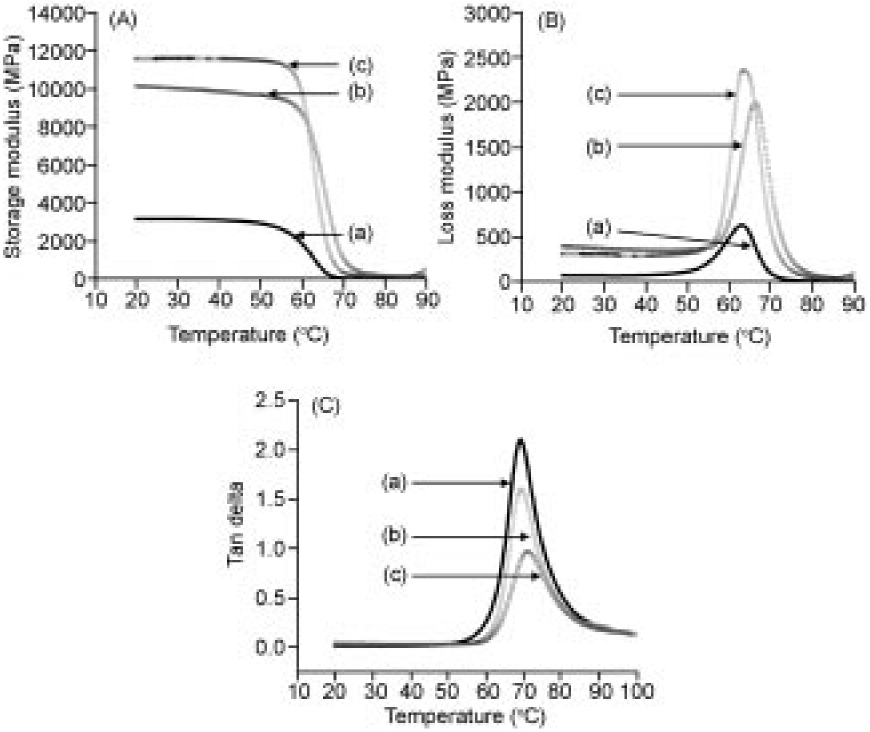
Figure 7.12 also shows that the impact strength of the PLA/bamboo fiber composite decreased after addition of bamboo fiber. It can be seen that the impact strength of treated fiber reinforced composites improves after the addition of treated fibers, since good filler/matrix interfacial adhesion provides an effective resistance to crack propagation during impact tests. For the PLA/silane-treated bamboo composite, impact strength increased significantly (33% improvement) compared with that of the untreated version with 30 wt% loading studied in these experiments, in contrast to a lower trend of these values for the silane-treated fiber reinforced composite processed in the same manner. Generally, the toughness of short fiber reinforced composites can be influenced by a number of factors such as the matrix intrinsic properties, fiber volume fraction, and interfacial bond strength. Therefore, strong interactions between the coupling agent and the hydroxyl groups of natural fibers are needed to overcome the incompatibility problem to increase impact, tensile, and flexural strengths of natural-fiber reinforced composites.

7.6 Thermo-mechanical characterization and thermal behavior

7.6.1 Dynamic mechanical analysis

The properties of composite materials can be determined by the characteristics of the polymer matrices, together with reinforcements, and the adhesion of matrix–fiber interface and the bonding strength at the interface.[119] As a consequence of these characteristics, sensitive techniques must be used, such as dynamic mechanical analysis (DMA), which monitors changes in the mechanical properties, and serves as an important thermal analysis technique for characterizing the fiber–matrix interface.[120–122] It is essential to understand the thermal behavior and phase morphology of the cellulose fiber reinforced composites, which may affect the mechanical properties and biodegradation behaviors. Figure 7.13 shows the storage modulus, loss modulus, and tan delta of the PLA and its composites, as a function of temperature. Here, the DMA was performed to show how exposing the microcomposites to elevated temperatures would affect the stiffness of the composite material. As seen in Fig. 7.13(A) and Table 7.6, the storage modulus of PLA-based composites is higher than that of the neat PLA matrix. This is due to the reinforcement imparted by the fibers, which allowed stress transfer from the matrix to the fiber.[101,102] There are two possible reasons for these high modulus values: the presence of intramolecular bonds and rigid skeletal conformation of the cellulose molecule.[61,109,110] The glass fiber reinforced PLA composite showed a high storage modulus of about 11.9 GPa at 25 °C (in Table 7.6), though it seems that the storage moduli of the RNCF reinforced PLA composites compared favorably with the corresponding storage modulus of glass fiber reinforced PLA composite.

Figure 7.13(B) shows the variation of the loss modulus of the PLA and its composites with temperature. From the loss modulus curves in Fig. 7.13(B), the glass transition temperature (T_g) was determined. The T_g is usually taken to be the peak of either the tan delta or the loss modulus curves obtained during the dynamic mechanical test.[112,123] As seen in Fig. 7.13(B) and Table 7.6, owing to the fiber present in the PLA matrix, the T_g of both PLA-based composites shifted to higher temperature. The shifting of T_g to higher temperatures can be



7.13 Temperature dependence of (a) storage modulus, (b) loss modulus, and (c) tan delta of PLA- and PLA-based composites: (a) PLA (100%), (b) PLA/RNCF (70/30); (c) PLA/glass (70/30).

associated with the decreased mobility of the matrix chains, due to the addition of fibers. Furthermore, the stress field surrounding the particles induces the shift in T_g. Since the loss modulus is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation, when different systems are compared at the same strain amplitude, the loss factors are very sensitive to molecular motions.[53,101] It can be also seen from Fig. 7.13(B) that the loss modulus peak values increases with 30 wt% fiber content. The most pronounced effect of the fiber has been the broadening of the transition region with the presence of the 30 wt% fiber content. Figure 7.13(C) shows that the height of the tan delta peak decreased with the presence of fibers. Generally, the damping in the transition region measures the imperfection in the elasticity and that much of the energy used to deform a material during DMA testing is transformed directly into heat.[123] Hence, the molecular mobility of the composites decreased and the mechanical loss to overcome inter-friction between molecular chains reduced after adding fibers.

As seen in Table 7.6, the addition of 30 wt% glass fibers increased the storage modulus of the PP matrix, i.e. the storage modulus of the PP/fiber composite

Table 7.6 The dynamic mechanical properties of the composites

Polymer/fibers (wt%)	T_g* (°C)	Storage modulus at 25 °C (GPa)	Storage modulus at 40 °C (GPa)	Storage modulus at 60 °C (GPa)	Modulus increase at 25 °C, vs. neat (%)
Neat PLA	63	3.2	3.1	1.8	n/a
PLA/glass (70/30)	65	11.9	11.6	9.7	240
PLA/RNCF (70/30)	67	10.1	9.9	8.6	188
PLA/wood (70/30)	77	10.2	10.0	9.2	218
Neat PP	13	2.9	2.4	1.4	n/a
PP/glass (70/30)	18	7.9	7.4	6.1	172
PP/RNCF (70/30)	4	6.5	5.5	3.8	124
PP/wood (70/30)	15	7.3	5.7	4.0	151

* T_g obtained from the loss modulus curves.

was higher than that of the PP matrix due to the reinforcement imparted by the fibers that allows stress transfer from the matrix to the fiber.[101] The storage modulus of the PP/fiber composite decreased with the increase of temperature. The reduction of modulus is associated with softening of the matrix at higher temperature.[124] As seen in Table 7.6, the T_g of PP/glass composite shifted to higher temperature due to the glass fibers present in the PP matrix.

7.6.2 Heat deflection temperature

As seen in Table 7.7, though it is difficult to achieve high heat deflection temperature (HDT) enhancement without strong interaction between PLA matrix and cellulose fibers at a stress of 0.46 MPa, the measurements of HDT suggested that the polymer appeared to have gone through a change. Since the elevated temperature performance of a structural composite is an important

Table 7.7 HDT of neat polymer and polymer/fiber composites

Polymer/fibers (wt%)	HDT (°C)
Neat PLA	64.5
PLA/glass (70/30)	73.9
PLA/RNCF (70/30)	80.2
PLA/wood (70/30)	66.1
Neat PP	106.3
PP/Glass (70/30)	172.9
PP/RNCF (70/30)	154.1
PP/wood (70/30)	139.4

consideration, the HDT of the fiber reinforced composites were determined. The HDT of PLA/RNCF (70/30) composite was 80.2 °C, relatively high compared with the PLA/glass (70/30) composite. This improvement in HDT might be derived from the increases in modulus as well as from the good dispersion of the RNCF that helps the reinforcement. These results of the HDT of RNCF composites demonstrated that the RNCF reinforced PLA composite would be useful for higher-temperature applications than the PLA/glass composite, because HDT is a property that would provide a basis for the selection of the material to be used at higher temperatures. In general, there are three options to increase the HDT of a polymer: increasing the T_g, increasing the crystallinity, and/or increasing the reinforcements. In this context, the increase of HDT of neat PLA by reinforcement with RNCF could be an important development. The measurements of HDT show that glass fiber reinforced PP composite has high HDT as seen in Table 7.7. One of the most striking effects of RNCF or wood fibers in composites is the great increase in HDT in the PP-based composites. The HDT of the wood fiber reinforced PP composites was higher than that of the PP resin. Even without reinforcement, the HDT of PP exceeded 106 °C.

7.6.3 Thermal behavior

The thermal behavior of natural fibers and natural-fiber reinforced composites is studied by differential scanning calorimetric study (DSC) and thermogravimetric analysis (TGA).[44,125,126] As the natural fibers are hydrophilic, a water desorption peak is observed around 100 °C. The amount of absorbed water depends on the ambient humidity. As reported in literature,[44] no polymer degradation takes place until 160 °C. The temperature at which significant weight loss starts is taken as a basis to compare the thermal stabilities of the respective fibers or composites.

Differential scanning calorimetry

The thermal properties such as glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) obtained from the DSC studies are summarized in Table 7.8. Using literature reference values for the PLA and PP melting enthalpies, under the assumption that the polymer is purely crystalline, it was possible to obtain the degree of crystallinity (χ%) in the composite, $\chi = \Delta H_m / \Delta H_m^o \times 100$; where $\Delta H_m =$ experimentally measured melting enthalpy (J/g) and $\Delta H_m^o =$ melting enthalpy of a purely crystalline PLA (93.7 J/g)[125] or PP (137.9 J/g).[126] The neat PLA had a 51.1% degree of crystallinity with a distinct glass transition at 54 °C.[109] Table 7.8 shows that with the addition of RNCF to the PLA matrix the T_g and T_m of the composites do not change significantly. Similar results were obtained in the case of PLA/glass (70/30) composite. The ΔH_m, ΔH_c and T_c of

Table 7.8 Thermal properties of neat polymer and polymer/fiber composites

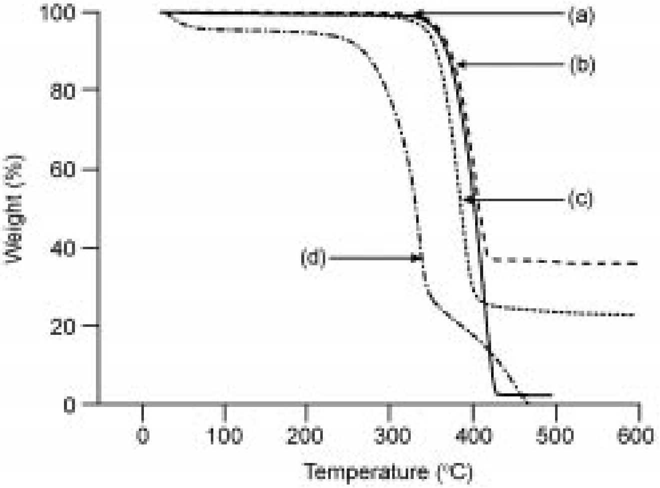
Polymer/RNCF (wt%)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	ΔH_m (J/g)	χ (%)	T_m (°C)
Neat PLA	54	96	27.8	47.9	51.1	172
PLA/glass (70/30)	57	91	20.4	41.7	44.5	170
PLA/RNCF (70/30)	56	90	21.2	44.3	47.4	170
Neat PP	−8	115	84.1	77.7	56.4	153
PP/RNCF (70/30)	−7	119	56.0	40.0	29.0	156

the PLA composites decreased in the presence of RNCF in the case of PLA/RNCF composite. These results suggest that RNCF do not significantly affect the crystallization properties of the PLA matrix. There are two main factors controlling the crystallization of polymeric composite systems.[109,127] First, the additives have a nucleating effect that results in an increase of crystallization temperature, which has a positive effect on the degree of crystallization. Second, additives hinder the migration and diffusion of polymer molecular chains to the surface of the growing polymer crystal in the composites, resulting in a decrease in the crystallization temperature, which has a negative effect on crystallization. In this study, the crystallization temperature of the RNCF reinforced composite decreases by up to 6 °C, which signifies that the cellulose fibers hinder the migration and diffusion of PLA molecular chains to the surface of the nucleus in the composites.[110,128] The crystallinity was found to decrease as a result of the addition of glass in the case of PLA/glass (70/30) composite. The crystallization temperature of PLA decreased by approximately 5 °C when glass was added.

The effect of the fibers on the thermal properties of PP has also been analyzed using DSC experiments. The results are reported in Table 7.8. The dynamic crystallization behavior shows a positive effect from the fibers on the crystallization behavior of PP. A marked increase of the crystallization peak temperature can be observed when the fibers are incorporated in the homopolymer matrix. The melting enthalpy and crystallization enthalpy decreased with the addition of RNCF. The composites T_g, T_m, and T_c remained consistent with neat PP. These results suggest that cellulose fibers significantly affected the crystallization kinetics of the PP matrix. The obtained data are in agreement with the results of Lopez-Manchado and Arroyo,[129] where the nucleating effect of cellulose fibers on the crystallization rate of polypropylene was demonstrated.

Thermogravimetric analysis

The thermal stability of pure PLA and fiber reinforced PLA composites was investigated with TGA. Figure 7.14 shows complete weight loss in a single step



7.14 Thermogravimetric curves of PLA, TC 1004 fiber, and PLA-based composites: (a) PLA (100%), (b) PLA/glass (70/30), (c) PLA/RNCF (70/30), and (d) RNCF (100%).

between 342 and 414 °C in the case of virgin PLA. Usually, an increase in the decomposition temperature results in a more thermally stable product. The 5, 25, 50, and 75% weight-loss temperatures (T_5, T_{25}, T_{50}, and T_{75}, respectively) are listed in Table 7.9. The first weight loss of the composite samples was between 200 and 250 °C. A 72% and 75% weight loss for the RNCF reinforced composite were observed at 400 °C and 432 °C, respectively, which indicated that the presence of cellulose fibers does affect the degradation process. The derivative of the TGA curve of 100% RNCF showed a 20% weight loss peak at 294 °C followed by another 60% weight loss peak was at 384 °C. In general, there were three stages of degradation throughout the temperature runs, especially in the case of RNCF. This was consistent with results reported by Van de Velde and Baetens.[130]

Table 7.9 TGA characterization of the neat polymer and polymer/fiber composites

Polymer/fibers (wt.%)	T_5 (°C)	T_{25} (°C)	T_{50} (°C)	T_{75} (°C)
Neat PLA	356	385	401	414
PLA/glass (70/30)	360	389	407	600
PLA/RNCF (70/30)	345	370	385	432
Neat RNCF	177	305	330	348

Morphological characterization/fracture surface analysis

The morphology of the fracture surface of notched Izod specimens of the composites was investigated by scanning electron microscopy (SEM).[35] SEM observations of the fracture surface of notched Izod specimens of PLA/glass composite indicated that glass fibers were well dispersed in the PLA matrix. The glass fibers are covered with a thin layer of matrix linking the fiber surface to the matrix, and thus better stress transfer could be expected. The state of the fiber–matrix interface in the PLA/RNCF composite was investigated by SEM. The micrographs indicated that the cellulose fiber have been separated during the extrusion process as well as being well dispersed into the PLA matrix. Some fibers are tightly connected with the matrix. Raj and Kokta reported that it is difficult to achieve a good dispersion of the fibers in the polymeric matrix.[131] In the case of the RNCF, a considerable improvement of the adhesion at the interface of the composite is observed when compared with our previous studies[35,132] due to the changes in the processing using the large mixer-compounder Werner and Pflider (WP) twin-screw system. Hence, there were fewer voids on the fractured surface, which indicated that the fibers were trapped by the PLA matrix. Closer observation revealed that some of the matrix could be found on the surface of the fiber, which was a good indication of enhanced fiber–matrix adhesion. It is probable that both RNCF and glass fibers have been covered with a thin layer of the matrix. This suggests that the fibers have some interaction with the matrix, which led to better stress transfer between the matrix and the reinforcing fibers.

SEM studies of fractured surfaces of PLA/glass and PP/glass composites revealed fewer voids in the PLA/glass composite. Glass fibers were seen outside the fractured surfaces indicating that during crack propagation, the glass fibers were broken and pulled out of the polymer matrix, although pull-out is the most important phenomenon.[133,134] The morphologies of the fractured surfaces of both PLA- and PP-based composites therefore show phase information, and fracture characteristics reflect the reasons why the mechanical properties have been changed and in turn decide the mechanical properties of these polymeric composites.

Measurement of water uptake

At ambient temperatures, natural fibers absorb moisture from the environment and this characteristic is desirable for seat cushion application. But for other applications, water absorption must be prevented because upon absorbing water, the composites suffer from dimensional instability. Thus it is very important to study the water uptake behavior of these composites. The measurement of water uptake behavior of natural fibers and natural-fiber reinforced composites has been reported by the researchers in many ways. Baltazar-y-Jimenez and Bismarck[135] reported on the wetting behavior, moisture uptake and electrokinetic properties of lignocellulosic fibers. They set up humidity chambers at 100% humidity using distilled water. They prepared the specimens from bundles of single fibers (flax fibers of different grades) bound together. The fibers were dried in an air oven at 60 °C for 24 h weighed to accuracy of 4 decimals (0.1 mg) and were then placed in the humidity chamber, held at room temperature. They measured the weight difference at different time intervals (as per DIN standard 53495) and the total water uptake was calculated using the following equation: $MC = \{[(m - m_d)/m] \times 100\}\%$, where MC = moisture content, m = mass of the sample after exposure to humidity and m_d = mass of the dried sample. They used three samples for each type of fiber. They also used 'measurement of zeta potential' method to determine the moisture content of the samples.[135]

Other ways have also been adopted by the researchers to measure the water uptake behavior of natural-fiber reinforced composites. Panigrahy *et al.*[136] used an economically viable microwave drying system by incorporating a halogen lamp/microwave combination oven in their experimental design to reduce the moisture of bast fiber before incorporation into a polymer matrix. They investigated the mechanical properties, water absorption, and weather resistance properties of these profiles and found that they can be used as a construction material for the housing industry.

7.7 Applications

7.7.1 Interior components

Natural fibers can be processed into door cladding, seatback linings and package shelves (the space behind the rear seats of sedans), etc. Coconut fiber is used to make seat bottoms, back cushions, and head restraints. Abaca (a cousin of the banana tree) is used in underfloor body panels. The present state of technology allows for the use of about 5–10 kg natural fibers per automobile. Table 7.10 shows the typical weight of natural fibers being incorporated for the automotive components in well-established applications. For mechanical performance

Table 7.10 Typical weight of natural fibers being incorporated in automotive components[29]

Automotive components	Typical weight of natural fibers (kg)
Seatbacks	1.6–2.0
Headrests	~2.5
Front door-liners	1.2–1.8
Rear door-liners	0.8–1.5
Parcel shelves	<2.0
Boot-liners	1.5–2.5
Sunroof interior shields	<0.4
Noise, vibration and harshness materials	>0.5

equivalent to that of glass fiber reinforced composites, press-molded panels can save weight and cost when hemp, flax and sisal are used, mainly for interior applications, including door trim, head-liners and trunk-liners. Practically all major vehicle manufacturers around the world now use natural-fiber composites in various applications such as those as listed in Table 7.11.

Daimler-Benz in Germany has been using the components made from different natural-fiber composites since 1994. Flax, hemp, sisal, wool and other natural fibers are used to make 50 Mercedes-Benz E-class components. Daimler-Benz in Germany is also working with a range of natural fibers – sisal, jute, coconut, European hemp, and flax – as reinforcing fibers in high-quality polypropylene components in order to replace glass fibers. Daimler-Benz has developed the dashboards and center armrest consoles along with seat shells and paneling on seatbacks. Daimler Chrysler increased the use of renewable materials in some vehicles by up to 98% over previous models by using natural materials such as flax and abaca fibers. The newest Mercedes S-class vehicle has 27 components made from natural-fiber composites which weigh 43 kg (73% more than previously).

The BMW Group incorporates a considerable amount of renewable raw materials into its vehicles, including 10 000 tonnes of natural fibers in 2004. Each BMW 7-series car boasts 24 kg of renewable raw materials, with flax and sisal in the interior door linings and panels, cotton in the soundproofing, wool in the upholstery and wood fiber in the seatback cushions. A kenaf and flax mixture has gone into package trays and door panel inserts for Saturn L300s and European-market Opel Vectras.

Toyota developed a biodegradable plastic made from starch extracted from sweet potatoes and other plants. This plastic was combined with natural fibers for use in the fuel-efficient ES3 concept car's pillar garnish and other interior parts.[63] Kenaf has been used to make Lexus package shelves, and it is also incorporated into the body structure of Toyota's i-foot and i-unit concept vehicles. Ford (Germany) is using kenaf fibres imported from Bangladesh[137] in their 'Mondeo' model and the door panels of the Mondeo are manufactured from kenaf reinforced PP composites. FlexForm is a composite made from natural fibers such as flax, jute, kenaf, hemp, and sisal blended with thermoplastic matrix materials such as PE and PP. FlexForm also offers good mechanical properties, claiming a 25% improvement in strength over wood fiber reinforced thermoplastics. Johnson Controls automotive launched its Eco-Cor™ material and process for use on door trim panels for Daimler Chrysler's 2001 Sebring Convertible. V Composite Products Inc. (CPI), Winona, MN, makes composites of PP and flax or kenaf. They are being field tested for door panels, instrument panels, package shelves, and cab back panels for SUVs or pick-ups. Findlay Industries (Findlay, OH) received a 4-star dynamic side-impact rating for door quarter panels made of a LoPreFin PP/PET/natural-fiber composite. The panels appeared on the '99 Saab 9S and are believed to be the first natural-fiber

Table 7.11 The applications of natural fibers in various automotive interior components

Model	Manufacturer	Applications
Rover 2000 and others	Rover	Rear storage shelf/panel, insulation
Vectra, Astra, Zafira	Opel	Door panels, pillar cover panel, head-liner panel, instrumental panel
Passat Variant, Golf A4, Bora	Volkswagen	Seatback, door panel, boot-lid finish panel, boot-liner
A2, A3, A4, A4 Avant, A6, A8, Roadstar, Coupe	Audi	Hat rack, boot-lining, spare tire-lining, side and back door panel, seatback
A, C, E, S class	Daimler-Chrysler	Pillar cover panel, door panels, windshield/dashboard, business table
3, 5 and 7 series and others	BMW	Seatback, headliner panel, boot-lining, door panels
Pilot	Honda	Cargo area
406	Peugeot	Front and rear door panels
Alfa Romeo 159	Fiat	Door panel
Cadillac DeVille, Chevrolet TrailBlazer	General Motors	Seatbacks, cargo area floor
ES3	Toyota	Pillar garnish and other interior parts
L300	Saturn	Package trays and door panel
V70, C70	Volvo	–
Mondeo	Ford	Floor trays, door inserts
–	Saab	Door panels
Clio	Renault	–
Raum	Toyota	Floor mats, spare tire cover
–	Mitsubishi	Cargo area floor, door panels, instrumental panel
C, S, E, and A classes	Mercedes-Benz	Door panels (flax/sisal/wood fibers with epoxy resin/UP matrix), glove box (cotton fibers/wood molded, flax/sisal), instrument panel support, insulation (cotton fiber), molding rod/apertures, seat backrest panel (cotton fiber), trunk panel (cotton with PP/PET fibers), seat surface/backrest (coconut fiber/natural rubber)
Mondeo CD 162, Focus, Freestar	Ford	Boot liner, door panels, B-pillar

composite to meet this stringent specification. VolcaLite is natural-fiber reinforced glass mat thermoplastic (GMT) Lite product, made with PP reinforced by long chopped basalt fiber. Its main advantages are higher service temperatures, higher modulus, and better chemical resistance than fiberglass. It is being targeted as a replacement for both glass and carbon fiber reinforcements in composites. VolcaLite has been targeted for headliners, offering ultra-thin profiles down to 3 mm, a 50% reduction over traditional GMT products. Currently, VolcaLite is being evaluated by multiple Tier 1 automotive suppliers.

Automotive parts supplier Cambridge Industries (Madison Heights, MI) is making flax/PP composites for Freightliner Century COE C-2 heavy trucks. Natural fibers are also being used in polyurethane composites. The first commercial example is the inner door panel for the 1999 S-class Mercedes-Benz, made in Germany of 35% Baypreg F semi-rigid polyurethane thermoplastic (PUR) elastomer from Bayer and 65% of a blend of flax, hemp, and sisal. For interior parts, the plastic resins used as matrices include the thermosetting resins polyurethanes and unsaturated polyester resins. The door inner trim panels were molded using mats of 60% natural fiber in a Baypreg polyurethane resin. Becker Group Europe GmbH developed a polyurethane/fiber, named Fibropur. The polyurethane/natural-fiber composite is elastic and does not tear, even in highly contoured areas such as door pull cups and armrests, according to Becker reports. Chemie Pelzer produces panels using combinations of natural and synthetic fiber felts, bonded with phenolic (thermosetting) or thermoplastics. Mercedes-Benz is producing a mixture of equal parts by weight of flax and sisal is used with a polyurethane matrix for door inner trim panels. The panels are claimed to cost less than similar glass fiber/polyurethane composite panels and the panels have a thickness of 1.7–1.8 mm and a unit weight of 1300–1600 g/m^2. Therefore, all of the major automotive manufacturers now use natural-fiber composites in applications such as listed in Table 7.11.

7.7.2 Exterior components

High-performance resins with reinforcing natural fibers along with suitable additives have helped these composites to meet the performance standards of various automotive components such as dashboards, bumpers, door and trim components, exterior body panels, etc. However, the high moisture absorption behavior of these composites has restricted their use as exterior components. This characteristic of natural fibers to store humidity is desired only for their application in seat cushions, for other applications water absorption must be prevented.[23,138] This is the main reason why the application of these composites is currently limited to the interior of the vehicles. New inventions are leading to the use of natural-fiber composites in the exterior components.[23,139,140] Daimler Chrysler's innovative application of abaca fiber in exterior underfloor paneling on the Mercedes A-class, manufactured from abaca plant fibers, which are extremely elastic and have impressive tensile strength, has recently been recognized.[139] Other exterior parts (front bumper, underfloor trim of bus, etc.) made from natural-fiber composites should be available shortly.[138,140] Mercedes-Benz used flax fibers to make exterior components for Travego and TopClass models.

7.8 Limitations in automotive applications

A major disadvantage of the natural-fiber reinforced composites for their application as automotive parts is the variation in the properties of the natural fibers. Since these fibers are grown all over the world, they have different histories, different geographic conditions and, most importantly, different kinds of processing and production routes. This results in a wide variation in the properties of the composites and this inconsistency creates a problem for the users. Apart from this, their high moisture absorption also limits their application as exterior automotive components. Dimensional instability and deterioration in properties due to ingress of moisture is a characteristic of natural-fiber composites. This restricts their application as exterior component.[4,141] Because of the possibility of fiber degradation and/or the possibility of volatile emissions that could affect composite properties, the lower processing temperature required is the one of the limitations of the use of natural fibers in composites. So, although it is possible to use higher temperatures for short periods, the processing temperature is limited to about 200 °C. The high moisture absorption of the natural fibers and their low microbial resistance are the other drawbacks. Good adhesion decreases the rate and amount of water absorbed in the interphase region of the composite. Owing to encapsulation by the polymer and good fiber–matrix bonding, the absorption of moisture by the natural fibers is minimized in the composite. The moisture absorption of the natural fibers can be significantly reduced through the acetylation of some of the hydroxyl groups present in the fiber.[14]

Another disadvantage of these composites is the variable price of natural fibers compared with the synthetic fibers such as glass fibers. These fibers in reinforced composite industry face a competition with the fibers in the textile industry, which, as a result, causes significant rise in their price. The cost of the glass fibers has remained stable for last many years, whereas, the price of natural fibers, e.g. flax, has had an increasing trend. So a critical cost analysis should be done to avoid this problem.

7.9 Future trends and conclusions

Natural-fiber composites are enjoying a renaissance for a variety of reasons. The quest for increased fuel efficiency in cars and a growing public awareness in environmental preservation are leading to further developments. New materials, stronger, cheaper and eco-friendly, should be achieved. Though natural-fiber composite components are competing with petroleum components in a small part of the automotive market, many new natural-fiber composite components may soon be entering the market. Since several European, Japanese, and US companies currently making natural-fiber-based composites, a number of commercially viable companies are producing natural-fiber components for use in millions of cars. From an economic point of view, natural fibers exhibit decent price stability, being less dependent on the price of oil than other materials and their use should be highly encouraged. Natural-fiber composites from plant-derived fibers and crop-derived polymers (biopolymers) would be of great importance to the materials world, not only as a solution to growing environmental threat but also as a solution to the uncertainty of petroleum supply.[3,6,29]

Natural-fiber reinforced composites have developed significantly over the past few years because of their ease of production, lower density, high specific strength, and renewable nature. However, interfacial adhesion with a synthetic matrix should be improved with suitable surface treatment. In any good composite, it is very important to create a good interphase, so that the applied stress can be transferred from the matrix to the fibers. Owing to significant weight and cost savings, these composites are becoming attractive alternatives to glass and carbon fiber reinforced polymer composites and automotive industries have begun to apply these composites in a variety of interior applications. However, further research is still required to overcome obstacles such as moisture absorption, odor reduction, and increased long-term stability for use as exterior components. Advances are required in areas such as construction of very large panels, structural design, and cost-effective manufacturing processes. Natural-fiber composite products for the automotive industry are the subject of increasing attention. With continuing advances in the basics of science and engineering of natural-fiber composites, their use will eventually surpass that of petroleum-based and synthetic alternatives.

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8

Natural-fibre composites in structural applications

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8.1 Introduction

Over the past ~60–70 years, the development of advanced polymeric composite materials, now primarily based on synthetic fibres (glass, carbon, aramid, etc.) has permitted the replacement of a great many traditional metallic, polymeric and ceramic materials. It could be said that the age of composite materials is now upon us, as their field of application extends from transport to medical to 'nanotech' and beyond. The acceptance of advanced composites, especially in the transport industries, as viable alternatives to more traditional materials is of course due to the impressive mechanical properties and low density of these materials, allowing their use in structural applications where light weight is also critical to the final design. In recent times, no other industry has embraced the technology of advanced composites more enthusiastically than the aerospace industry. Commercial aircraft such as the new Boeing 787 will shed hundreds of kilograms of weight with the extensive substitution of aluminium alloys for carbon fibre composites in the primary structures.

Changes in US and European legislation (and to a lesser extent in other parts of the world) are now driving an insatiable hunger for new recyclable and/or biodegradable materials to avoid the financial penalties that these new directives impose on manufacturers, especially in the automotive sector. A change that has been readily apparent in materials science is the increased interest in and usage of natural fibres extracted from wood or from plants such as hemp, flax, jute, kenaf, ramie and sisal. Natural fibres offer biodegradability, appropriate mechanical properties attributed to their high cellulose content (Bodig and Jayne, 1982; Taiz and Zeiger, 1991) and sustainability, making them attractive alternatives to synthetic reinforcing fibres used in polymer composites (Mohanty *et al.*, 2000). Hence, there has been a strong resurgence in interest in natural fibres over the past decade or so, particularly for reinforcing polymeric materials. Natural fibres, if used in combination with a degradable polymer matrix, also serve as an inexpensive, renewable and less toxic alternative to synthetic fibres, while offering high specific strength and stiffness.

The strong interest in developing biocomposites is mainly due to two factors: (a) environmental concerns over the disposal of existing non-recyclable polymer composites and (b) concerns over the continued use of materials solely based on petroleum resources (i.e., the vast majority of polymers and composites in use today). Although biocomposites have the potential for 'greening' our planet and reducing our dependence on petroleum resources, the uptake of biocomposites by industry in structural applications has been limited by the apparent difficulties in taking full advantage of the mechanical properties of natural fibres. The potential strength of natural fibres is very large if estimated from the theoretical strength of a cellulose molecule. However, in practice it has not been possible to exploit the inherently high properties of cellulose due to naturally occurring structural defects within the fibre, defects introduced during processing of the fibre and chemical incompatibilities with the polymer matrix which impede stress transfer to the natural fibre. The initial excitement over natural-fibre composites has now been tempered somewhat by the realisation that achieving theoretical strengths might not be possible, at least in the near future. Thus, it would be reasonable to speculate that, compared with the widespread acceptance of advanced composites, the path to adoption of natural-fibre composites in structural applications will be hindered by technical challenges yet to be overcome.

This chapter primarily focuses on the current use of biocomposites in semi-structural and structural applications in which they face their greatest challenges – to be able to compete against synthetic fibre polymer composites in a wider range of load-bearing applications. One question that arises before we begin: how do we define 'semi-structural' and 'structural' applications? We make this distinction here quite arbitrarily, by defining semi-structural applications as those that require the component to at least support its own weight in addition to bearing light external loads such as soft knocks or impacts. Structural applications are loosely defined as those that play a major or principal role in supporting the structure of the final designed component (e.g., aircraft airframe, vehicle chassis, load-bearing members used in construction, ballistics). From this latter definition, we take note that biocomposites have had only limited success in structural applications, whereas semi-structural applications for biocomposites have increased rapidly in the past few years. It will become obvious in the next section that much more research is still required to give biocomposites the 'structural' status for which they have some potential, as mentioned earlier.

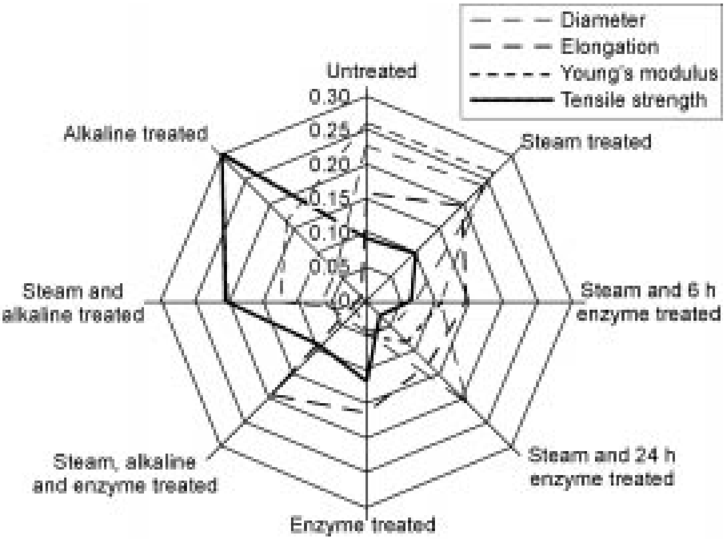
This review is organised into seven main sections. First is an introduction to discuss the potential of natural fibres and biocomposites in structural applications. A historical perspective on the use of biocomposites in semi-structural and structural applications is then given. The next two sections are an overview of the two major classes of biocomposites based on thermoset and thermoplastic polymers, respectively. The literature is reviewed to provide up-to-date information on the range of materials and their properties, state-of-the-art developments in processing and preparation and examples of semi-structural and structural applications. The current limitations of biocomposites are then discussed and this is followed by a future outlook on biocomposites in structural applications and the emerging trends in the development of novel biocomposites aimed at structural applications.

8.2 The potential of natural fibres as structural materials

8.2.1 Introduction

The theoretical elastic modulus of a cellulose molecule is predicted to be around 138 GPa (Nishino *et al.*, 1995). The theoretical tensile strength of cellulose I, cellulose II and amorphous cellulose is 13–17 GPa (Cottrell, 1964), ~9 GPa (Cottrell, 1964) and 800 ± 100 MPa (Chen *et al.*, 2004a,b), respectively. Hence, the theoretical mechanical properties paint a very positive picture for the use of natural fibres as a structural material, especially when considering that the cellulose content of bast and leaf fibres varies from ~45 to 75% depending on the species. As a consequence, much effort has been expended on the optimisation of fibre extraction methods for (i) the separation of fibre bundles and (ii) removal of the non-cellulose components found in natural fibres. The main objective of fibre processing by chemical, thermal or enzymatic means is to remove pectin from the middle lamella, thereby separating fibre bundles into their individual cells (also variously referred to as primary or ultimate fibres) (Sharma and Van Sumere, 1992; Evans *et al.*, 2002). The fibrillation of fibre bundles increases the surface area available for bonding to a polymer matrix (Ouajai and Shanks, 2005; Prasad *et al.*, 2004). In addition, fibre treatments may increase surface roughness of the fibre, resulting in improved mechanical interlocking with the polymer matrix (Bisanda, 2000). The degree of chemical and/or mechanical bonding between fibre and polymer determines the strength of the overall composite, since composite strength depends on the applied load being transferred to the fibre and away from the relatively low strength polymer matrix (Gassan *et al.*, 2000). The treatment of fibres is an essential requirement for the production of viable composites due to various limiting issues such as strong water absorption (Bismarck *et al.*, 2002; Prasad *et al.*, 2004), low resistance to microbiological attack (Mwaikambo and Ansell, 1999) and incompatible surface properties for bonding with a polymer matrix (Mwaikambo and Ansell, 1999). However, it must be noted that the above benefits of fibre treatment may come at a price – a decrease in the mechanical properties of the natural fibre may accompany some treatments, as shown in Fig. 8.1.

The first availability of compatibilised synthetic fibres and cold cure resins in the 1940s (see historical review below) effectively spelled the end of natural-fibre usage in composites. Synthetic fibres offer the advantage of consistency – something more difficult to achieve in a naturally grown fibre. Natural fibres are vulnerable to seasonal variations in growing and soil conditions. The variation during growth is a major disadvantage since manufacturers expect that materials



8.1 The effect of different fibre treatments on the tensile properties of hemp fibre (adapted from Korte, 2006).

provided will have consistent properties. Traditional methods of preparing the fibres (e.g., dew retting), in which processing is difficult to control, further compounds the problem of inconsistent material properties. Methods of fibre preparation (chemical, thermal or enzymatic) that can ensure consistent material properties are a key requirement in an industrial context and are still a major area of research in the biocomposites field. The full potential of biocomposites will not be realised until further progress is made in the areas of fibre processing and fibre–polymer matrix compatibilisation.

The specific tensile strengths of natural fibres are similar to those of glass fibre, although not competitive with carbon or aramid fibres. Worldwide, glass reinforced plastics are used in large quantities in structural applications, especially in the marine, automotive and aerospace industries. As a consequence, 'fibreglass' is commonly used as the yardstick by which to measure the performance of biocomposites. E-glass fibre composites also have the lowest mechanical properties within the family of engineering composites, thus their replacement with biocomposites is a sensible aim.

8.2.2 The mechanical properties of natural fibres

The mechanical properties of cellulose should be a good indication of the high potential of natural fibres in load-bearing applications. Raman spectroscopy has shown that the elastic modulus of microcrystalline cellulose (i.e., cellulose I) is 25 ± 4 GPa (Eichhorn and Young, 2001), and X-ray spectroscopy has indicated even higher values. For example, Ishikawa *et al.* (1997) and Nishino *et al.* (1995) have recorded Young's moduli of at least 90 GPa and 1–13 GPa for the crystalline and amorphous portions of native ramie cellulose fibres, respectively. Thus, the experimentally determined properties of cellulose in the larger fibre forms fall short of the theoretical properties mentioned above. For instance, Kroon-Batenburg *et al.* (1990) reported the highest tensile strength of cellulose to date: a value of 2 GPa. Recent modelling work by Chen *et al.* (2004a) predicts a Young's modulus of 10.42 ± 1.08 GPa for amorphous cellulose.

Taking the hierarchal structure of cellulose fibres one step further, the elastic modulus of natural fibres containing cellulose, hemicellulose and lignin has been modelled by several authors (e.g. Gassan *et al.*). In these studies, the elastic modulus appears to fall in the range of 40–80 GPa (depending on the chosen theoretical modulus for cellulose) for most natural fibres of interest in biocomposites. However, little modelling work has been done on the theoretical strength of natural fibres, owing to an incomplete understanding of the supermolecular architecture and deformation mechanisms during the failure of natural fibres. The experimentally determined mechanical properties for a range of different natural fibres are shown in Table 8.1. The large spread in properties is related to (i) the variation in cellulose content of different fibre types and (ii) the natural heterogeneity of the fibres themselves.

There have been many investigations of the strength of natural fibres, although it is not usually appropriate to compare data from different laboratories. Natural fibres exist mainly as bundles of smaller primary fibres that contain various microstructural defects. Thus, testing a bundle is not a good indication of the strength of the primary fibres, since failure is prematurely initiated by the defects present in the bundle at the microstructural level. Additionally, the statistical nature of the microstructural defects means that a thicker fibre bundle will also have greater numbers of defects and thus a decrease in properties would be expected with increasing bundle diameter (e.g., see Fig. 8.2). One further key problem in testing fibre bundles is that the primary fibre might be only a few micrometres in diameter and at most a few millimetres long. Gripping such a small sample and measuring its extension is a challenge for experimenters. Alternative methods to mechanical testing, such as Raman spectroscopy, have allowed measurements of elastic modulus but not ultimate strengths (Eichhorn *et al.*, 2003). It is likely that the comparison of mechanical property data from different investigations reported in the literature will continue to be problematic until approaches to measuring the mechanical properties of natural fibres are standardised.

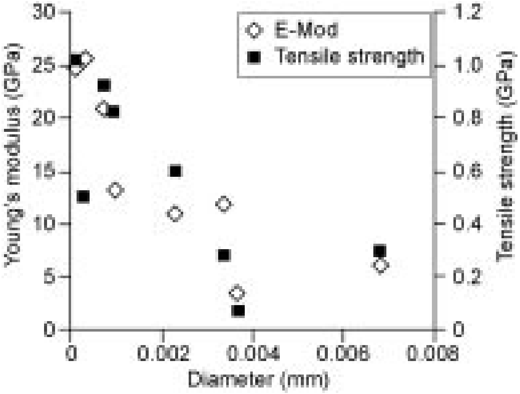
8.3 Historical perspective on structural applications of biocomposites

To begin this section, it is worthwhile considering how composite can be usefully defined (see Matthews and Rawlings, 1994, as an example). The normal definition of a composite is a material consisting of a dispersion of different phases with differing functions. Strictly, biocomposites are such materials, in which the

Table 8.1 Mechanical properties of natural fibres as compared to conventional reinforcing fibres (except where shown adapted from Bledzki and Glassan 1999; Mohanty *et al.*, 2000)

Fibre	Density (kg/m^3)	Elongation (%)	Tensile strength (MPa)	Specific tensile strength ($MPa.kg^{-}$)	Young's modulus (GPa)	Specific Young's modulus ($GPa.kg^{-1}$)
Cotton *(Gossypium sp.)*	1500–1600	7.0–8.0	287–597	0.179–0.398	5.5–12.6	0.00344–0.0084
Jute (*Corchorus capsularis*)	1300	1.5–1.8	393–773	0.302–0.595	26.5	0.00204
Flax (*Linum usitatissimum*)	1500	2.7–3.2	345–1035	0.230–0.690	27.6	0.00184
Hemp (*Cannabis sativa*)*	1480	111.6	690	0.209–0.507	30–60	0.00203–0.00405
Ramie *(Boehmeria nivea)*	1500[†]	3.6–3.8	400–938	0.267–0.625	61.4–128	0.00409–0.00853
Sisal *(Agave sisalana)*	1500	2.0–2.5	511–635	0.341–0.423	9.4–22	0.0063–0.00147
Coir *(Cocos nucifera)*	1200	30	175	0.146	4–6	0.0033–0.005
Viscose (cord)	1520	11.4	593	0.390	11	0.0072
Softwood Kraft fibre	1500	–	1000	0.667	40	0.00267
E-glass (alumino-borosilicate glass)	2500	2.5	2000–3500	0.800–0.1400	70	0.0028
S-glass (high strength glass)	2500	2.8	4570	0.1828	86	0.00344
Aramid (Dupont Kevlar-49) fibre	1400	3.3–3.7	300–3150	0.2571–0.2929	63–67	0.00936
Carbon fibre[‡]	2050	–	1960	0.956	522	0.002546

* Tucker and Johnson (2004); [†] Baillie (2004); [‡] mesophase pitch fibre data from Kelly (1994)



8.2 Young's modulus and tensile strength of hemp fibre as a function of the fibre bundle diameter (adapted from Korte, 2006).

two phases are sourced from plant or animal origin. However, in practical terms, one or the other phase may be artificial in origin, as with flax–polypropylene materials used for interior automotive trim parts. Without doubt then, wood, horn, bone and plant stems all pass the test to be considered as biocomposites, but to make this historical overview manageable, articles made entirely from wood, tanned leather or plant fibres (e.g., rope) will not be considered.

The human race has always used biocomposite materials, although the biodegradable nature of biocomposite materials serves to limit the number of surviving examples from history, and probably to skew the proportion of early examples towards areas with hot dry climates and a culture with an enthusiasm for equipping the dead with articles for the afterlife. The entrepreneurial prehistoric artisan had a choice of bone, shell and wood to augment the use of stone as a resistant material for cutting, scraping and hammering, with skin, sinew and plant fibre for fastening and fixing. The range and sophistication of implements increased in parallel with knowledge of manufacturing technologies and materials science. Later, for instance, gums and glues assisted fastening articles together, and tanning chemistries increased durability and water resistance. The following timeline sketch for the ebb and flow of the use of biocomposites over the past four millennia shows how the history of biocomposites is inextricably tied to the development of manufacturing technologies.

From about 2000 BCE, happy accidents of preservation at a few European burial sites indicate the early use of leather, wood and bone for armour (Carman and Harding, 2004). The bow and arrow has been with us since prehistory and examples from numerous cultures show the early application of knowledge of material properties in the construction of laminated horn and wood bows. A composite bow is typically shorter than the equivalent single material long bow, and therefore more suitable for use by mounted archers (Gordon, 1976; Turnbull, 1998; Carman and Harding, 2004; Holmes, 2006).

In the 5th century BCE, Herodotus (translated by Macaulay, 1890) notes that certain Egyptian priests wore shoes made of papyrus, and Gordon (1976) says that mummy cases were also made from papyrus papier-mâché. Circa 8 BCE, in Homer's description of the siege of Troy, the Locrian warrior Ajax is slightly damned for wearing the linothorax, a laminated or quilted linen breastplate: 'He was a little man, and his breastplate was made of linen, but in use of the spear he excelled all the Hellenes and Achaeans' (translation by Butler, 1898).

By the 13th century AD, Japanese Samurai warrior armour in the style known as Yoroi used a scale-like structure, mixing lacquered leather and iron lamellae (for the more vulnerable parts) to make a full suit of armour weighing about 30 kg (Turnbull, 1998). However, by the 1500s in Europe, the development of relatively mass-produced firearms from blast furnace iron and the difficulties of producing hardened steel armour in quantity put the use of steel armour into a decline (Williams, 1986) that lasted until the invention of composite body armour in the latter years of the 20th century.

Tyres are commonly used composite articles, but unusual in that they operate at well above the glass transition temperature of the resin. The pneumatic tyre was first invented by R W Thomson in Scotland in 1845, and then again in 1888 by another Scot, Dr J W Dunlop in Belfast (Kelly, 1994), originally inspired by a desire to make his son's tricycle ride more smoothly across the Belfast cobbles. Tyres were made of natural rubber with reinforcement cording of cotton, until rubber shortages in the Second World War encouraged the development of synthetic rubber substitutes, and the requirement for higher performance replaced natural-fibre reinforcing cordage with rayon and steel.

In 1860 Frederick Walton patented a mixture of linseed oil, rosin, wood flour, cork powder and pigments, which was rolled onto a jute fibre backing known as linoleum (Smith, 1946), and is still in use today as a heavy-duty floor covering.

At the turn of the 19th century, demand for large volumes of insulating board for the nascent electrical industry (Couzens and Yarsley, 1956) inspired the development of replacements for shellac as a matrix material. (Shellac is the harvested secretion of the *Laccifer lacca* beetle (Tucker and Johnson, 2004) and is still in use as a wood polish and an edible glaze.) Leo H Baekeland developed a mouldable thermosetting phenol formaldehyde resin (Baekeland, 1909) that became known as Bakelite. Bakelite is in part made from renewable materials – formaldehyde potentially of renewable origin, and the wood flour filler-extender.

In the early 1900s, aircraft evolved as large, lightweight biocomposite structures, presumably building on the previous best practice of kite making. A wooden, bamboo and ply space-frame was covered in cotton or Irish linen fabric and starched by the application of gelatinised sago starch (Penrose, 1967). By the beginning of 1911, covering technology was advanced by the introduction of cellulose nitrate dope (Smith, 1919), having the advantages of shrinking upon drying, and thus making the covering drum-tight and, unlike sago, weatherproof: it was, however, highly inflammable, and was readily penetrated by castor oil from the total-loss engine lubrication systems. This oil penetration caused the covering material to slacken off. By the middle of 1911, cellulose acetate dopes (resulting from the work of Eichengrün in Berlin and the Dreyfus brothers in Basle) became available. Cellulose acetate dopes were less inflammable and capable of being plasticised to produce a tough covering that does not creep under load (Britton, 1927).

As is usual during wars, technology developed apace. In 1914, aeroplane propellers were carved out of wood by skilled artisans. By the end of the First World War, propellers were being mass-produced by compression moulding of canvas reinforcement bound with Bakelite resin (Fenichell, 1996), a material known as Micarta. After the war, the material was taken up by the Meadows Company to make the impeller for its highly successful washing machine (Fenichell, 1996).

In 1925 Charles Ducas took out a patent for a method of making printed circuit boards (PCB) (Ducas, 1925); the substrate would have almost certainly been a phenolic resin-impregnated cotton or paper (Smith, 1947), examples of which include Haefelyte, invented by Emil Haefely in 1904 (Seymour, 1987), and the phenol formaldehyde laminates Tufnol and Paxolin (Smith, 1946). The role of the circuit board is certainly structural, and the use of natural-fibre composites for PCB continues to this day.

Inspired by difficulties in the aluminium supply chain in 1940, Aero Research Ltd, made a flax–phenolic resin composite Spitfire fighter body (Anonymous, 1945). This passed static loading tests, but was never assembled into a flying machine. Flax was chosen as the reinforcing material because suitable glass fibres were not yet available (Kelly, 2000). Cellulose laminates (Gordon, 1976) were used for the production version of the pilot seat in the Spitfire fighter plane.

Henry Ford was an enthusiastic member of the interwar Chemurgy movement (Finlay, 2004). Chemurgy was the notion of using crop origin materials as industrial raw materials. Ford promoted the use of soya oil and fibre, patenting a soya composite skinned space-framed automobile design in 1942 (Ford, 1942).

In 1942, Geoffrey Pyke proposed making an aircraft carrier out of a biocomposite (Collins 2002). HMS *Habbakuk* (*sic*) was to be 2000 ft (600 m) long, 300 ft (90 m) wide, with walls 40 ft (12 m) thick, and weighed 2 million tons. The biocomposite, dubbed ‘Pykrete’, although also proposed by Mark and Hohenstein of the Brooklyn Polytechnic University (Goodeve, 2008) consisted of between 2% (Gordon, 1976) and 14% (Collins, 2002) of wood pulp reinforcement added to water as a matrix: the composite was then frozen into the solid state in the manner of a thermoplastic. This material was between 2 and 14 times stronger than ice in beam failure, and significantly more resistant to melting than unreinforced ice. The manufacture of HMS *Habbakuk* never progressed beyond the pilot stage, as the strategic need for mid-Atlantic floating aircraft bases receded, and the limitations of the materials due to its creep properties became better understood.

During the 1950s the ready availability of glass fibre and cold-curing polyester resins and a low capital cost open mould manufacturing route (Couzens

Table 8.2 Examples of companies producing commercial quantities of biopolymers

Company	Thermoset or thermoplastic	Country	Trade name	Polymer type
Novamont	TP	Italy	Mater-Bi	Starch-PLA
BASF	TP	Germany	Ecoflex	Co-polyester
Union Carbide	TP	USA	Tone	Polycaprolactone
Showa	TP	Japan	Bionelle	Poly Butyl Succinate
Solvay-Interox	TP	UK	Capa	Polycaprolactone
Cargill-Dow	TP	USA	NatureWorks	Polylactide
Sustainable Composites Ltd	TS	UK	Ecocomp	Polyurethane
Urethane Soy Systems Co.	TS	USA	SoyOyl	Polyurethane

and Yarsley, 1956) pushed plant fibres into the background as reinforcing materials. In 1957 the Eastern Bloc car manufacturer VEB Sachsenring Automobilwerke Zwickau began production of the Trabant motor car with component body parts made of Duroplast – a phenolic resin reinforced with cotton waste (Maxwell, 1999). The Trabant remained in production until 1991, with a production run of about 3 000 000 vehicles.

Following the first oil crisis in the early 1970s and the predictions of the Club of Rome, drawing attention to the finite nature of oil resources, consideration was given to the manufacture of polymers from non-fossil resources (biopolymers). There are now a considerable number of companies with commercially available biopolymers (Table 8.2).

A corresponding revival in interest in natural-fibre composites (see automotive examples in Table 8.3) has been driven by the need to reduce polymer article cost and weight in the traditional way by the use of fillers and extenders. Thus, over the past few years, Mercedes, BMW and other automotive original equipment manufacturers (OEMs) and first-tier suppliers have adopted mainly flax- and hemp-reinforced polypropylene for non-structural applications such as door-liners. At present, though, these panels are at best semi-structural, and do not yet exploit the full potential of crop origin raw materials.

Table 8.3 Examples of automotive suppliers using natural-fibre composites

Company	Item
Johann Borgers	Insulation
Concargo	Parcel shelf
Johnson Controls	Seats
Lear Corporation Europe	Interior trim
MIP (Textron)	Interior parts
Empe Findlay	Interior trim

The above recent revival is often presented as an example of the greening of manufacturing and consumption, given an increasing need to be perceived as 'green' by customers, but the more obviously quantifiable drivers are the increasing end-of-life disposal costs for polymer matrix composite articles, and the additional fact that in European markets, legislation dictates that the cost of disposal should be borne by the manufacturer. These external drivers are derived from the 'polluter pays' dictum, and from the notion of the 'triple bottom line', whereby the social and environmental effects of manufacturing are considered as well as financial measures.

There is a high perceived value of good environmental stewardship, both in terms of good corporate citizenship, and in response to legislation. The increased interest in the production and usage of biocomposite materials can, in part, be attributed to a perception by consumers of the finite nature of fossil resources and that the consumption of these fossil resources contributes to the damage of the environment (Heyde, 1998). However, in Europe the major factor has without doubt been legislation making end-of-life disposal via landfilling and incineration less attractive due to increased taxes. European waste disposal legislation has set targets for recovery of end-of-life articles (e.g., scrap cars – see Table 8.4) and for the consequent fate of the recovered materials, and composite materials allow greater leeway in how the manufacturers dispose of returned end-of-life articles. Natural-fibre composite materials can be burnt to a low ash residue at the end of life, which is particularly important because, as Monk (2003) observes in Germany, polymer composites with natural fibres do not count towards the thermal recycling quota, and can be thermally treated (burnt, perhaps to recover energy) without penalty.

In a similar vein, the US Government issued an executive order in 1999 directing researchers to work towards the replacement of fossil resources with plant material in both raw materials and fuel (Gerngross and Slater, 2000).

Table 8.4 Planned targets for disposal methods in European End-of-life Vehicle Directive (after Tucker and Lindsey, 2002)

Action	Definition	Current	2015
Recovery	Entry into a waste management system and the recovery of energy, materials or other products from waste	$\geq$85%	$\geq$95%
Reuse of material	Reconditioned spare parts	$\geq$80%	$\geq$85%
Recycling of material	Using recovered stuff as a feedstock (can include composting)	$\geq$80%	$\geq$85%
Thermal energy conversion	Burning	$\leq$5%	$\leq$10%
Landfill	Burying	$\leq$15%	$\leq$5%

However, Lomborg (2001) asserts the view that fossil raw materials have yet to demonstrate the expected increases in price associated with long-term scarcity, and that owing to a change in methods of waste disposal (more composting and incineration) landfill sites are filling at lower than projected rates. Nonetheless, setting targets for reduction of waste streams results in increasing pressure on manufacturing industry to improve its environmental performance, particularly in relation to end-of-life disposal issues, and also in the matter of choice of raw materials.

One of the barriers to the uptake of crop origin materials is the perceived uncontrolled variability in properties. High-volume throughput of tightly specified manufactured articles is not assisted by the need to continually retune the process to cope with material variation. On the assembly line, variation in material properties makes the rapid and accurate assembly of complex structures more difficult. For example, a reliable snap-fit requires precise mechanical properties – neither too stiff to fit, nor too flexible to stay in place.

In addition to the difficulties associated with proving the performance and suitability of any 'new' material, the problems facing the introduction of biocomposites include the demonstration of biodegradability and the separation of biodegradable materials from mixed waste streams. In the former case, standards and product marking systems are required, and in the latter economic production and recovery routes.

Overall, though, the above discussion can be taken as a healthy sign for biocomposites because the industry is accepting natural fibres, and building up a store of knowledge and experience in the application of such materials. In terms of technical development of biomaterials, reinterpretation of materials science already developed for non-renewable resource composites is also likely to reap rewards in establishing a profitable market for these materials. It is the authors' opinion that the use of hybrids of sustainable materials (in this case flax) and non-sustainable ones (polypropylene) are an essential development stage in the widespread acceptance and uptake of such materials into current manufacturing.

8.4 Natural-fibre–thermosetting biocomposites

8.4.1 Introduction

This section considers the use of thermosetting resins as matrix materials. These resins are broadly characterised by being relatively high cost compared with thermoplastics, but processable by low capital cost methods. Thermoset resins are traditionally used to make high-performance composites, the reasons for this being a combination of the high intrinsic mechanical properties of the resins coupled with processing routes that allow the production of high fibre loadings with controlled fibre orientation in the finished article. Table 8.5 shows some

Table 8.5 Examples of crop-based thermoset resins

Resin type	Crop origin component	Non-renewable component
Polyurethane	Rapeseed[*] (*Brassica napus*) oil polyol (polyols are also produced from castor (*Ricinus communis*) oil[*])	Isocyanate curing agent
Epoxy	Epoxidised soya[*] (*Glycine max*) oil	Hexamethylene diamine curing agent
Phenolic	Cashew (*Anacardium occidentale*) nut shell liquid	Sodium hydroxide (NaOH) Formaldehyde[†]
Urea formaldehyde	–	Urea (potentially a bioproduct, but made from ammonia and CO_2 by the Bosch–Meiser urea process) Formaldehyde[†]
Lignin	Lignin (a by-product of the paper industry)	Glutaric dialdehyde and hexamethylene diamine (Wrezesniewska-Tosik *et al.*, 2001)
Condensed tannins	Tannin (from mimosa (*Acacia mimosa*), quebracho (*Schinopsis* sp.), pecan nut (*Carya illinoinesis*), pine (*Pinus* sp.) and gambie (*Uncaria gambia*) (Johnson *et al.*, 2003)	Formaldehyde[†]
Casein	Casein (from milk)	Hydrated lime ($CaCo_3.6H_2O$) Sodium hydroxide (NaOH) Formaldehyde[†] or glycerol and polyphosphate (Fossen *et al.*, 2000)
Latex	Latex (from the *Hevea brasiliensis* or rubber tree)	Sulphur crosslinker, thiocarbanilide accelerator

[*] This triglyceride-based chemistry can produce either polyurethanes or epoxies from these source materials.
[†] Formaldehyde is made from methanol, which was originally isolated from wood but is more usually made on the industrial scale from natural gas or coal.

examples of renewable origin thermoset resins, illustrating the state of the art at the time of writing in the use of sustainable origin materials. None of the resin systems is completely sustainable in origin, but they all represent significant stages on the route to entirely biodegradable thermoset composites. Similarly, the use of non-sustainable origin reinforcements such as glass is a necessary stage in the development of entirely renewable origin materials. The full consideration of minimising the environmental impact of composite manufacturing is beyond the scope of this chapter, but by way of introducing the debate on this subject, the reader is invited to consider the environmental desirability or otherwise of making composite articles from a whale oil-based resin, reinforced by panda fur. Note that ‘crop origin’ or ‘sustainable’ should not be taken to mean non-toxic. Thermoset resins of whatever origin are characterised by small highly reactive molecules, and need to be treated with the appropriate degree of respect.

The low molecular weight of thermoset resins means that they are usually supplied as a liquid to which an extra component must be added (often called a catalyst or curing agent) to start the chemical process of solidification to a solid product. The low viscosity of the resin means that the process of infusing the resin through a packed bed of reinforcement is a practical processing route, and the stiff nature of the highly chemically crosslinked cured resin means that thermoset resins are particularly useful in making long fibre reinforced articles with a high mechanical performance.

The chemical nature of the solidification process means that the resins cannot be re-liquefied without disrupting some of the chemical bonds formed during manufacture, and hence degrading the material. The plus side of this is that the service temperatures of the finished article will be higher than thermoplastic alternatives.

The chemical nature of the solidification of thermoset resins also means that they are less soluble than the thermoplastic equivalents. This insolubility also means that the composite is less prone to biodegradation – the physical process of dissolving being a much faster route to disintegration than attack by micro-organisms. This does not mean that thermoset composites will not biodegrade. Work by Mwaikambo (L Y Mwaikambo, 2007, personal communication) indicates that the presence of natural-fibre reinforcement significantly speeds up the process of biodegradation, probably by increasing the effective surface area of the material by providing routes for moisture ingress into the bulk of the material.

Table 8.6 shows the main methods used for thermoset composite manufacture and gives an indication of the level of environmental impact inherent in each method.

8.4.2 Overview of mechanical properties of natural fibre–thermoset composites

Table 8.1 shows natural fibres with a density of about half that of glass, but it should be noted that this apparent low density may not result in corresponding low density composites. Plant fibres are hollow and can therefore either fill with resin or collapse under processing pressure.

Depending on the degree of processing, natural fibres are usually cheaper than the synthetic equivalents. Some processing routes are cheap, but not

Table 8.6 Estimates of the environmental impact of manufacturing with thermoset composites (modified from Baillie, 2000)

Method	Long or short fibre reinforcement	Blend/ compound/ mix	Process heating	Post-process heating[†] and and cooling	In-process waste	Total*
Injection moulding	Short	2	3	–	2 (non-reusable scrap from sprue etc.)	7
Contact moulding	Long	1	–	–	7 (trimmings from stock materials and exposure of workers to the uncured resin system)	8
Sheet and dough moulding (SMC/DMC)	Short	3	3	3	1	10
SRIM/RRIM	Long (SRIM)/ short (RRIM)	2	3	3 (optional for best properties)	1 (long fibre reinforcement trimmings)	6–9
Resin transfer moulding (RTM)	Long	1	3	3 (optional for best properties)	2 (reinforcement trimmings & purging solvents	6–9
Vacuum infusion	Long	1	2	3 (optional for best properties)	4 (diffusion materials are all one trip)	7–10
Pultrusion	Long	1	2	0	1 (production of constant section geometries only)	3

SRIM is structural reaction injection moulding, RRIM is reinforced reaction injection moulding.

[†] Heating the finished composite (often called 'post-cure') to above the glass transition point of the matrix maximises the degree of chemical crosslinking and degree of removal of any non-reacting process solvents, and hence tending to maximise mechanical properties.

* Scale is arbitrary the larger the number, the greater the environmental impact (related to the amount of energy used and the amount of process scrap produced). For detailed descriptions of these processes the reader is referred to Tucker and Lindsey (2002).

Table 8.7 Comparison of specimen material properties for jute, hemp, and glass long fibre reinforced thermoset composites

Fibre/resin	Fibre volume fraction (%)	Tensile strength (MPa)	Young's modulus (GPa)	Charpy impact strength (kJ/m^2)	Interlaminar shear strength (ILSS) (MPa)	Source
Chopped strand mat glass/polyester	30 (25–35)	95 (60–150)	8 (6–9)	40–80[‡]	25 (20–30)	Johnson (1994)
Jute (*Corchorus* sp.)/ polyester	45	60	7	29	10	Gowda *et al.* (1999)
Hemp[*]/low-OH *Euphobia*[†] polyurethane	21	23 (1.06)	2 (0.53)	19 (2.17)	3 (0.54)	Mwaikambo *et al.* (2007)
Hemp[*]/high-OH *Euphorbia*[†] polyurethane	19	27 (1.85)	3 (0.92)	7 (1.13)	3 (0.45)	Mwaikambo *et al.* (2007)
Alkalised hemp[*]/high-OH *Euphorbia*[†] polyurethane	20	35 (3.76)	3 (1.05)	9 (1.64)	5 (0.76)	Mwaikambo *et al.* (2007)

Figures in brackets are the range of values.
[*] *Cannabis sativa*, [†] *Euphorbia lagascae*, [‡] IZOD un-notched to BS27782 – section 306a.

necessarily very satisfactory for composite use. Needled felts are a case in point: the high degree of fibre entanglement makes it difficult to mould compound shapes without fibre rupture.

The higher elongation to failure of natural fibres offers the opportunity for the production of tough materials (see also Chapter 3). Natural-fibre composites have the potential to deliver mechanical properties per unit cost that are similar to established synthetic materials, but with lower embodied energy consumption.

8.4.3 Comparison of synthetic–thermoset composites with natural-fibre alternatives

Table 8.7 shows a comparison of properties of some natural-fibre composites with a typical glass–polyester composite. The fibre volume fraction achieved is in the range expected for a hand-laid composite. The hemp composites are made with two different *Euphorbia lagascae* seed oil-based polyurethane resin formulations, with low or high levels of attachment of hydroxyl groups. The level of attachment of the OH groups is related to the degree of adhesion between fibre and matrix. The highest tensile strengths, moduli and interlaminar shear strength (ILSS) are obtained from the high-adhesion high-OH composites, while the low-OH composites show higher impact strength. Pre-treatment of the hemp fibre mats with NaOH increases the tensile strength, stiffness and ILSS, but has little effect on impact strength. The high impact strengths of the synthetic composites are related to the high degree of control of the degree of adhesion between fibre and matrix achieved in the past half century of material development.

With regard to short fibre composites, Nangia *et al.* (2000) describe work by Fabtech Industries & Technology (with support from the Central Glass & Ceramics Research Institute (CGCRI), Calcutta) to develop jute and glass fibre composite components such as louvre shutters for windows and axle box covers for railway coaches. The composites were made from sheet moulding and dough moulding compounds. The low moisture absorption values are attributed to using glass surface veil layers: see Table 8.8 for details.

8.4.4 Examples of structural and semi-structural applications

The Ecoboard environmentally friendly surfboard

Originally surfboards were wooden structures, but since the availability of cold cure polyester resins, the typical board is now a glass reinforced polyester skin over a cast and shaped polyurethane foam core (Neal, 2006). There is currently a thriving worldwide demand for surfboards, and the sport has experienced a phenomenal growth rate in recent years, becoming a distinctly mainstream

Table 8.8 Comparison of properties of jute and glass short fibre laminates tested to Government of India – Ministry of Railways Research Designs and Standards Organisation specifications

Properties	Fibre glass sheet moulding compound	Jute–glass-based hybrid composite
Specific gravity	1.75–2.0	1.41
Hardness (units not specified)	48	50
Tensile strength (MPa)	70	88 ± 5
Cross breaking strength (MPa)	150	169 ± 37
Izod impact (J/m)	450	574 ± 42
Water absorption (with edge sealing)	0.5%	0.4%
Resistance to boiling water (after 4 h boiling)	80%	85%

activity. The surf industry is the largest growing sector of the leisure industry in the south-west of England and continues to grow annually.

Currently semi-finished raw materials (known as blanks in this industry) and some finished surfboards are imported from the European Union, the United States, and the Far East. The service life of a surfboard is on average between 6 and 12 months. Manufacture of boards in the south-west of England is the province of a number of small to medium sized enterprises. The companies employ skilled workers, who typically work with imported foam blanks, shaping the blank to suit the demands of the customer, and then hand laying a glass polyester composite outer skin on to the foam blank. The board is then sanded and polished to a smooth finish. This craftsman approach is time and material intensive. It is estimated that about a third of the raw materials entering the workshop end up either stuck to the floor, or in the rubbish skip (R. Henty, 2002, personal communication).

Responding to a perceived need for a surfboard with a low environmental impact, a group of composites manufacturers in the south-west of England have formulated resins for a polyurethane foam core blank (Ecoblank®) made from 40% castor oil and a resin system (EcoComp® UV-L resin), which has a claimed 96% linseed oil content. The principal partners are sister companies Sustainable Composites Ltd and Movevirgo Ltd, based in Redruth, Cornwall (Tunbridge, 2007). The EcoBoard is made by a third local company, Laminations Ltd, using hand-laid hemp fibre reinforcement, and is claimed to have a 55% renewable content. The linseed UV cure system wastes less resin than the conventional polyester system owing to the very long pot life (cure is not initiated until the resin is exposed to UV light), and the workforce is not exposed to styrene fumes, nor is acetone required for cleaning up (N. Frost, 2007, personal communication).

Brake pads

Brake pads are composite materials, in which short fibres are added to the formulation to prevent settling of the mix components during mould filling, before the pad is compression-moulded. This prevention of mix segregation produces a brake with constant performance during its service life. Phenolic resins based on cashew nut shell liquid (CNSL) are being used as binders for friction materials such as brakes and clutches (Johnson *et al.*, 2003). The addition of cured CNSL dust and rubber dust reduces brake squeal, and CNSL is also used an insulator to prevent heat being transmitted from the brake pad to the braking mechanism (Chan and Stachowiak, 2004).

John Deere tractor engine covers

The John Deere agricultural equipment company is using soy-based polyurethane (branded as SoyOyl from the Urethane Soy Systems Company) resins in its line of farm equipment. The 'HarvestForm' panels are made by reaction injection moulding (RIM) and sheet moulding compound (SMC) reinforced with short glass fibre. It is asserted that the move to biopolymers and biocomposites will reduce the environmental impact of the vehicles; the company suggests that every 1 lb (0.5 kg) of soybean oil used can be considered to be equivalent to the removal of almost 3 lb (1.5 kg) of carbon dioxide from the atmosphere (Niemann, 2004).

Fishing rods

CelluComp Ltd use a method of extracting fundamental fibrous material from vegetable feed stocks (carrots are used as an example) to produce an epoxy-based mouldable thermoset composite material with properties between glass and carbon (Hepworth and Whale, 2006). Reinforced composites are claimed to have strength figures of 5 GPa and strain to failure of over 5% (see Table 8.9 for claimed fibre properties). The material is used in the manufacture of fishing rods, with performance said to be greater than or equal to carbon fibre equivalents.

Table 8.9 Material property data for Curran reinforcement fibres (from http://www.cellucomp.com/ – accessed 13 June 2007)

Stiffness (GPa)	Strength (GPa)	Energy absorbed to failure (MJ/m^3)	Density (g/cm^3)
130	5	100	1.5

Rail rolling stock internal partitions

Duroflex Limited, Bangalore, (manufacturers of rubberised coir materials) are developing jute-coir composite boards with oriented facings of jute veneer and coir/rubber wood inside. Natural fibres such as coir and jute impregnated with phenolic resins are used for its manufacture. 80% of the materials used in the composite are claimed as these jute and coir natural fibres. The product range developed by Duroflex is being marketed as medium density fibreboard (MDF) substitutes, and has been tested satisfactorily for railcar application at the Indian Plywood Industrial Research & Training Institute (IPIRTI) (Nangia *et al.*, 2000).

8.5 Natural-fibre–thermoplastic biocomposites

8.5.1 Introduction

A great deal of emphasis has been placed on developing biocomposites using a matrix based on thermoplastics, especially the petroleum-derived thermoplastics polyethylene (PE) and polypropylene (PP), which are the two most commonly produced thermoplastics. Despite their lower thermomechanical properties, there is great interest in developing biocomposites with a thermoplastic rather than thermoset matrix, primarily due to their recyclability. Indeed, the choice of a thermoplastic matrix fits well within the eco-theme of biocomposites. However, there are some important limitations on the recyclability and mechanical properties of thermoplastics. First, it is important to realise that thermoplastics have a finite life and that the properties of thermoplastics decline with each recycling event, requiring blending with virgin material to maintain these properties. In general, the mechanical properties of thermoplastics fail to compete with thermosets, exhibiting lower moduli and strength values. Additionally, a dramatic loss in properties is observed above the glass transition temperature, leading to decreases in other thermally sensitive properties such as creep resistance. On the plus side, thermoplastics generally show greater fracture toughness than thermosets and thus are more useful in resisting impact loads. The addition of natural fibres can further enhance the fracture toughness of thermoplastics.

The limit on thermoplastic recycling was recognised early on in the development of biocomposites. This has led to increased interest in thermoplastic biopolymers that could be derived from biomass, with the aim of decreasing our reliance on petroleum-derived thermoplastics. Biopolymers derived from biomass offer greater sustainability and reduce our dependence on petroleum-derived plastics. The best example is the polylactide (PLA) family of biopolymers that are derived from corn starch and were one of the first biopolymers to be produced in commercial quantities (Cargill Dow LLC, PURAC, Hycail, etc.). The availability and outstanding mechanical properties of polylactides have led to this matrix system being one of the most thoroughly investigated in the biocomposites literature. Furthermore, PLA can be processed in the same manner as polyethylene terephthalate (PET), making it amenable to a large range of different processing routes. The polymer structure of PLA can also range from semicrystalline to completely amorphous. Using a combination of natural fibres and biopolymer matrix it is possible to create a true eco-material. It also becomes less of a necessity to recycle biopolymers since they are biodegradable and thus do not contribute to landfill at their end of life. Furthermore, if incineration of the material at the end of life is a viable option then the CO_2 emitted does not lead to accumulated CO_2 as is the case for incineration of petrochemical-based plastics that are derived from fossil fuels. Moreover, since biomass is a huge, self-replenishing resource, future biopolymer production will be essentially unlimited, in contrast to petrochemical-based plastics.

Although thermoplastics can be recycled, their main deficiency is that in general their mechanical properties are not as high as thermosets, particularly under hygrothermal conditions (i.e., combined exposure to moisture and heat). Traditionally, the use of advanced composites based on glass, carbon or aramid fibres has depended heavily on thermosets in most structural applications. As discussed earlier, the development of new types of bio-derived thermosetting resins aims to provide sustainable, polymer matrix systems that will fulfil biocomposite eco-principles while offering high mechanical properties, especially under hygrothermal conditions. However, at a recent workshop ('Naturfaserverstärkte Kunststoffe', 2007) held by the AVK (Federation of Reinforced Plastics),[1] it was widely recognised that biopolymers were not likely to tap into the industrial market in the near future unless costs could be lowered and processability improved.

8.5.2 Manufacturing of thermoplastic biocomposites

The various processes used for manufacturing thermoplastic composites include injection moulding, compression moulding, pultrusion and filament winding. Aside from injection moulding, the remainder of these processes rely on feedstock in the form of a 'prepreg'. The prepreg consists of the thermoplastic and reinforcement already combined in the form of a sheet, tape or fibre. The purpose of the prepreg is to reduce production cycle times by reducing the melt flow distances for wetting out of the reinforcement during processing. Table 8.10 gives a summary of these processes, and the type of fibre reinforcement and feedstock typically used.

Obviously for structural applications those processes that allow the use of continuous fibres hold the most promise for producing composites with good structural properties. Unfortunately, nature does not produce natural fibres in a continuous form and in fact most natural fibres range in length from only a few

[1] http://www.avk-frankfurt.de/www_avktv/press_225_73_0_f.htm (accessed on 16 June 2007).

Table 8.10 Summary of possible processing routes for thermoplastic composites

Process	Fibre type	Feedstock
Injection moulding	Short	Short fibres and thermoplastic pellets, or composite pellets from extrusion processes
Compression moulding	Short or continuous	Glass mat reinforced thermoplastic (GMT) Long fibre reinforced thermoplastic (LFT) Textiles of commingled yarns
Pultrusion	Continuous	Commingled fibres or tows
Filament winding	Continuous	Pre-impregnated tows or tape

millimetres to 20–30 mm in length. This is a limitation for natural fibres compared with continuous synthetic fibres, but another equally important factor is that the fibres are well bonded with the thermoplastic matrix to allow effective stress transfer (see Chapter 3).

The most common way to use natural fibres in biocomposites has been as a short fibre as extracted from the plant, with the fibre bundles being partially fibrillated by treatments to increase the aspect ratio and surface area per unit volume of the fibre bundles. Below a critical aspect ratio, the fibres will behave as a filler rather than reinforcement (for example, see Takagi and Ichihara, 2004). The production of continuous fibre in the form of a yarn is also possible. A further development of natural-fibre yarns for biocomposites is to use a commingled yarn that combines both natural and thermoplastic fibres to help improve fibre wetting by bringing the thermoplastic into closer contact with the reinforcement.

Compression moulding, and variants on the process, is a very popular method for producing short and continuous glass fibre reinforced thermoplastics. The feedstock is either a pre-impregnated glass fibre mat (GMT, random, short fibre arrangement) or a pre-impregnated long glass fibre mat (LFT, long fibres woven into a textile). The glass fibre in this type of composite product has been replaced with natural fibres (mainly jute, kenaf, sisal and European flax, and to a lesser extent coir, abaca and hemp[2]) in mainly automotive applications where GMT and LFT are already used extensively. The main difference in processing conditions is that an upper temperature limit of about 200 °C is necessary to avoid degradation of cellulose, which also effectively limits the matrix choice to lower-temperature thermoplastics. A ‘green’ bulk moulding compound (BMC) that uses the injection or injection-compression moulding processes is in development, although a commercial product (from Menzolit SA, Vineuil, France) is not yet market-ready.

[2] http://www.nova-institut.de/nr (accessed on 16 June 2007).

8.5.3 Structural properties of thermoplastic biocomposites

Commodity thermoplastics such as PE and PP have played a central role in the development of biocomposites. The projected market value of biocomposites (using a petrochemical-derived thermoplastic matrix) is projected to be at least €290 million worldwide by 2009 (Foster *et al.*, 2006).

The widespread use of thermoplastics has been chiefly due to their large-scale availability, recyclability and low cost. The type of natural fibres used and mechanical properties achieved has varied tremendously. Numerous studies of wood-, flax- and hemp-reinforced PE or PP have been reported. The mechanical properties for a selection of natural-fibre–thermoplastic biocomposites are summarised in Table 8.11. The most commonly studied bio-derived thermoplastic has been polylactide, mainly due to its excellent mechanical properties that allow it to compete with the commodity polyolefins. An excellent review of polylactic acid (PLA) is presented by Plackett and Sodergard (2005).

In general, the commodity polyolefins struggle to compete with glass fibre thermoset composites, even if the glass fibres are short and randomly arranged. There is some hope for some combinations, however, with work by Ochi *et al.* being particularly promising. Ochi *et al.* (2003a,b) have looked at continuous fibre arrangements of hemp and bamboo in starch thermoplastics that yield

Table 8.11 Overview of the mechanical properties of selected natural-fibre biocomposites compared with traditional glass fibre composites

Fibre/resin	Fibre volume fraction (wt%)	Tensile strength (MPa)	Young's modulus (GPa)	Source
Chopped strand mat glass/polyester	25–35	60–150	6–9	Johnson (1994)
Kenaf–PLA	40–80	~45–62	4.5–6.3	Nishino *et al.* (2003)
Flax–PLA	20	66	5.7	Bogoeva-Gaceva *et al.* (2007)
Bamboo–PP	20	16	2.5	Bogoeva-Gaceva *et al.* (2007)
Sugar cane–PP	20	16	0.6	Bogoeva-Gaceva *et al.* (2007)
Sisal–LDPE	20	16.5	0.93	
Wood–PP	30	38	–	*
Oil palm fibre–HDPE	30–60	6.3–12.5	0.4–0.65	*
Hemp–starch	50	153	–	Ochi *et al.* (2003b)

* Partially adapted from *Natural Fibres, Biopolymers and Biocomposites* by Mohanty AK, Misra M, Drzal LT (2005), CRC Press, Boca Raton, FL.

strengths of up to 188 MPa using compression moulding and taking particular care not to damage the natural fibres during moulding. With such strengths, these materials have the great potential for structural applications. PLA thermoplastics also show great promise as a high-strength matrix for natural fibres. Based on the results to date, much more development work is required on thermoplastic biocomposites if they are to be used in structural applications. However, it should be noted that a thermoplastic matrix composite is being used to make the leading edge of the wing of the A380 Airbus Superjumbo (Gardiner, 2006). This is a highly significant departure from normal practice because similar previous parts have been made from aluminium or thermoset composites, and it indicates that thermoplastic materials are not inherently unsuitable for structural applications.

8.5.4 Examples of structural and semi-structural applications

Examples of natural-fibre thermoplastic biocomposites used in true structural applications are extremely rare. At the time of writing, thermoplastic biocomposites are still largely restricted to semi-structural applications. However, with further development of these materials in terms of fibre processing and compatibilisation with a thermoplastic matrix, thermoplastic biocomposites will be able to meet the requirements of more demanding applications in the future.

Automotive applications

According to a Nova-Institut survey,[3] 19 000 tonnes of natural fibres was used by the German automotive sector alone in 2005. Despite this growth over 2004–2006, the long-term future of natural fibres in the automotive sector is still unclear and some believe that the uptake of biocomposites may have now reached a peak. However, there is a new EU End-of-Life Vehicle Directive currently under review which could further force the automotive sector down the green materials path.

Since some of the first trials of natural-fibre biocomposites, this industry sector has seen a large growth of ~10% per annum in the usage of these materials. Some of the first trials were undertaken by Toyota, which exhibited the Eco Spirit cubic (ES3) concept car at the International Frankfurt Motor Show in 2001. Toyota used a new starch-based thermoplastic combined with natural fibres for a range of different semi-structural interior parts.

First-tier suppliers to the automotive industry such as Techni-Lin (France) are now supplying interior door panels for 2000 vehicles/day for companies such as Opel and Citroen. The panels are fabricated by compression moulding of needle-

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[3] http://www.nova-institut.de/nr (accessed on 16 June 2007).

punched non-woven mats consisting of 50:50 flax:PP fibres. Another major supplier to the automotive industry, Faurecia (France), is also currently developing new wood fibre–thermoplastic door panels and other semi-structural parts for the automotive industry. Rieter Automotive System (Switzerland) in partnership with Daimler Chrysler AG (Germany) and Manila Cordage Co. (Philippines) has developed a composite based on leaf fibre from abaca (*Musa textilis*) fibre reinforcement of a PP matrix, in which the abaca fibre is being used as a glass fibre substitute.[4] The main application is in underfloor components. The natural-fibre option appears to be both competitive and sustainable.

Toyota Auto Body is the main division of Toyota that produces minivans and sports utility vehicles (SUVs). Ansell (2005) reports that the company is actively engaged in the development of car components made from natural fibres in natural resin matrices. Kenaf (*Hibiscus cannabinus*) is the fibre of choice of the company for composites manufacture. Toyota Auto Body has its own kenaf plantation in Indonesia and automotive panels are also pressed in their factory in Indonesia. Considerable care is taken over the quality control of germination, the sowing of seed and rotating the crop on a monthly basis. Following retting in water the bast fibres are separated mechanically. After drying, the fibres are cut to size in the factory, refined and converted into pre-board by combining the fibres with thermoplastic polymer and heating the mixture to consolidate it. This product may then be exported to Japan and elsewhere and hot-pressed into automotive components.

Two types of thermoplastic polymer are used:

- PP (oil-based but readily recycled);
- PLA (synthesised from lignin extracted from the core of the kenaf stem).

Manufacture of door trims began in 1999, using kenaf fibres in a phenolic resin matrix. PP and PLA-based products followed, and the spare wheel trim for the Raum car is a truly sustainable biocomposite product made from kenaf–PLA preform. Toyota Auto Body exhibited its first all-kenaf composite car at the 2003 Tokyo Motor Show.

Construction applications

Tecnaro GmbH are marketing a natural fibre biocomposite (ARBOFORM®) that uses lignin as the thermoplastic matrix material.[5] Approximately 50 million tonnes of lignin per year is produced worldwide as a by-product of the pulp industry. The biocomposites can be used in the construction industry for applications such as slabs, parquet flooring, hand railing and window frame sections. The biocomposite can also be foamed to a give a lightweight structural

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[4] http://www.rieter.com (accessed on 17 June 2007).

[5] http://www.mellikids.de/tecnaro (accessed on 16 June 2007).

material. The Aquasolv digestion process used to produce ARBOFORM® was initially developed by Eisenreich in 1986.

The manufacture of biocomposites that use a lignin matrix has also been developed and patented (2002) by LignoTech Developments Ltd (New Zealand) with proposed structural applications in furniture, joinery, flooring and roofing.[6]

More traditional wood fibre filled composites (WPCs) based on petrochemical thermoplastics, such as virgin polypropylene, recycled polyethylene and to a lesser extent PVC, are used extensively in construction applications including decking, furniture and window applications. A good example of this technology is being marketed by Tipco Industries (India),[7] which is offering WPCs claimed to be suitable for door panels, trims, office cabinet, marine flooring, furniture and various artificial wood products.

Electronics applications

NEC has developed the first mobile phone with an outer casing manufactured from a biocomposite.[8] The casing is made from a kenaf fibre reinforced PLA biocomposite that contains around 90% natural fibre. The high fibre content reduces the amount of PLA used, improves heat deflection and almost doubles the impact resistance of the casing compared with an unfilled PLA casing. This is an encouraging initiative by the electronics sector, since millions of mobile phones are produced annually with a typical lifespan of only 1–2 years.

8.6 Current limitations

8.6.1 Supply and consistency

Robson *et al.* (1993) suggest three sources of fibre for composite manufacture:

1. *Established fibre crops* (see Table 8.12). Timber figures are quoted in m^3, and are in the region of 300 000 million m^3 of timber per annum. About half of this amount is used for biomass fuel, a third for sawn products, and the remainder for pulp.
2. *Potential fibre crops*, examples are banana (*Musa cavendishi* and *M. sapientum*), members of the *Palmae* family – palm trees, members of the *Asclepiadoideae* subfamily – e.g. milkweeds and lianas, *Miscanthus giganteus* grown for biomass fuel and animal bedding in the UK by Bical Ltd and used by Napac in Switzerland for the manufacture of biodegradable plant pots by a proprietary compression moulding method, and the common nettle (*Urtica* sp.) and broom (*Genisteae*).

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[6] http://www.lignotech.co.nz (accessed on 17 June 2007).

[7] http://www.tipco-india.com (accessed on 17 June 2007).

[8] http://www.nec.co.jp/eco/en/annual2006/02/2-1.html (accessed on 16 June 2007).

Table 8.12 Commercially important fibre sources (NB: legislative constraints on growing hemp mean this value is likely to be under-reported)

Fibre source	World production (10^3 tonnes)	Region
Cotton lint (*Gossyphium* sp.)	18 450	E, W
Jute (*Corchorus* sp.)	2 300	W
Kenaf (*Hibiscus cannabinus*)	970	E, W
Flax (*Linum usitatissimum*)	830	UK, E, W
Sisal (*Agave sisilana*)	378	W
Roselle (*Hibiscus sabdariffa*)	250	W
Hemp (*Cannabis sativa*)	214	UK, E, W
Coir (*Cocos nucifera*)	100	W
Ramie (*Boehmeria nivea*)	100	W
Abaca (*Musa textiles*)	70	W
Sunn hemp (*Crotalaria juncea*)	70	W
Urena (*Urena lobata*)	?	W
Henequen (*Agave fourcroydes*)	?	W
NZ flax (*Phormium tenax*)	?	W
Pineapple (*Ananas comosus*)	?	W
Bamboo (*tribe: Bambuseae*)	10	W

UK = United Kingdom, E = Europe, W = Rest of the World.

3. *Agricultural wastes* – such as straw from cereals (100 million tonnes per year) and oil seed production, fibre from sugar extraction, known as bagasse. Bagasse production is estimated to be about 15 million tonnes per year.

It is clear that quantity and variety of fibres are not limitations to the uptake of natural-fibre composites, but there may be issues associated with quality and consistency of fibres. Note that Toyota Auto Body uses water retting for its fibre production. This method was traditionally used to produce high-quality fibres (for example for linen production) but the large quantities of highly eutrophic (and evil smelling) liquor produced by this process have reduced the popularity of this technique.

There are standard agricultural techniques to reduce the season-to-season variability of crop products. These usually involve retaining a stock from year to year, and blending to produce a more consistent product. In terms of establishing a supply chain for composite materials, fibres from by-products are favourite, as usable quantities are available on demand and the financial risk to growers are minimised.

8.6.2 Hygrothermal effects

All composites suffer from problems of water ingress. In glass fibre composites the path of ingress is either via protruding fibres or reaction between water and unreacted elements of the gel coat. This reaction causes ultimate failure of the gel coat and the underlying laminate is capable of absorbing water 'like a sponge' (Anonymous, 2003) via further reaction with silane coupling agents used to control the degree of adhesion between fibre and matrix: this process is often described as 'osmosis'. The usual method of coping with this is by the provision of a resin-rich layer at the surface.

Hart-Smith (1993) suggests that (for artificial fibre composites) a maximum fibre loading of 55 vol.% is used, noting that the weight saving effects achieved by higher fibre loadings are offset by the need for additional surface coatings to cover pin-hole surface porosity.

In the case of biocomposites, some degree of water ingress is in fact desirable. For biodegradation – the consumption of end-of-life articles by microorganisms – water is necessary. Observations by Mwaikambo (L Y Mwaikambo, 2007, personal communication) on the increase in biodegradation resulting from the addition of hemp fibre to thermoset cashew nut shell liquid resin mouldings illustrate this effect.

Thermoplastic biopolymers are usually, to a degree, water soluble. This fact can be exploited to provide a manufacturing route (Johnson *et al.*, 2007). The polymer is dissolved, and then mixed in solution with the reinforcing fibre. The mixture is then dried and hammer milled to a suitable size for further processing for example, by injection moulding. The method could also be applied to make long fibre pre-pregs.

8.7 Future trends

In general the current philosophy of production of biocomposite materials is based on the notion of taking large complex biological systems (e.g., the stem of a hemp plant or the trunk of a tree) and reducing it to some form of component parts – say a bast fibre, throwing away the unusable residue, then reorganising the material into a mat, and then binding the material back into an article by means of pressure and a resinous glue. Given the complexity of the process route, the consequent opportunities for fibre damage, and possible incompatibilities between fibre and resin, it is perhaps not surprising that the resulting materials are disappointing in terms of cost and performance.

This is at odds with the construction methods used in nature, where molecular assemblies form into composite materials from constituent components by processes that do not require too much in the way of external impetus. Natural composites neatly sidestep the main problems that beset existing artificial biocomposites, namely poor impact properties, and a degree of uncertainty in finished article physical properties. The process of reducing existing biocomposite structures to components by comminution, and then reassembling the components by traditional manufacturing techniques, is at best inelegant and at worst counterproductive in that the artificial biocomposites rarely outperform their precursor materials (for example, wood) as tough structures of least weight.

It is therefore to be expected that we will see developments in manufacturing biocomposite structures from the bottom-up, rather than the current top-down approach.

8.8 Sources of further information and advice

A recent review of applications of natural fibre composites is given by Bogoeva-Gaceva *et al.* (2007) in which there is some coverage of structural applications. Natural fibres are examined in detail by Gordon-Cook (2004).

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9

Natural-fibre–biodegradable polymer composites for packaging

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9.1 Introduction

In late 2006, the Food and Agricultural Organisation (FAO) of the United Nations declared 2009 as the International Year of Natural Fibres in order to raise consumer awareness and strengthen demand for natural-fibre-based products.[1] One area where natural fibres have scope for consideration is the packaging industry. Globally, the packaging sector accounts for approximately 40% of total plastics consumption, and results in an inexhaustible waste stream.[2] Legislation prompted by environmental reasons has begun to encourage the use of biodegradable polymers; however, the cost of these materials is still too high. Biodegradable polymers reinforced with natural fibres provide the next logical step in an effort to provide environmentally friendly cost-effective solutions for the packaging industry.

The main goals for the use of natural fibres in packaging are to provide additional stiffness and strength, minimise weight and reduce cost by lowering polymer content. In addition, when combined with biodegradable polymers, natural fibres allow the biodegradability of the packaging material to be maintained.

This chapter endeavours to identify the extent to which natural-fibre-based packaging is being utilised in industry at present and the potential future applications. It will in particular:

- identify biodegradable polymers used in packaging with the potential for natural-fibre reinforcement and the relevant natural fibres;
- review structural properties of biodegradable natural-fibre composites and other material property requirements relevant to the packaging industry; and finally
- review biodegradable natural-fibre composites which are in use already or are being developed and tested with packaging applications in mind.

9.1.1 What is packaging?

Packaging is the process of preparing an item for preservation, storage, transportation and display. The materials with which this is done depend on the category of packaging and the requirements of the item itself. In general, the packaging should:

- protect the item against physical and chemical damage;
- provide convenience during handling and transportation; and at the final stage
- encourage consumers to purchase the product.

9.1.2 Categories of packaging

Packaging materials can be broken up into three categories: primary, secondary and tertiary packaging.[3] Primary packaging materials are those that come into direct contact with, but can be separated from, the product, while secondary packaging is used for physical protection of the product. Tertiary packaging considers the storage and handling requirements of the product and its purpose is to protect against mechanical damage and weather conditions during transportation.[3] There are examples of the use of natural fibres in all three categories of packaging materials. For primary packaging, food trays and containers; secondary packaging, natural fibre incorporated loose fill foam and rigid packaging for non-food consumer items, for example electronics and tertiary, lightweight composite pallets and containers. Another special category of packaging materials is made up of edible coatings and films which do not facilitate the addition of natural fibres.

9.1.3 Materials for biodegradable packaging

Plastics used for packaging are very often used once and then discarded, creating an unending waste stream. In the past, efforts to reduce this waste focused on either the use of natural fibres in non-biodegradable polymers[4] or the use of biodegradable polymers. However, knowledge of these two types of biomaterials has evolved to a stage where they can start to be used together effectively.

The importance of biodegradable polymers for sustainable development is paramount. The harvest of precursor materials, manufacture, use, collection and composting of biodegradable plastics waste can become a yearly renewable cycle. Composting biopolymers can create much-needed carbon-rich soil, even helping to reduce the consumption of chemical fertilisers.[5]

The latest New Zealand national waste data report issued in 1997 shows that packaging contributes 10–14% of the total landfill waste. However, this figure includes all types of packaging materials, not only plastics.[6] In July 2004, as part of a general drive towards sustainable development, the Packaging Council of

Table 9.1 Consumption and recovery of packaging materials for 2007 and targets for 2008[8]

	Aluminium	Glass	Paper	Plastics	Steel	Total
Consumption (tonnes)	6270	208 240	336 500	156 359	21 340	728 709
Recovery (tonnes)	3900	109 860	256 200	34 891	12 245	417 096
Recovery/ consumption	62%	53%	76%	22%	57%	57%
2008 Targets	65%	55%	70%	23%	43%	

New Zealand and the Sustainable Industry Group brought together packaging brand owners, users, retailers, importers, recyclers and local governments to negotiate a New Zealand Packaging Accord. The accord is a voluntary industry and government initiative to make the use of packaging more sustainable.[7] The most recent report from the Packaging Council of New Zealand shows figures for the use and recovery of various packaging materials in New Zealand from 1994 to 2005, while the targets to be met by 2008 can also be found at the Packaging Council website.[8] Table 9.1 shows the use and recovery data for the latest year, 2007 along with 2008 targets.

The most interesting figure to note is the very low recovery rate of plastics compared with the other packaging materials. The reason for this is the problem of sorting. In order to recycle plastics, a pure stream of categorised waste must be achieved so that manufacturers have access to materials with properties equal to that of virgin plastics. However, manual sorting is very labour intensive and costly. Newer methods of automated sorting are currently in development but also pose a few technical problems such as the sorting of contaminated plastics or products that use a combination of polymers. Finally, even if recovery is achieved, it is often tricky to find an appropriate use for the recycled plastic.

Fortunately, current trends and legislation point towards the use of renewable, biodegradable polymers or natural fibres reinforcing biodegradable polymers for future packaging materials, with the aim of providing packaging solutions that not only meet consumer needs but also preserve the quality of our environment.

Biodegradable polymers

Degradation of polymers can take several different forms, including degradation resulting from the exposure to light, oxygen (oxidation), water (hydrolysis) or the action of enzymes, and chemical decomposition associated with living organisms, such as bacteria, fungi, etc., and their secretion products. The latter is defined as biodegradation where any metabolites released during degradation should be non-toxic to the environment and redistributed through the carbon, nitrogen and sulphur cycles. Organic material can be degraded aerobically (with oxygen), or anaerobically (without oxygen). There are four main degradation environments for polymers and polymer composites:

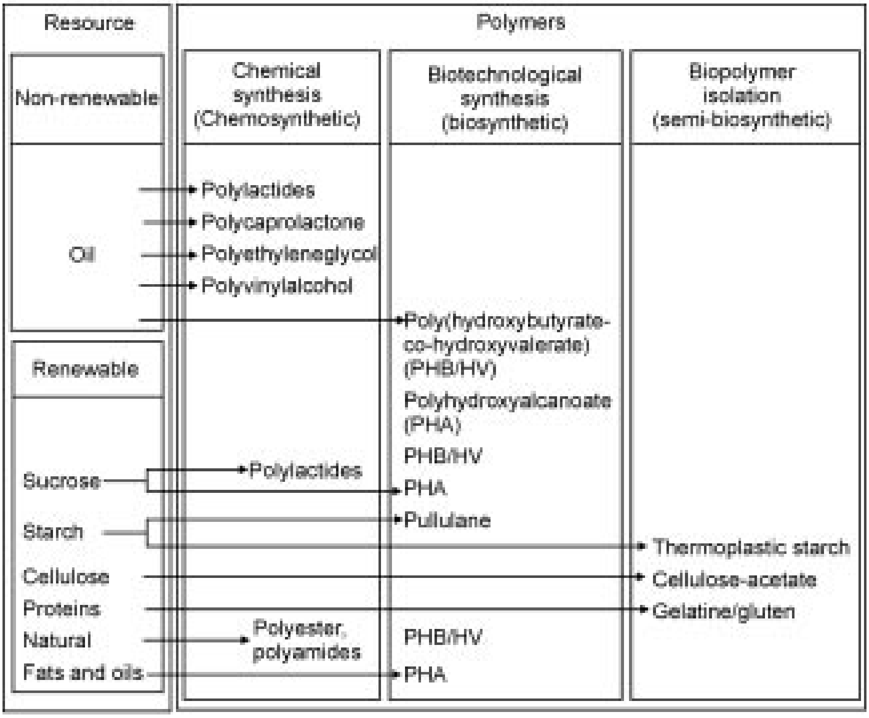
- soil;
- water;
- landfill; and
- compost.

Biodegradable polymers are classed as:[9,10]

- biosynthetic, e.g. poly-β-hydroxyalkanoates (PHAs);
- semi-biosynthetic, e.g. cellulose-acetate; or
- chemosynthetic, e.g. polylactides (PLAs).

Figure 9.1 illustrates the classification of biodegradable polymers and details the renewable or non-renewable resources from which they are derived.

It is important to note that not all polymers of biological origin (biopolymers) are easily biodegraded; an example of this is thermosets made from cashew nut shell liquid.[12] However, as can be seen from Fig. 9.1, some readily biodegrad-



9.1 Classification of biodegradable polymers and the resources from which they are derived (after Stapert *et al.*[11]).

able polymers are not from renewable resources. For a polymer to meet the requirements of sustainability, biodegradability and useful life cycle it should ideally:[11,12]

- be renewable and biological in origin;
- be degradable into non-toxic or usable products (e.g., water, carbon dioxide, ethanol, methane) and CO_2 neutral;
- be completely biodegraded at a predetermined rate by the end of its defined lifespan;
- be comparable in mechanical properties to common non-degradable polymers (e.g., polyethylene (PE), polypropylene (PP) and polystyrene (PS));
- be price competitive with common non-degradable polymers (e.g., PE, PP, PS); and
- have a lifespan appropriate to the application (e.g., resorbable medical products such as sutures, and short-term packaging applications).

Strictly speaking the term biodegradable must incorporate specified periods of time for these types of reactions to occur to certain levels. It should also consider disposal pathways to ensure biodegradation occurs safely and does not negatively impact the use of the end product resulting from disposal, for example the compost created or the water or air quality.[13] Over the past ten years a lot of effort has gone into developing international standards and test methods for measuring biodegradability, Bastioli[13] dedicates an entire chapter to this topic. In Europe, additional legislation (European Standard EN 13432, 2000) allows biopolymers to be marked with a 'compostable' symbol if they break down by 90% (without toxic effects on the compost) within 6 months. Polylactide (PLA) film under 20 μm is an example of this level of biodegradability.

Over the past 10–15 years a large number of bio-based polymers (biopolymers) have been in development and are now beginning to emerge as commercially viable replacements for commonly used consumer product polymers. However, to date, biopolymers have struggled to be price competitive with commodity polymers such as PE, PP and PS. Relatively low yield rates and demand have kept manufacturing rates low and hence prices high. This has limited the use of biopolymers to niche products, such as bioresorbable implants and sutures in medical applications. However, increasing environmental awareness, improved yields and manufacturing processes, as well as new legislation have seen an increasing focus on the use of biopolymers for applications such as polymer bags, food packaging, nappies and cosmetic containers. Recently Sainsbury's, a leading UK supermarket, announced that it will use biodegradable packaging for its house-brand foods and carrier bags. Cargill-Dow LLC, the company that produces the NatureWorks range of PLA, offers its high-quality PLA product in various grades suitable for injection moulding, extrusion/thermoforming, film and blow-moulding.

In addition to price, the degree of biodegradability in polymers often has a detrimental effect on performance characteristics such as strength, flexibility and brittleness. Therefore, both price and performance have been key drivers in the move towards biopolymer composites.

PHAs, PLAs and starch are commercially prevalent natural polymers that have been the focus of research into biopolymer composites. Table 9.2 presents some of the current commercially available PHAs, PLAs and starches (including blends) along with other synthetically produced biodegradable polymers and their manufacturers.

Natural fibres for composites

Natural fibres have been used throughout history for the production of commodity (paper, textiles and ropes) and decorative products (wall hangings, bags and jewellery). However, with the advent of low-cost synthetics, the conventional applications of natural fibres have greatly diminished.[15]

Interest in natural-fibre reinforced composites has grown with increasing awareness of the environmental impact of plastics and non-recyclable materials on landfill. Natural fibres are generally suitable for reinforcing both thermoset and thermoplastic polymers, making them suitable substitutes for glass fibres. The advantages associated with natural fibres include:[9,16–18]

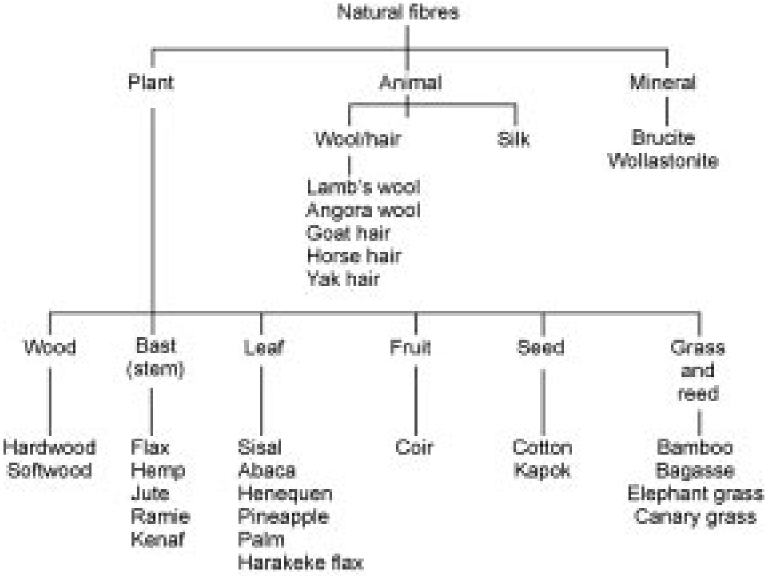
- low cost;
- abundantly available;
- sustainable;
- CO_2 neutral;
- low density;
- often have good specific strength properties;
- high toughness;
- low abrasion, and therefore tool wear;
- non-toxic;
- recyclable;
- biodegradable;
- good fibre–matrix adhesion with polar matrix materials; and
- low energy consumption.

The main drawbacks with natural fibres are:[9,16–19]

- inhomogeneous quality;
- thermal instability over ~200 °C, limiting the use of some thermoplastics; and
- hydrophilic nature:
  - can cause water absorption and associated problems, limiting the product applicability,
  - may cause bonding problems when using hydrophobic polymer matrices.

Table 9.2 Biodegradable polymer materials currently available in the market[3,9,10,12,14]

Polymer type	Manufacturer	Product name
Polyhydroxyalkanoates	Metabolix, Inc.	Biopol$^{\text{TM}}$, PHA
	Procter and Gamble	Nodax$^{\text{TM}}$
	Biomer	Biomer$^{\text{TM}}$
	Biomatera Inc.	
	PHB Industrial S/A	
Cellulose acetate	Courtaulds	
	Mazzucchelli	Bioceta
Polylactides	Cargill-Dow LLC	NatureWorks$^{\text{TM}}$
	Galactic SA	Galactic
	Birmingham Polymers, Inc.	Lactel, Absorbable
	Boehringer Ingelheim	Resomer®
	Mitsubishi Plastics, Inc	Ecoloju
	Mitsui	LACEA
	PURAC	Purasorb®
	Shimadzu Corporation	Lacty
	Hycail	
	Biomer	
Starches and starch blends	VTT Chemical Technology	Cohpol$^{\text{TM}}$
	BIOTECH GmbH	Bioplast®, Bioflex®, Biopur®
	Novamont	Mater-Bi
	Avebe	Paragon
	Earth Shell	Starch-based composite
	Bioplastic (Michigan)	Envar$^{\text{TM}}$
	Hayashibara	Pullulan
	National Starch	Eco-Foam®
	Groen Granulaat	Ecoplast
	Rodenburg Biopolymers	Solanyl
	Starch Tech	RenEW, ST1, ST2, ST3
	Supol	Supol
	Vegemat	Vegemat®
	Biop	Biopar
	Biochemical Labs	
Other biodegradable polymers based wholly on synthetics		
Copolyester	BASF	Ecoflex
	Eastmen Chemical	Eastar Bio
Polycaprolactone	Union Carbide	Tone polymer
Polybutylene succinate	Solvay	CAPA
	Showa Highpolymer	Bionolle
Polyesteramide	Bayer	BAK
Polyesterurethane	Bayer	MHP 9029
Polyester co-polymer	Bayer	Degranil VPSP42002
Polylactic acid	Fortum	
Polyester	Dupont	Biomax



9.2 Categories of natural fibres.

Natural fibres fall into three main categories depending on their origin (plant, animal, and mineral) as shown in Fig. 9.2.

However, natural-fibre composites are generally reinforced with plant fibres.[15] These vegetable or lignocellulosic fibres are generally classed into four categories, depending on which part of the plant they are extracted from.[15,19] Table 9.3 details the regions that produce the most common natural fibres for reinforcing composites. The production of cellulose-based fibres peaked in the early 1980s at approximately 3 million tonnes.[20] Since that time there has also been a regional shift in the production of natural fibres, with a decline in European-sourced fibres and increasing Asian production. In 2002, Asian production accounted for 69% of the global production of cellulosic fibres.[20]

9.1.4 Natural-fibre–biopolymer thermoplastic composite materials for packaging

The development of natural-fibre–biopolymer composites is the next step in providing fit-for-use, environmentally friendly consumer products with a reduced environmental footprint. Though a considerable body of work has been established, there are relatively few products commercially available, particularly in the packaging industry. However, wider adoption is being driven by the improved cost and availability of biopolymers, as well as by government legislation around landfilling and recycling.

Table 9.3 Production of natural-fibre types by region[21–24]

Fibre type	Production region
Sisal	Central and South America, Africa, Indonesia, West Indies, India
Henequen	Mexico
Abaca	Philippines, Malaysia, Uganda, Bolivia, Ecuador
Hemp	Serbia, Croatia, China, Philippines, Central Asia, Russian Federation, Ukraine, EU
Flax	Malaysia, EU, Canada, Argentina, Russian Federation, Ukraine, India
Ramie	China, Brazil, Thailand, Japan, USA, Honduras, Mauritius
Kenaf	Iraq, Tanzania, Jamaica, South Africa, Cuba, Togo, Thailand, India, North America, South America
Softwood kraft	EU, North America
Coir	India, Sri Lanka, Philippines, Malaysia
Bamboo	Asia, South America, India
Cotton	Southern parts of North America
Jute	India, China, Bangladesh, Egypt, Guyana, Jamaica, Ghana, Malawi, Sudan, Tanzania

It is difficult to compete with wood and cardboard in secondary and tertiary packaging applications; they are after all a form of natural-fibre composite themselves and are very recyclable and mostly biodegradable. Corrugated cardboard, for example, exhibits density values between 30 and 90 kg/m^3 in its packaging form and 180 and 300 kg/m^3 when compacted, while wood densities vary between 170 and 500 kg/m^3 in the case of balsa wood and pine.[25] In order to compete with these materials, natural-fibre composites need to show additional value while maintaining very low densities. This could be achieved by foaming the plastic; better resistance to water absorption could also be addressed if required. It is the ability to tailor the mechanical and chemical characteristics to the packaging requirements that is the main advantage of natural-fibre composites. In order for natural-fibre composites to be fully utilised in packaging, the concepts behind the design of packaging may need to be re-examined. Table 9.4 compares some of the properties required for packaging materials.

9.1.5 Processing of natural-fibre–biopolymer composites

As previously discussed on page 306, the main issues with processing any composite utilising natural fibres are thermal instability, inhomogeneous quality

Table 9.4 Comparative trends in properties of the existing types of packaging materials

Packaging material property	*Excellent*						*Poor*
Structural properties	Metals (aluminium, steel)	**Bioplastics/ biocomposites**	Plastics	Glass	Wood	Paper/board Moulded pulp	Textile
Manufacturability	Plastics	**Bioplastics/ biocomposites**	Paper/board Moulded pulp	Metals (aluminium, steel)	Glass	Textile	Wood
Barrier properties	Metals (aluminium, steel)	Glass	Plastics	**Bioplastics/ biocomposites**	Wood	Paper/board Moulded pulp	Textile
Environmentally friendly	**Bioplastics/ biocomposites**	Paper/board Moulded pulp	Wood	Metals (aluminium, steel)	Textile	Plastics	Glass
Non-structural functionality	Paper/board Moulded pulp	Plastics	**Bioplastics/ biocomposites**	Metals (aluminium, steel)	Wood	Glass	Textile
Light weight	Paper/board Moulded pulp	**Bioplastics/ biocomposites**	Textile	Plastics	Wood	Metals (aluminium, steel)	Glass

and their hydrophilic nature. Biopolymers with melt temperatures below 200 °C must be selected to minimise fibre degradation.

Various methods of preparing natural-fibre–biopolymer composites have been researched.[15,16,19,26–37] Fibre length determines to a great extent what methodologies are available. However, the general methods used are:

- sheetforming or compression moulding;
- extrusion;
- injection moulding; and
- filament winding.

Long fibres may be compression moulded or filament wound (if the fibres have been spun), and this maintains the lengths of the fibres. However, fibre attrition is significant in most extrusion and compounding processes, which often precede injection moulding. These are therefore not suitable if fibre length needs to be maintained.

In order to optimise fibre dispersion (particularly for extruded and injection moulded samples), there is often some form of mixing required before the final processing of specimens. Mixers, such as Brabender kneaders or extruders, are often used to do this, sometimes in series. However, the lack of compatibility between natural fibres and matrices often has more to do with differences in the polarity. Fibre and matrix modifications are often used with success to improve dispersion and fibre–matrix adhesion.[27]

Some methods of processing natural-fibre composites result in significant fibre attrition. In particular, specimens that undergo mixing followed by a granulation step before being injection moulded see significant fibre length reductions.[16,27] For example, Gatenholm *et al.*[27] found that in processing polyhydroxybutyrate (PHB) with cellulose, the fibre size reduction of cellulose was related to the reduction in molecular weight of the PHB. They proposed that chain scission of the PHB was occurring during processing; this resulted in the formation of crotonic acid, which hydrolysed the cellulose. The result was significant fibre attrition, but also improved fibre dispersion.

Owing to the hydrophilic nature of natural fibres, care must also be taken to dry the fibres before processing in order to optimise the mechanical properties. The reasons for this are twofold:

- Water reduces the strength of the fibre–matrix interface, acting as a separating agent[15]
- Water evaporates at 100 °C, causing voids in the composites.

Tensile strength and modulus improvements of 10% and 20%, respectively, have been achieved by maximally drying fibres.[15]

9.2 Structure and property issues related to the use of natural-fibre composites in packaging

9.2.1 Available test methods and standards

A large number of test methods exist for packaging materials. These range from general tests for compression strength of filled transport packaging to abrasion resistance testing of printed materials. For plastics, gas/barrier properties along with burst and tear strength are common, while corrugated board and paper board have their own long list of test methods. There are various companies[38–40] that specialise in the testing of packaging materials and provide the testing services shown in Table 9.5.

9.2.2 Categories of properties

Most of the test methods that are available for packaging materials are usually related to plastics or paper/paperboard since these materials are the most used (see Table 9.1 for consumption data). As a result, the use of natural-fibre composite materials may require the development of a combination of these test methods or newer composite materials-based test methods.

Structural

These test methods consider the structural properties of the packaging material under loading conditions specific to packaging applications. An interesting consideration is how natural-fibre composites rank compared with other packaging materials with regards to mechanical properties. Although com-

Table 9.5 Categories of tests for packaging materials

Category of test	Examples
Structural	Tensile properties, tear strength, bending stiffness, compression strength, edge crush resistance, burst strength, puncture resistance, folding endurance, wet strength, delamination
Degradability/compostability	Compost biodegradation tests, disintegration test, compost quality test
Barrier and absorption properties	Air permeability, water absorption, water vapour transmission rate
Manufacturability and manufacturing quality	Thickness uniformity, density uniformity, moisture content
Non-structural functionality	Abrasion resistance of printed materials, static and kinetic friction

parative data for properties such as tear strength and puncture resistance are unavailable, one can obtain a reasonable idea of the suitability for a particular application by comparing some typical structural properties.

Aside from the properties of the constituent materials, the mechanical properties of natural-fibre–biopolymer composites are dependent on fibre content, fibre orientation, interfacial bonding and the processing methodology by which they are formed. Table 9.6 details the mechanical properties of some key biocomposite materials.

There is a difference in the mechanical properties of biopolymers reinforced with natural fibres compared with synthetic polymers. In their review of cellulose-based composites, Bledzki and Gassan[15] state that most composites reinforced with unmodified natural fibres exhibit a reduction in tensile strength, and that the property attrition is proportional to increasing volume of fibres. However, this is not always the case for natural-fibre reinforced biopolymers.

For unidirectional fibre orientations, tensile properties of the composite in the longitudinal direction show significant improvements, with enhancements being proportional to increasing fibre mass fraction.[46,47,50] For example, 100–150% improvements in fibre-reinforced poly(hydroxybutyrate-co-hydroxylvalerate) (PHBV) tensile strength have been observed.[32,54] These composites are most often reinforced with long fibres, and are formed by compression moulding or filament winding. However, for unidirectional composites, properties in the transverse direction are often lower than those of the pure polymer and diminish with increasing fibre content.[32,34,45,54] For short fibre composites, and long fibre composites with a balanced laminate stacking sequence (i.e. 0/90/90/0), tensile modulus is usually enhanced.[26,27,35,36,41,48,52] Tensile strength is most often enhanced proportionately with increasing fibre content.[16,27,32,35,36,41,45,52] However, several studies have also found tensile strength to be diminished with the addition of fibres.[37,48,51,55] There have also been some studies where tensile properties increase up to an ‘optimum’ level of fibre addition, after which properties remain static or decline with increasing fibre content.[42,46]

Fibre inclusion also reduces the elongation to break of natural-fibre–biopolymer composites.[26,27,33,35] For composites with PHBV as the matrix, elongation at break and fibre pull-out increase proportionately with increasing percentages of hydroxylvalerate (HV).[27] Fibre modification can enhance bonding, and therefore mechanical properties, though not all treatments are effective.[56] Of note, Wollerdorfer and Bader[16] observed negligible improvements in PHBV reinforced with regenerated cellulose treated with Rokramar 3030.

Experimental results are usually lower than those predicted by the rule of mixtures and modifications thereof.[33,37] Additionally, the disparity usually increases with fibre content. This has been explained by the increase in voids at higher mass fractions, as well as lower interfacial shear strength (IFSS).[33] Lower IFSS limits the transfer of stress from the matrix to the fibre, and causes the disparity increase with increasing fibre mass fraction.

Table 9.6 Tensile properties of selected biopolymer composite materials

Composites	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Processing method
PHB–pineapple fibre (20wt% – 0/90/0 orientation)[32]	46.0	2.158	3.0	Compression moulding
Biopol™ – regenerated cellulose fibre (25 wt%)[16]	30.05			Twin-screw extrusion–injection moulding
Biopol™ – jute fibre (25 wt%)[16]	33.58			
Thermoplastic starch–flax (20 wt%)[16]	36.42			
Mater-Bi–Ramie (15 wt%)[16]	25.10			
Biopol™ – regenerated cellulose fibre (9.9 wt%–0 orientation)[34]	128	5.8	3.4	Compression moulding
Biopol™ – regenerated cellulose fibre (10.1 wt% – 90 orientation)[34]	11	1.6	1.4	
Biopol™ – regenerated cellulose fibre (26.5 wt% – 0 orientation)[34]	278	11.4	4.3	
Biopol™ – regenerated cellulose fibre (28 wt% – 90 orientation)[34]	3.3	1.2	0.1	
Biopol™ – straw (10 wt%)[26]	14	1.4	1.7	Mixing–compression moulding
Biopol™ – straw (30 wt%)[26]	14	1.7	1.4	
Thermoplastic starch–wood-fibre (16 wt%)[35]	11	0.32	11	
Soy protein isolate – Ramie (20 wt%)[37]	17	0.55	10	
PHB–cellulose (40%)[27]		6.21	1.07	Brabender extrusion–injection moulding
PHB/15%HV–cellulose (40%)[27]		4.14	1.75	
PES–bamboo (28%)[36]	85.5	8.5		Compression moulding
PLA–cellulose (30 wt%)[41]	68.69	4.65		Extrusion–injection moulding

BAK 1095–jute (32 wt% – alkali modified fibres)[42]	35.8			Compression moulding
Soy flour and BAK 1095-pineapple fibres (30 wt%)[43]	∼30	∼3.75	1.18	Extrusion–injection moulding
Glutaraldehyde modified soy protein concentrate–flax fabric (45 wt%) [warp direction][44]	50.3	1.01	21.0	Compression moulding
Glutaraldehyde and PVA modified soy protein concentrate–flax yarn (45 wt%) (longitudinal)[45]	126	2.24	11.6%	
TPS–flax fibre (40 wt%) (longitudinal)[46]	73 ± 3	5.9 ± 0.6		Compression moulding
TPS–flax fibre (40 wt %) (transverse)[46]	53 ± 5	4.5 ± 0.5		
Glutaraldehyde-modified soy flour–flax yarn (60 wt%) (longitudinal)[47]	259.5	3.71		
PLA–flax fibres (30 wt%)[48]	53 ± 3.1	8.3 ± 0.6	1.0 ± 0.2	Extrusion–compression moulding
Phytagel® modified (20%) soy protein isolate–flax yarn (45 wt%)[49]	220.2 ± 28.5	4.11 ± 0.16	7.5 ± 0.7	Compression moulding
GA and PVA modified soy protein concentrate–flax yarn (45 wt%) (longitudinal)[50]	125	2.25		Compression moulding
PHB–flax (20%)[51]	22.9	3.621	4.63	Extrusion–injection moulding
PLA–flax (20%)[51]	64.4	6.197	6.21	
Mater-Bi Z (TPS)–flax cellulose pulp fibres (40 wt%)[52]	21.0	1.736		
PHBV–lyocell (63.2 wt%)[53]	108.8	2.46	10.6	Compression moulding
PLA–lyocell (62.1%)[53]	100.5	5.55	6.4	

Effects of ageing

Ageing experiments, including water absorption, accelerated weathering and physical ageing (usually utilising storage trials), are used to determine the likely usefulness of composites in commercial applications. Physical ageing of solid thermoplastic materials generally results in hardness and brittleness increasing proportionately with time. During ageing, the amorphous regions of the semicrystalline polymer move towards a denser equilibrium packing state.[57] This denser packing of the amorphous region inhibits chain motion, creating the harder, more brittle material.

PHB and its copolymer PHBV undergo an ageing process at room temperature.[58–60] Over days or weeks the polymer became increasingly brittle, evidenced by increasing tensile strength and modulus, and a reduction in elongation at break and impact strength. De Koning and Lemstra[60] showed that the embrittlement levels off after 150 days. However, they also demonstrated that this embrittlement is not solely due to physical ageing because it is not reversible once the sample is again heated above the glass transition temperature. PHBV undergoes a process of secondary crystallisation; however, this occurs over a relatively short timeframe (days) and does not fully account for the embrittlement seen over the extended (150 days) timeframe.

Effects of water absorption

Water absorption experiments are most often conducted to verify the effectiveness of fibre modification techniques for natural fibres. Some research has been conducted on the water absorption of natural-fibre–biopolymer composites.[61] A large number of studies have also been conducted on natural-fibre–synthetic polymer composites,[62–66] and comparisons can be drawn from the observations of similar experiments and the ageing mechanisms described.

Curvelo *et al.*[35] investigated the water absorption of *Eucalyptus* pulp–thermoplastic starch composites stored at 25 ºC and 100% humidity. It was found that the addition of fibres actually decreased the water absorption (almost 50%) compared with the polymer alone. This was attributed to the fact that starch is more hydrophilic than cellulose. In addition, they hypothesised that the fibres absorb some of the glycerin from the matrix, which is a plasticiser, but also enhances water uptake. These two factors combined to reduce the water absorbency of the composite compared to the polymer. Although this is a natural-fibre–biopolymer composite, it can be seen that these results are not particularly useful for drawing conclusions about non-starch biopolymer composites. However, they do serve to highlight one of the key problems of starch-based composites.

Joseph *et al.*[63] conducted two types of weathering tests on sisal–low-density polyethylene (LDPE) composites, some of which had fibres modified with toluene diisocyanate. Prior to ageing, the tensile strength of the composites increased proportionately with fibre mass fraction, with the treated fibres clearly enhancing performance. The first weathering test involved boiling samples for 7 h under atmospheric pressure. In all cases the mechanical properties decreased with increasing exposure time. Composites with untreated fibres experienced higher losses of tensile strength than those with treated fibres. Of significant interest was that after 7 h exposure to boiling water, the untreated sisal–LDPE composites had similar tensile strengths, irrespective of fibre loading. In contrast, the modified sisal–LDPE composites showed good retention of tensile strength, which still increased with fibre loading. This clearly showed that modification of the fibres minimised water absorption. The second weathering test kept sisal–LDPE composites at 80 °C for 7 days. After 12 h exposure, it was found that tensile strength increased, and this was attributed to annealing. However, after 7 days, the mechanical properties for both the treated and untreated composites were inferior to the unaged specimens. The attrition of mechanical properties was attributed to decomposition of volatile extractives in the fibres, causing voids at the interface, resulting in poor adhesion and tensile performance.

Biodegradation and compostability

A large focus in the packaging industry has been placed on biodegradability or compostability, especially since these materials have a very short useful life relative to the actual products. The maximum acceptable timeframe for biodegradation is usually 6 months.[13] Composting time for a biodegradable polymer such as PLA is typically 0.5–1.5 months; however, it is important to note that degradation is also dependent on particle size. Four to six months composting time is typical for particle sizes commonly used in packaging applications and would be a feature considered during the design of the packaging.[3] The biodegradation rate of composites is dependent on several factors:

- biodegradability of the constituent materials;
- fibre content;
- interface; and
- degradation environment.

Mohanty *et al.*[54] investigated the degradation of Biopol™ and jute–fabric Biopol™ composites in compost. After 150 days Biopol lost 34% mass, while 15 wt% hessian cloth (jute) reinforced lost between 34% and 56% mass, depending on the fibre surface modification. The largest mass loss, 56%, was observed for dewaxed fibres, which had the weakest interfacial bonding. Surface modification also affected the biodegradation of jute–BAK 1095 composites in compost, with 5–10% mass loss being observed after 15 days.[42] Similarly, Peterson *et al.*[18] found that wood fibre–PHBV composites degraded faster than PHBV during incubation in sewage-amended soil at 40 °C for 5 weeks. In this research, the rate of degradation was examined using specimens of varying fibre mass fraction. The effect of sewage content was also examined. The study, which considers fibre mass fractions between 0 and 25%, shows the greatest rate of degradation for a fibre mass fraction of 25%. It is concluded that the addition of the natural fibres actually encourages biodegradation of the polymer by allowing access pathways for microorganisms, particularly at the fibre–matrix interface along the length of the fibres. This has also been observed by other researchers such as Keller *et al.*[67] Varying the amount of sewage-amended soil was seen to have little effect.[68] The significance of this is that natural fibres could be used to provide a kind of timing mechanism for biodegradation.

In contrast, Avella *et al.*[26] found no discernible difference between the degradability of PHBV and wheat straw–PHBV composites using either modified Sturm tests, or soil burial tests. Further tests in compost showed that PHBV and 10 wt% straw–PHBV composites degraded similarly, and significantly after 36 days. However, 20 wt% and 30 wt% straw–PHBV composites degraded to a lesser, but similar, degree after 67 days. The higher mass fractions were observed to degrade more 'homogeneously' than the 10 wt% fibre composites. It was also suggested that the lower mass loss may be attributable to higher fibre contents, since lignin requires fungi to degrade, which are not favoured in compost conditions.

Barrier properties

Another important issue related to degradability is the degradation of the packaged item itself. In most cases, food degradation is caused by permeation of gases, bacteria or water vapour into or out of the food product through the packaging material. Natural fibres themselves do not have very good barrier properties; therefore it is unlikely that they will improve barrier properties of the material to which they are added. However, to minimise the loss in barrier properties care must be taken to ensure good bonding between the fibres and the polymer in order to minimise air gaps, allowing easy permeation pathways.

9.3 Applications

9.3.1 Currently available materials and applications

Tetrapak

Tetrapak's packaging solutions, the tetra brik aseptic and its other arrays of cartons, are a prime example of successfully implemented use of natural-fibre composites for packaging applications. This packaging material uses a laminate of three materials: high-quality paperboard (75%), polyethylene (20%) and aluminium (5%).[69] The composite contains a total of six layers; from the inside, two layers of polyethylene, an ultra-thin layer of aluminium foil to provide a barrier against light and oxygen, a layer of paperboard for stiffness and strength and a final layer of polyethylene to keep the exterior dry. Recently, the Swedish-based company has produced microwaveable versions of its products by replacing the aluminium layer with polyethylene terephthalic silicon oxide which provides good barrier properties to oxygen and keeps the product it holds well preserved.[69] It is likely that in the near future, copolymers of biodegradable plastics including PLA and PHA (which have much better oxygen barrier properties than polyethylene[3]) could be used to add a biodegradable edge to this already successful natural-fibre packaging product.

PPM100 & 200 from Biosphere Industries

Another product already available on the market is the range of packaging solutions from Biosphere Industries. The products are a type of rigid foam made from starches such as tapioca and potatoes and a small percentage of grass fibres.[70] Along with being ovenable and microwaveable, they are also edible and can even be scented and flavoured.[70] The products have been targeted for applications such as fast food service packs, fresh meat, fish and poultry trays. Two grades of the material currently exist. PPM100 grade is targeted towards dry consumer items and low-moisture food products such as packaging for batteries, cell phones, toys and dry foods including fruit. The other grade, PPM200, is geared towards elevated moisture food products such as coffee, cold beverages, soups, meat, noodle and pasta dishes. Both grades of product are fully microwave, oven and freezer compatible and biodegrade 98% in 28 days and 100% in less than 40 days; see Fig. 9.3.

9.3 Applications for Biosphere Industries PPM100/200 products (courtesy of Biosphere Industries).[70]

Earthcycle palm fibre packaging

Earthcycle has produced a packaging solution that utilises palm fibres, a waste product discarded when the palm fruit is harvested throughout the year for its oil to make food items and cosmetics. The fibre itself has natural water repellent properties due to the natural wax present in the fibres, but is mixed with food-grade additives to further increase its water and oil repellency and forms a pulp which is processed into containers suitable for fresh fruit and vegetable packaging solutions as shown in Fig. 9.4. The long strands of palm fibres also make the material strong and durable. After its useful life, the non-genetically modified material is biodegradable and compostable (according to ASTM D6400) and decomposes into an organic soil component called humus after less than 90 days.

9.3.2 Research

Natural fibres for biodegradable loose fill packaging

The use of natural fibres as reinforcing agents in biodegradable foamed packaging materials is one research area of particular interest. There are, however, only a limited number of studies available which consider this possibility. In one article by Carr *et al.*,[72] the addition of short cassava fibres or wheat fibres (1%, 2% and 3%) on the mechanical properties of cassava starch foams is investigated. The results show that the starch foam containing 1% of fibres had the greatest compression strength after which the addition of further fibres exhibits a decrease. A similar result is observed for flexibility where the addition of more than 2% fibres decreases the flexibility of the foam. The decrease in properties is attributed to non-homogeneity of fibre distribution within the foam. In another

9.4 Applications for Earthcycle's Palm Fibre Packaging Solutions (courtesy of Earthcycle).[71]

study by Ganjyal *et al.*[73] corn stalk fibres were used in mass fractions up to 14%. Again, enhanced mechanical properties were observed up to 10%, after which an increase in density and decrease in expansion ratio occur. Non-uniformity and poor fibre distribution are again highlighted as the reason for poor mechanical properties with higher fibre content.

Sheet formability studies

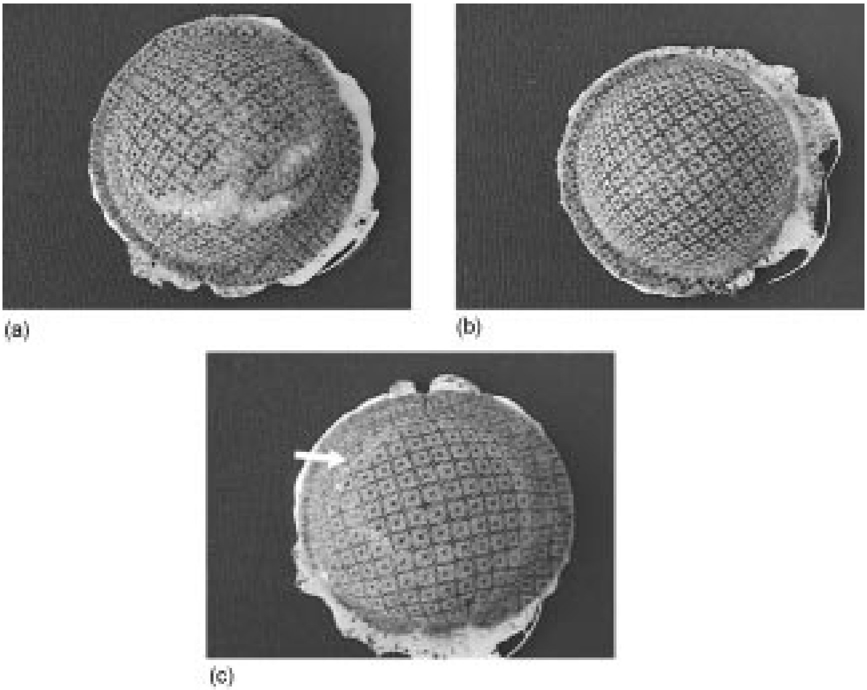
The inclusion of fibres also has a significant effect on sheet formability. Sheet forming is a widely used forming method for a large variety of consumer products packaging quite often requiring double curvature shapes. The research done by Peterson[18] investigates the sheet formability of one type of biodegradable composite, wood-fibre–Biopol™ using matched-die (with and without vacuum) and air-pressure dome-forming. Matched-die consists of a male punch/stamper (able to move vertically), which pushes the heated blank into a matching female hemispherical dome shaped cavity. For air-pressure forming, the heated blank is held between deformable diaphragms (usually under vacuum), and air instead of a male die, forces the blank to conform to the female cavity. The forming of domes, despite the relatively simplistic hemispherical shape, requires double curvature deformation and is often the starting point for an investigation into the three-dimensional forming behaviour of composite materials.

Matched-die thermoforming

One of the most significant findings of this work was the inability to form wood-fibre–Biopol™ composites within the thermoforming range of 110–160 °C. In all cases, for the 20 wt% fibre composite, where the forming temperature was below the melting point (160 °C) fracture occurred in the dome. Changing the forming rate, forming temperature and die temperature seemed to have no obvious effect on the resulting dome. Once forming was undertaken above the melting point, 160 °C (163 ± 2 °C) there were no further fracture problems. In order to maintain the blank temperature above the melting point, the die temperature also had to be 160 °C or above.

Effect of fibre mass fraction on matched-die thermoforming

From this investigation it was found that Biopol™, on its own, did not form very good domes. With the addition of wood-fibres, the resulting composite material thermoformed significantly better using the matched-die apparatus. The composite domes had a much more consistent thickness distribution for the finished product. It is believed that the addition of wood-fibres helped to maintain the integrity of the blank, and dome during the forming process.

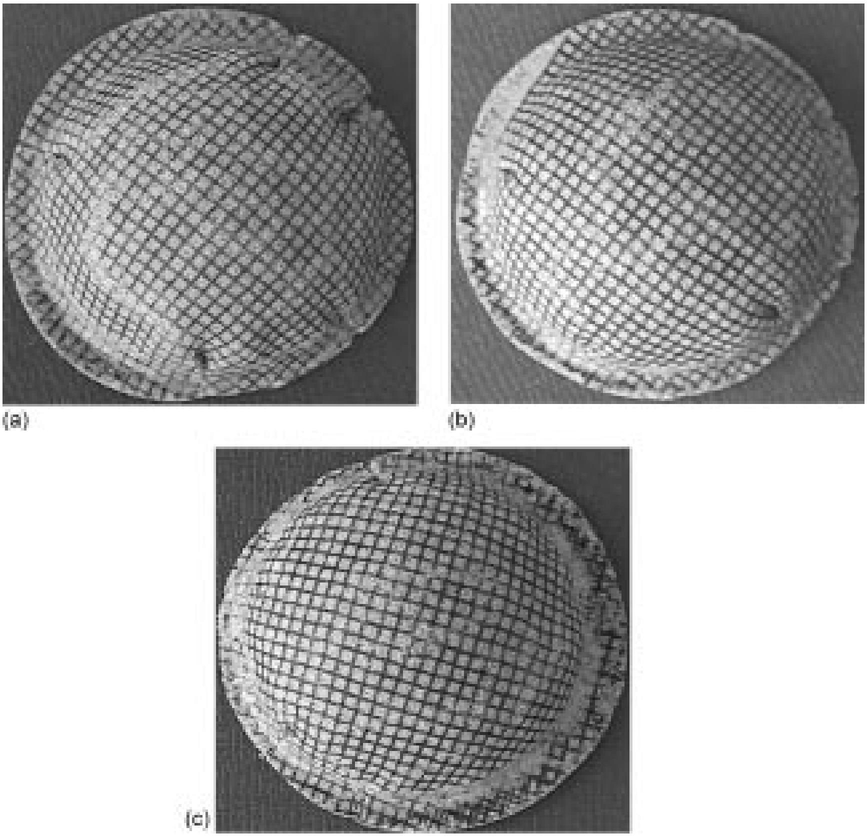


9.5 10 wt% matched-die thermoforming specimens, formed at various cross-head speeds. Preheat temperature 170 °C, thermoforming temperature 165 °C, die temperature 163 °C: (a) 20 mm/min; (b) and (c) 40 mm/min.

The forming of 10 wt% fibre composites at 20 mm/min resulted in failure by fibre pullout in the dome wall, as seen in Fig. 9.5(a). However, when the forming rate was increased to 40 mm/min, the domes formed a lot better. Figure 9.5(b) shows a perfectly formed 10 wt% fibre composite dome. Some domes formed at 40 mm/min did show early signs of fracture beginning to occur in walls as highlighted by the arrow in Fig. 9.5(c); also, squeeze-out was observed in all cases for domes with 10 wt% of fibres.

Figure 9.6 shows examples of domes containing 20 wt% wood-fibres. Of note is that with each successive forming rate increase (doubling each time), the occurrence of wrinkles diminishes. There is, however, a limit to the benefit of increasing forming rate. High forming rates result in greater thinning at the dome apex, and this is not desirable in a thermoformed product, where consistent product thickness is preferable.

Once the fibre mass fraction reaches 25 wt% and above, the ability to produce good domes without significant buckling or fracture diminishes. A less than perfect surface finish was also observed on domes containing fibre mass fraction above 25 wt% formed at any rate. The problem was thought to be a result of the



9.6 20 wt% matched-die thermoforming specimens, formed at various crosshead speeds. Preheat temperature 170 °C, thermoforming temperature 165 °C, die temperature 163 °C: (a) 10 mm/min; (b) 20 mm/min; and (c) 40 mm/min.

higher residual stresses induced by the higher pressure required to manufacture the preform sheets.

At 20 mm/min forming rates, the composites buckled and started to impinge on the ability of the composite to form a true dome shape. When formed at 40 mm/min, the 25–35 wt% fibre composites fractured in every trial. Therefore, it may be concluded that wood-fibre–Biopol^{TM} composites above 25 wt% fibre fraction are not able to be dome-formed to a sufficient standard.

The analysis of the effect of fibre mass fraction on 3D curvature forming performance of wood-fibre–Biopol^{TM} using matched-die forming showed that there appears to be an optimum mass percentage of fibres for obtaining the best double curvature components, and this was found to be between 15 and 20 wt%. Domes formed in this range are very good, as evidenced in Figs 9.5 and 9.6, while domes manufactured from 10 wt% tended to fracture, and buckling and fracture occurred in domes with 25 wt% and above. In all cases, manufacturing at the higher forming rate (40 mm/min) produced the better dome.

9.4 Future trends

9.4.1 Challenges facing natural-fibre composites in packaging

Cost and consumer acceptance

Natural fibres are a relatively cheap bio-based material; wood-fibre is approximately 10 cents per kilogram in comparison with 5–50 US$/kg at the present introductory stage for many biodegradable polymers.[3] However, this is expected to drop to 1–10 US$/kg in the future, which is in the range of current highly utilised commercial polymers such as polypropylene and polyethylene, as producers of these materials increase their output capacities. In any case, the addition of natural fibres has very good potential to reduce the cost at the raw material level. However, the processing cost is where the addition of natural fibres incur their greatest cost factor. If the sum of the material and processing costs exceeds that of current plastics then there would be no incentive to use natural fibres. Consumers' points of view and whether they are willing to accept the technology depends a lot on education and marketing.

New technologies

Two rapidly advancing areas in composites research over the past decade have been the development of natural-fibre composites and micro- and nanocomposite materials. In a marriage of these two research areas, work involving the use of cellulosic whiskers derived from wood, cotton or sugar beet pulp,[74] as a reinforcement material for plastics or even bioplastics such as starch[75] has evolved. However, this may be too high-tech for use in present-day packaging applications, as potential uses cited involve applications such as security paper and reinforcing agents for low-thickness polymer electrolytes for lithium batteries.[74]

9.5 Summary

The packaging sector is the largest consumer of plastics in the different regions of the world. Plastic products used for packaging are often discarded after a single use, resulting in a never-ending supply of waste polymeric materials. Recovery rates of plastics from the waste stream are very low owing to problems associated with sorting the various types, the presence of contamination, and the presence of products consisting of combinations of polymers. Therefore, it is sensible to consider the use of biodegradable polymers for packaging applications.

Natural fibres come from renewable resources and are relatively inexpensive. While their tensile strengths and moduli are generally inferior to those of synthetic fibres, they often exhibit significantly larger elongation, giving them better damage tolerance. The addition of natural fibres to reinforce biodegradable polymers will impart additional stiffness and strength to the resulting packaging materials and allow for the complete biodegradability of these materials.

Biopolymer–natural-fibre composite may not suit all areas of packaging, but there are areas where it can compete. Current trends in packaging are directed towards the use of materials such as grass fibre-starch and palm fibre-food additives. The development of more such environmentally friendly materials for packaging applications is crucial. However, it should be pointed out that the addition of natural fibres to biodegradable polymers should render the resulting packaging materials viable in the areas of mechanical properties, manufacturability and economics for any serious changes to occur in the packaging sector.

9.6 Acknowledgements

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10

Opportunities for using wood and biofibers for energy, chemical feedstocks, and structural applications

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10.1 Introduction

Other chapters in this book outline many exciting new opportunities for creating enhanced performance and high-value products from wood, forest residues, and other bio-based materials. In addition to traditional value-added products, such as lumber, paper, and composites, exciting new opportunities are on the horizon for biorefining to produce electricity, transportation fuels, chemical feedstocks, and cellulose nanofibers. Cellulose nanofibers, a residual from the biorefining process, will be used to manufacture innovative high-strength biocomposites necessary for advanced structures. This chapter describes '*integrated biomass technologies*', a systematic approach for maximizing value, performance, resource sustainability, and profitability in the agriculture and forest products industries. The fundamental principles of *integrated biomass technologies* provide a global roadmap to a bio-based economy based on the systematic use of many less-desirable lignocellulosic resources to produce liquid biofuels and chemical feedstocks, advanced biocomposites, and advanced structures. This switch in approach to meeting user needs will lead to a bio-based society using sustainable technologies rather than a society based on the use of non-renewable, non-sustainable resources.

Globally, a vast lignocellulosic resource (biomass) is available for industrial use, but everyone needs to recognize that it must be used in a systematic and sustainable manner. This lignocellulosic resource includes small-diameter timber, forest residues (i.e., tree tops, branches, and leaves), high-yield plantation-grown timber (e.g., hybrid poplar), invasive species (e.g., salt-cedar, one-seed western juniper, and eastern red cedar), recycled paper, lumber and composites, and both woody and agricultural crop residues.

Integrated biomass technologies allow industry to (1) adapt to ever-changing forest and lignocellulosic feedstocks, (2) use market-driven models to determine the best use of resources on the basis of current market prices for various commodities, (3) modify production of chemical feedstocks, transportation fuels, and advanced products in accordance with these models, (4) adjust raw materials and manufacturing processes to maximize process and product performance, (5) develop new markets for innovative products, and (6) ensure that products meet structural, fire, and durability requirements for residential and commercial structures. *Integrated biomass technologies* also help forest and land managers improve forest health by working collaboratively with industry to remove less-desirable biomass and thereby offset the costs associated with efforts to restore damaged ecosystems. This further promotes sustainable forest management practices while simultaneously promoting the production and use of environmentally sensitive value-added products.

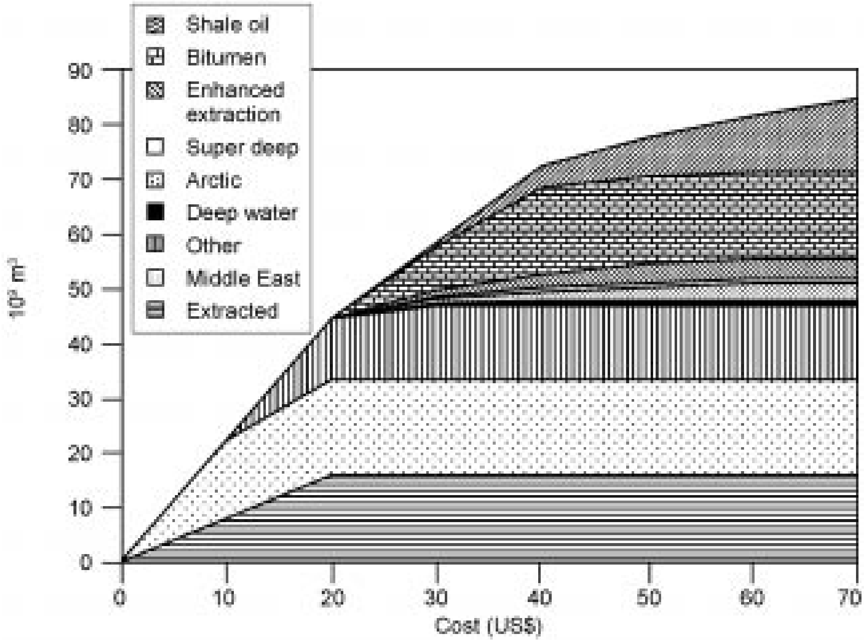
10.2 Biorefining

Biorefining is the first step in applying an *integrated biomass technologies* approach. Biorefining encompasses the use of all components of biomass to yield products, such as liquid transportation fuels, chemical feedstocks, and energy. In this section we will review the background leading to the current state of forests in North America, the fluctuations of oil prices over the past 50 years, and explore opportunities for producing transportation fuels from biomass. Biorefineries offer the potential for offsetting the cost of forest management, decreasing dependence on fossil fuels, and mitigating greenhouse gases. Fuels derived from biomass are generally regarded as greenhouse gas neutral because the amount of CO_2 released on combustion equals the amount absorbed from the atmosphere and sequestered by the plant through photosynthesis. As international concerns over global warming and greenhouse gas generation rise, government support for fuels from biomass is increasing and may give more confidence for investment in biomaterials for energy. This is an exciting time as many scientific, social, natural resource, political, and economic considerations seem to be aligning to create an environment for producing transportation fuel, chemical feedstocks, and advanced biocomposite products from biomass.

10.2.1 Past and future of petroleum

The invention of a practical internal combustion engine by Nikolaus Otto and Gottlieb Daimler in 1876 can be considered the start of the petroleum age. More than any other devices, gasoline and diesel engines have created demand for liquid fuels. Since then, every time there has been a shortage of petroleum, there have been efforts to produce ethanol from biomass. Increased demand and disruption of the supply chain created interest during the First and Second World Wars, the formation of the Organization of Petroleum Exporting Countries (OPEC) and ensuing oil embargo of 1975, and most recently, the increase in demand in Asia with supply disruptions from wars in the Middle East, all caused an increase in activity on use of biomass for energy. Unique among new incentives to develop biomass sources of energy is the current concern over global warming.

In addition to variable demand, there have long been concerns over fossil fuel reserves. The history of petroleum extraction is one of discovery and depletion. Many original oil fields were discovered because of oil leaking to the surface and most of these have long since been exhausted. By evaluating the various sources of data available on known oil reserves, a vision emerges of future supply. Known reserves continue to increase as supply companies get better at finding new oil fields and in developing new capability for extracting petroleum from deeper wells and more formidable environments. But many of these sources require higher costs to develop and only become profitable with sustained high prices (Fig. 10.1). The most recent statistics from the Energy Information Administration indicate that known reserves increased by 1% between 2006 and 2007 but production rose by just 0.035% between 2005 and 2006.[2] This difference probably reflects the increased extraction costs associated with many new reserve supplies. Still, it does not appear that the world will run out of oil in the near future. As prices rise, other sources of petroleum will become cost competitive. Considerable quantities of oil are available in heavy bitumen and oil shale. These are considered profitable at around US$25 per barrel for existing production capacity, and about US$50 per barrel for new



10.1 Price versus availability of various crude oil reserves from different sources.[1]

capacity. Stable long-term pricing of crude oil at US$40–50/barrel will also facilitate development of alternate sources for transportation fuels. Recent price increases offer a unique opportunity to forestry and bio-based fuels industries.

The US National Renewable Energy Laboratory (NREL) has several production estimates for cellulosic ethanol. These estimates generally show profitability when oil costs between US$46 and US$60 per barrel. By comparison, the cost of ethanol from corn is US$52/barrel at current (2007) corn pricing. Although current crude oil prices are near US$50/barrel, investing in facilities to produce ethanol from biomass is tempered by concerns over a return to lower oil prices.

10.3 Energy from biomass

The concept of the forest as a source of energy and chemicals is not new. Since humans first harnessed fire, wood, and other lignocellulosic biomass it has been a source of heat, light, and power. Before petroleum and petroleum-based chemistries became commonplace, wood and biomass were the primary source of chemicals providing methanol, and acetic acid by destructive distillation, turpentine by steam distillation, and pine tar, rosin, and rubber extracted by wounding trees. With industrial advances, larger quantities and more concentrated sources of energy were required, and thus petroleum and coal largely displaced wood. Although firewood is still important in some less-developed countries, in most developed countries it is used only for residential wood stoves and, to some extent, for commercial electrical power generation. The primary use for wood is as a raw material for furniture and building products.

Once again the increased cost of fossil fuels has renewed interest in using lignocellulosics from wood and natural biofiber materials for production of both transportation fuels and chemical feedstocks. Processes for converting wood and other biomass resources into liquid fuels and chemical feedstock are now once again becoming cost competitive. One exciting ongoing development is the growing interest in development of chemical feedstocks for making bio-based plastics. This work now includes several commercial applications using bioplastics as binders for biodegradable thermoplastic composite products. Other developments include the use of bio-based resins to replace thermoset adhesives for engineered composites and paper, or extracted resins for imparting moisture or decay resistance to non-durable wood and biocomposites.

One of the primary tenants of biorefining is the conversion of biomass to energy. The forest products industry in the United States uses almost 90 million dry tonnes of wood waste annually for energy. These companies have begun installing wood waste gasifiers to convert additional biomass. The gas resulting from this thermal decomposition, especially in wood gasifier technology, is called ‘product gas’ and it can replace natural gas. There is also renewed interest in production of ethanol and other chemicals from wood. The agricultural industry already produces ethanol from corn and has intense interests in both gasification and fermentation processes to make use of the agricultural residuals. At present, the only commercial processes are fermentation of corn kernels to produce ethanol and esterification of crop oils for diesel fuel. The corn ethanol industry continues to expand and in 2006 consumed about 15% of the total US corn crop. To meet increased demand for ethanol, alternate sources of biomass will become necessary and materials such as corn stover, wheat straw, and wood are considered likely alternatives.

The US Department of Agriculture estimates that 325 million dry tonnes of wood are available in the United States on an annual basis and could be used for the production of energy.[3] Another 540 million dry tonnes of agricultural residuals can be harvested without reducing the productivity of agricultural land. The cost and uncertainty associated with delivering this material to commercial biorefineries are major factors that determine economic feasibility. For typical biorefinery models, raw material costs are projected to be greater than 50% of total operating costs. Many site-specific factors determine the delivered price, including road infrastructure, transportation method, harvesting costs, and the quality, quantity, and type of material available.

10.4 Chemical and biochemical methods for producing fuels from biomass

There are two major routes for producing chemicals and liquid fuels from biomass. The wood can be processed into sugars using chemical and biochemical methods and the sugars are subsequently fermented to ethanol or, the wood can be converted thermochemically to pyrolysis oil or product gas and these intermediates further processed to provide liquid fuels or electricity.

Increasing the yield of ethanol from wood and other cellulosic materials has been a goal of researchers for many years. Fundamental research on the kinetics of hemicellulose and cellulose hydrolysis led to the ‘trickle-bed dilute-acid saccharification process’ in 1945. It became the standard for chemical saccharification processes and was capable of providing enough sugar to produce 266 liters of ethanol per tonne of wood. This process[4] was implemented in a commercial-scale facility in Oregon during the Second World War. However, the project was abandoned before the plant was completed when the war ended. This concept became the basis for the US Department of Energy (DOE) research on ‘dilute-acid hydrolysis’ at Oak Ridge (Tennessee) and the National Renewable Energy Laboratory (NREL) at Golden, Colorado. Today, the DOE has largely abandoned this approach in favor of ‘enzymatic saccharification’. The bulk of the research throughout the 1980s and 1990s replaced the second stage of acid hydrolysis with enzymatic saccharification. Enzyme manufacturers have had considerable success in accelerating the saccharification process and reducing the costs of the enzymes, but these successes have yet to translate into improved ethanol yields or commercial processes.

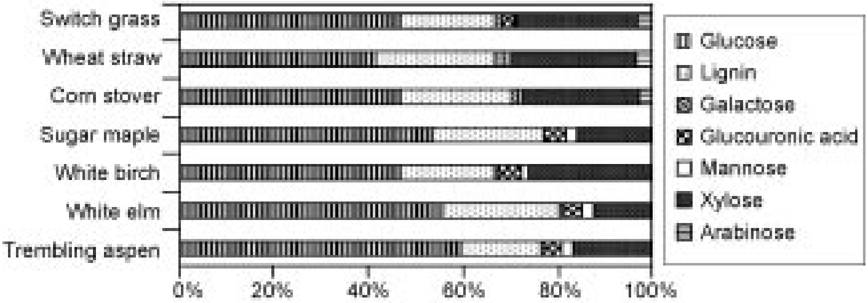
10.4.1 Enzymatic fermentation

Hardwoods and many agricultural residuals are rich in five carbon sugars or pentoses (xylose, arabanose). Xylose is a particularly abundant sugar in the hemicellulose of hardwood species (from 12% to 26%) and many grasses (Fig. 10.2). Xylose and arabinose are considerably harder to ferment than glucose and the other six carbon sugars and research continues on developing more robust organisms to improve conversion.

There is much less xylose obtained in hydrolysis of softwoods (6.6%), but considerably more mannose (10%) and the galactose and arabinose combine for another 5%.[8] Six-carbon hemicellulose sugars such as galactose and mannose are fermented by common brewer's yeast *Saccharomyces cerevisiae*, with rates and yields with mannose approaching that obtained with glucose. Pretreatment processes to remove hemicellulose can recover 50% to 90% of the available hemicellulose sugars in both hardwoods and softwoods.

10.4.2 Thermochemical methods

Thermochemical methods involve heating biomass under controlled conditions. In general, they include gasification or pyrolysis, two processes in which the target product is a gas or a liquid fuel, respectively. In either process, the goal is to convert complex heterogeneous biomass to simple chemicals. Rapid heating of wood in an oxygen-depleted environment forms gases, liquids, and solids. The relative proportion of the three components depends on heating rate and temperature. The gas phase is largely hydrogen, methane, carbon monoxide, carbon dioxide, and water. The liquid phase, or pyrolysis oil, contains thousands of compounds, many of which are unstable and polymerize over time.[9,10] The solid phase, or char, is largely carbon. The product gas produced in gasification can be used in a gas turbine with relatively little clean-up, but for producing other compounds such as liquid fuels, the carbon dioxide and water must be removed and the ratio of hydrogen and carbon monoxide adjusted using the



10.2 Proximate composition of selected wood and agricultural species.[5–7] water gas shift reaction to optimize the yield in the reforming processes. This reformulated gas mixture is generally referred to as synthesis gas or syngas.

One of the best developed synthesis gas processes is production of methanol over Cu/ZnO catalysts. In this process, a mixture of 3:1 hydrogen:carbon monoxide is passed over a catalyst bed at high temperature and pressure. With product separation and recycle, conversion efficiencies greater than 99% can be achieved. Reforming the product gas into hydrogen is currently the most energy-efficient process, recovering 60% of the original biomass energy. Reforming it into methanol is slightly less efficient, recovering just 55% of the starting biomass energy in the product. Processes for producing other products such as longer chain length alcohols or hydrocarbons are less efficient.[11] The projected yields of transportation fuels in the NREL analysis are 291 to 437 litres per tonne of biomass for ethanol and about 416 litres per tonne of biomass for methanol. A similar analysis from the Netherlands also suggested that the best overall energy yields were for hydrogen and methanol. Unfortunately, hydrogen is a difficult fuel to store and transport, and the energy in methanol is just 76% of the heat of combustion of ethanol.[12]

Use of pyrolysis oils from thermochemical processes has received a lot of attention, but has a number of problems that have delayed progress. Pyrolysis oil contains a complex mixture of hydrocarbons and hydroxy acids with 10–20% water. The pH is typically 1.5 to 3.0. The resulting liquid is corrosive and unstable, degassing and polymerizing on storage. Pyrolysis oil cannot be used directly in gasoline or diesel engines but can be further processed to make transportation fuels or could be used directly in boilers and other combustion devices.

10.5 Improving yields of fuels from biomass

Past research on improving yields of fuels from biomass has focused primarily on exclusive production of ethanol and did not seriously consider ethanol as a partial component as in the *integrated biomass technologies* approach. As we consider additional research needs, we believe it will be critical to consider solutions within the context of such an integrated approach. That way industry can leverage the cost of ethanol production by selling an array of by-products. Research needs and opportunities include pretreatment, value prior to processing, cellulose hydrolysis and thermomechanical methods.

10.5.1 Pretreatment

Pretreatment processes have proven to be necessary for both acid and enzymatic saccharification. Both processes are diffusion dependent, therefore wood needs to be reduced to small particle size to improve the rate at which reactants penetrate the wood and products are removed. Large molecules such as enzymes diffuse much more slowly than do small molecules. This makes the pretreatment processes used with enzymatic saccharification even more critical than for acids. The pretreatment typically involves shredding the biomass and a dilute acid or water autohydrolysis that removes the readily hydrolyzed hemicellulose and much of the amorphous cellulose.[13] Pretreatment processes that remove more of the lignin or minimize the number and size of the crystallized regions in cellulose would provide a breakthrough. Research on pretreatment is focusing on obtaining products from lignin and/or reducing cellulose crystallinity to improve saccharification yield.

10.5.2 Value prior to processing

Value prior to processing (VPP) is a pretreatment strategy with different goals from those of traditional saccharification pretreatments. VPP envisions collecting components of wood that are not critical to or maybe even in some cases detract from the eventual performance of a traditional product (such as paper or fiberboard). The collected material is subsequently used to make other products. Most of the current interest is to produce ethanol because the market is large enough to absorb the additional production without a major change in pricing. In some cases, VPP can improve the properties of the traditional product or improve the economics by decreasing overall energy consumption. Cellulose is the highest strength component of wood, therefore paper and board products require high amounts of cellulose. Cellulose concentration is increased by removing lignin and hemicellulose and these by-products are then available for other purposes.

Two proven methods have been used to remove hemicellulose: alkaline and acidic extraction. Alkaline methods extract oligomeric hemicellulose components and some small lignin fragments from the wood. They are more expensive and but tend to produce fewer unwanted by-products than acid extraction. They work best on hardwoods and result in a sugar extract that is very rich in five carbon sugars. Alkaline pretreatments have been evaluated for production of sugars and hydroxy acids.[14–17] Because many pulping processes use alkaline methods, it is envisioned that an alkaline pretreatment will still produce a high-quality paper product.

Acidic methods, including autohydrolysis, tend to hydrolyze the hemicellulose and produce sugars and low molecular weight polymers. The acid hydrolysis reaction is less selective and results in partial depolymerization of the cellulose as well. Carried too far, acid hydrolysis can also result in the formation of potentially toxic degradation products from the sugars. Acid pretreatments are used by the dissolving pulp industry and thus have a history in this application.[18] They are now being explored for the potential to make a secondary product while maintaining paper grade pulp properties.

As part of *integrated biomass technologies*, a critical advantage of VPP is that new products are more valuable than they were in the original process. In traditional kraft pulping, lignin and carbohydrates that are not included in the paper are burned to produce energy. Redirecting these chemical feedstock materials to production of higher-value products such as transportation fuels or resins may improve the profitability of the entire process. Whole-mill analysis is required to ensure that any new VPP process will be profitable.

10.5.3 Cellulose hydrolysis

Concentrated acids work very well to hydrolyze cellulose. Strong acids are cellulose solvents and because they can dissolve the cellulose as well as hydrolyze it, they can give near quantitative yields of sugars. Cellulose can be dissolved in concentrated sulfuric acid (72%) or hydrochloric acid (45%). If the temperature is low and oxygen avoided, the cellulose can be precipitated by water dilution, with relatively little degradation.[19] Strong acid conditions are also very effective at hydrolyzing lignocellulose.[20] At such conditions, the hydrolysis rate is fast enough and the temperature required low enough to avoid most of the decomposition reactions. This process proceeds relatively smoothly, leaving most of the lignin as an insoluble product. Much of the sugar remains as low molecular weight oligomers, but these are readily hydrolyzed in the diluted acid to give near quantitative yields of monomer. Concentrated acid hydrolysis has been known for over a century. But concentrated acids are expensive and energy-intensive compounds. The key technology needed to develop a viable strong acid process is acid recovery. This presents many challenges, but some recent reports suggest that engineers have successfully pilot-tested a strong acid process with acid recovery.

Dilute acid saccharification of lignocellulose proceeds at approximately three non-distinct rates. Easiest to hydrolyze are the hemicellulose polymers, which can often be removed by autohydrolysis and temperatures between 120 °C and 140 °C.[21] The amorphous cellulose is hydrolyzed at a slightly slower rate. The hemicellulose sugars are very sensitive to acid degradation, and the pre-hydrolysis conditions are usually optimized to remove as much of the amorphous cellulose as possible without excessive degradation of the sugars. After about half the cellulose has been removed, hydrolysis enters a much slower phase due to cellulose crystallinity. At this point, the rate of degradation of sugars to hydroxymethyl-furfural and levulinic acid is similar to the rate of sugar production, and thus further hydrolysis is usually not justified.[21,22] Enzymatic saccharification also slows down once the amorphous cellulose has been hydrolyzed. With enzymes, the decomposition reactions are no longer a major concern so that when the enzymes are allowed to continue, they are capable of hydrolyzing nearly all the cellulose in some substrates. But the retention time required to accomplish this is well beyond an economically viable process limit. The crystallinity of cellulose is the most important barrier to increasing the yield of sugars from wood hydrolysis and has been the barrier to developing a profitable wood-based ethanol process for a century or more.

10.5.4 Dispersed resources/production scaling

Stand-alone thermochemical processes to produce chemicals and fuels appear to require too large a scale to fit nicely into the dispersed nature of traditional supplies of biomass. A modern pulp and paper mill is handling about 2 million tonnes of dry wood annually. The largest petroleum refineries consume as much as 17 million tonnes of crude in a year. This difference in supply scale seriously impedes the ability to produce hydrocarbon products comparatively with the petroleum industry. An alternative approach is to produce pyrolysis oil as a higher value and higher energy density intermediate that could be economically shipped to larger conversion facilities. Pyrolysis oil has several characteristics that have prevented many direct uses but these are less of a concern when the oil is intended for thermochemical decomposition to a product gas. It will still be necessary to stabilize the oil to minimize degassing and polymerization in transit, but it does not need to achieve parity with gasoline or diesel. There is considerable work needed to determine if small-scale pyrolysis units can be constructed and operated economically. Operating both a pyrolysis plant and a gasification plant to perform work that could readily be carried out in one step in a gasification plant is not a good start on profitability. But this concept has the potential to overcome the single biggest impediment to biofuels – the distributed nature of biomass and match the economy of scale achieved in the petroleum industry.

10.6 Technology transfer and outlook for biorefining

Obtaining high-value products from biomass prior to kraft pulping or thermomechanical pulping (TMP) continue to have strong interest in the paper industry and transfer of new biorefining technology should be easily implemented. Acid prehydrolysis liquor is commercially available from one dissolving pulp mill and at least one hardwood sulfite mill. There is growing commercial interest in prehydrolysis prior to refining for the production of newsprint grade pulps. There is also strong interest by industry for pursuing waste fuel (bark) gasifiers, evaluating gas clean-up and gas reforming technologies.

Changes in scientific, social, natural resource, political, and economic areas have created opportunities for producing transportation fuel, chemicals, and other products from biomass. As process technology emerges from this research, engineering, and economic analysis will be used to present compelling business cases for transferring this technology to industrial partners. Success in biorefining will: (1) promote sustainable social development, (2) decrease global dependence on crude oil imports, (3) decrease greenhouse gases, and (4) promote sustainability of our precious natural resources.

In summary, the success of *integrated biomass technologies* will depend on both its economic and social feasibility. Economic, environmental, and social analyses need to determine the feasibility for using various biorefinery and related biomass conversions. Any implementation of *integrated biomass technologies* will need to consider the full spectrum of costs, prices, and revenues, but it must also consider environmental impacts and societal goals.

10.7 Advanced wood and bio-based natural-fiber composites

The next tenet of *integrated biomass technologies* (advanced biocomposites) is further advancing the development of wood and bio-based natural-fiber composites on the basis of performance and sustainability. This science began with the invention of plywood by ancient Egyptians about 3000 years ago. Modern wood composites technology began about 100 years ago with the invention of particle-board, flake-board, hardboard, and a variety of other wood-based composites. These products have created substantial commercial markets for value-added wood-based products in structures and furniture. Wood composite technologies are based on breaking woody material down to smaller elements, such as a veneer, particle, flake/strand, or fiber, then reassembling these elements using an adhesive or natural fiber–fiber hydrogen bonding to create a wood-based composite product. More recently, new innovative bio-based composite products using natural fibers, such as agricultural fibers or residues, or hybrid systems using combinations of both wood and natural fibers, have also become available. Youngquist identified over 1000 citations on ag-fiber or lignocellulosic composites.[23] Globally, many lignocellulosic options exist to manufacture composites and these options include composites employing thermoset resins, inorganic binders, or thermoplastic resins.[24] New hybrid products using wood– or natural fiber–plastic composites, have recently become popular for automobile components, especially door and deck panels and for building products such as decking, siding, roofing, fenestration, and millwork.

In North America, wood-based composites now represent more than 40% of the total materials used in residential construction making them the largest single material type used in residential construction. Wood-based composites are used because they are readily available, light, strong, easily worked, and cost effective. However, to expand into other markets, such as non-residential and commercial construction and consumer goods, composites need to achieve enhanced performance, serviceability, durability, and reliability. Users of many of today's wood and wood-composite products commonly refer to the same recurring problems. These common perceptions concern:

- low strength and stiffness with eventual rheological/creep problems;
- poor durability and water-related problems;
- limited service life;
- limited or poor fire performance;
- wood products harvesting and manufacturing not currently viewed as a fully 'green technology' and thus are not being given preference in some 'green' certification programs;
- existing wood and bio-composites only garner 10–20% of the ultimate strength of many lignocellulosic fibers, advanced composites will greatly increase that efficiency.

Advanced wood and lignocellulosic composites are needed to meet the diverse needs of users for high-performance building and commodity products. These products need to be developed to expand beyond current saturated wood products markets and must be proven to represent the state-of-the-art in sustainable forestry and agricultural practices.

10.7.1 Sustainable natural resource use

As worldwide demand for timber and lignocellulosic resources (biomass) increase, people in resource management, government, and research must develop a shared vision with industry for long-term sustainable management of this biomass and bio-based economic development that is in concert with sustainable use of this biomass.[25] Sustainability in this context denotes a balance between conservation and use to serve local and global environmental, social, and economic needs.[26] Sustainable management of natural resources becomes more complex as increasing worldwide populations place increased demand on these resources. At present in North America, there is excess of biomass available and resurgence in commercial interest for using this resource. Composites manufactured from biomass have unique performance, particularly with regard to strength/weight ratio and offer environmental advantages to non-renewable mineral- or petrochemical-based resources.[27]

10.7.2 Characteristics of wood versus agricultural fibers in biocomposites

Natural lignocellulosic-based raw materials from wood (fibers, particles, flakes, strands, and veneers) differ from agricultural crops (stems, bast, leaves, seed-pods). It is desirable for lignocellulosic materials (flakes, particles, and fiber) used for composite manufacture to be uniform and consistent, but various lignocellulosic materials are known to differ widely among species.[24] For example, fiber from hemp is vastly different from fiber from white pine. Fiber from white pine is different from fiber from white oak. Even within the same species, growth region, growth rate, and climate affect fiber properties.[28] Wood fiber results from many years of tree growth (decades or even centuries), but they are usually shorter than other natural fibers. Wood fibers have cellulose contents similar to fibers obtained from agricultural crops (agro-based fiber), but have higher lignin and lower pectin/extractives contents (Fig. 10.2).[27] Pectins are complex carbohydrates with a glucouronic acid/rhamnan main-chains and rhamnan, galactan, and arabinan side-chains. For an in-depth review of the composition of lignocellulosic materials, refer to Rowell *et al.*[29]

Agro-based lignocellulosics intended for use in composite products can be categorized into two types: agricultural residues and lignocellulosics grown specifically for their fiber.[24] The residue-types are characterized by species such as sugar cane bagasse, cereal straws, coconut coir, corn or cotton stalks, whereas the latter is characterized by species such as jute, kenaf, and industrial hemp. For a rigorous examination of properties and processing of wood- and agro-based lignocellulosic composites, refer to Maloney[30] or English *et al.*[24]

Many non-wood agricultural fibers that are common worldwide are usually annual crops and available seasonally. Harvesting must be done at certain times and production potential and infrastructure for collection, storage, drying, separating, cleaning, and delivery vary widely.[26,27] The overall limitations for using agricultural-based lignocellulosic materials include: lack of established delivery systems, processing complications caused by fiber density and morphology, process-temperature limitations, risk of decay, and odor emission during processing and use.[27]

Low thermal-degrade temperatures, potential for high volatile emissions, and high moisture absorption of agro-fibers may also limit processing options.[26] But compared with wood fiber, agro-fibers have lower density, higher stiffness-to-weight ratio and pliability, and enhanced recyclability and biodegradability.[26,27] Although inorganic fibers such as fiberglass have better mechanical properties, bio-fibers have desirable balance of strength and weight.[27] Natural fibers used in composites include: wood flour (i.e., used as a filler), wood particles, and fibers; short agro-fibers (i.e., used as reinforcements) and long agro-fibers such as jute, kenaf, and flax. Natural fibers with high strength and stiffness usually possess a high cellulosic content and low microfibril angle.[26]

10.7.3 Transitioning to a bio-based, sustainable future

If our society embraces the concept of a global economy, then we must commit ourselves to promoting renewable, recyclable, and reusable materials.[25] To do this, we must develop the fundamental and applied science and technology necessary to provide improved value, service-life, and utility while at the same time meeting the needs of consumers for a wide array of sustainable materials. This will require networking with international collaborators to provide a broad range of tools to resource managers that, regardless of resource type or quality, promote sustainability and recyclability, increase economic value-added, and reduce adverse environmental impacts.

In increasingly more instances, engineered wood- and biocomposites allow us to achieve resource sustainability and meet user needs in highly industrial, emerging, and third world countries, many with growing populations and growing demand for materials. Wood- and biocomposite technologies provide a tool for resource managers to add value to low- or no-value bio-based resources and thereby promote demand for diverse wood and lignocellulosic-feedstocks including small-diameter timber, fast plantation-grown timber, removals of invasive species, removals of hazardous forest-fuels, and agricultural residues.[25] At the same time, engineered wood composites can serve as a tool for economic development of rural communities and provide urban communities with sustainable, value-added commodity and non-traditional products. Biocomposite technologies can also promote value-added uses for post-consumer and/or post-industrial waste materials.

We must develop tools to address resource sustainability by enhancing reuse and recyclability, and minimizing the environmental impacts of composite processing. Then as forest resource options change, as discarded wood and fiber from waste-streams become available, as alternative non-wood and non-lignocellulosic materials become more economical, and/or as air- and water-quality regulations become more stringent, we can adapt and sustainably address each of these issues. Engineered lignocellulosic biocomposite materials provide technology that is adaptable to a changing resource base. These products can incorporate a variety of wood and natural lignocellulosic-based raw materials in the form of fibers, particles, flakes, strands, and veneers. But engineered biocomposites must also be durable, have specific performance properties, and generally serve for many years regardless of use condition.

Whether they are manufactured from a variety of natural fibrous sources alone or combined as hybrid products with non-wood materials such as cement, ceramics, plastics, or synthetic fibers, advanced composite technologies will provide the means to engineer and produce biocomposite materials with enhanced physical and structural performance characteristics to achieve special properties. Advanced composites will further enhance our ability to meet global needs for improved performance and for value-added products that promote long-term resource sustainability. They will also decrease environmental impacts relative to those of existing non-renewable products.

10.7.4 Recent advances in biocomposites

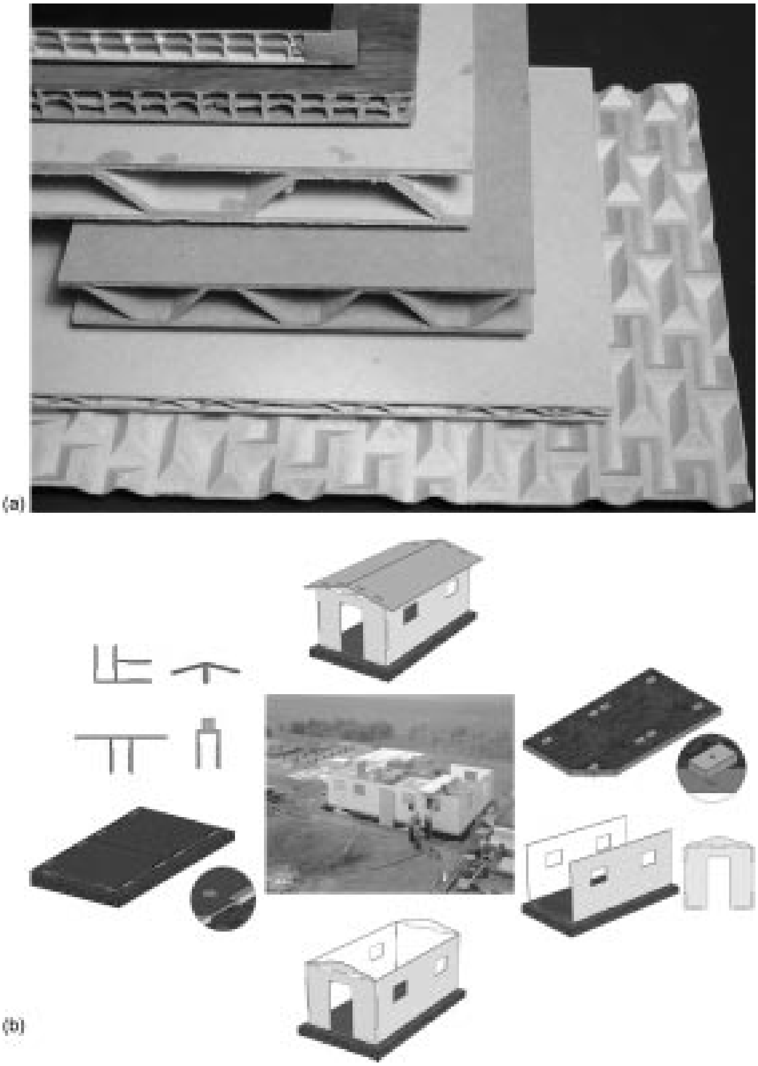
Recent advances within the international wood and biocomposites research community are just beginning to lead to the early stages of a fundamental understanding of the relationships between materials, process, and composite performance properties. These advances in science-based biocomposite processing technologies will eventually allow us to use a diverse array of bio-based raw materials and precisely control the composite manufacturing process on-the-fly. This in turn will also enable us to produce high value-added engineered biocomposites with reliable and consistent performance properties from virtually any bioresource. For example, biocomposite processing technologies allow us to use diverse species and an ever-changing quality of wood and other natural biofiber feedstocks, including small-diameter timber, fast plantation-grown timber, agricultural fiber, biofiber residues, non-desirable invasive species, and burnt timber.

Another major advance in engineered wood and biocomposites is in product and performance enhancement. Advanced engineered biocomposites are currently being developed that will simultaneously meet the diverse needs of users for high-performance and economical commodity products (Figs 10.3 and 10.4). These new engineered biocomposite products can be made from numerous bio-based feedstocks and can serve as tools to address forest management and global sustainability issues.[31,33] For another example, wood is approximately 30–40% cellulose and about half of that is crystalline cellulose. Recent advancements in nanotechnology will soon lead to the commercial isolation of nanocrystalline cellulose (Fig. 10.5). While nanocrystalline cellulose may be only one-tenth as strong as carbon nanotubes[35,36] (currently the strongest known structural material) it may cost 50–1000 times less to produce.[37,38] Engineered biocomposites employing nanocrystalline cellulose reinforcement could someday soon provide advanced performance, durability, value, service-life, and utility while at the same time being a fully sustainable technology.

10.7.5 Future advances in biocomposites

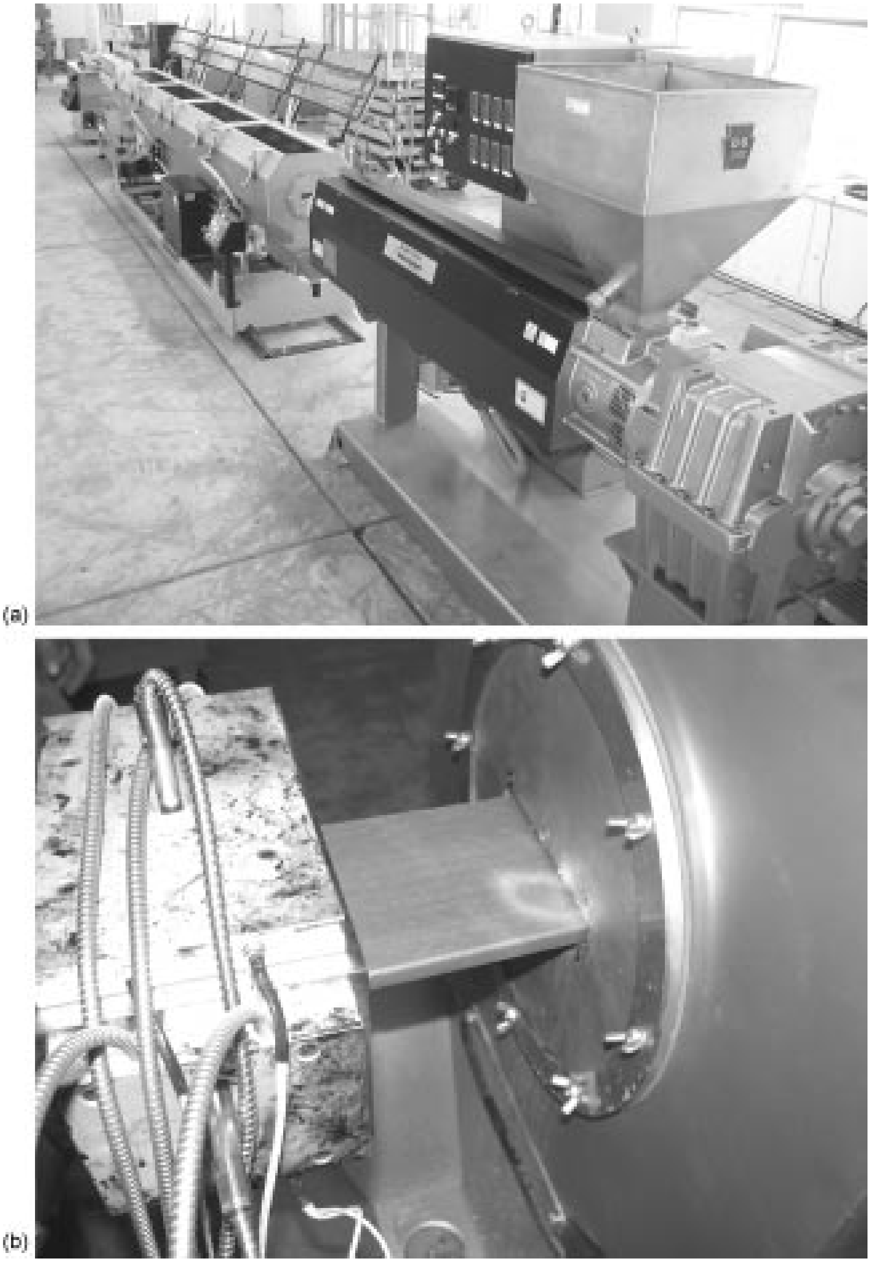
The next generation of engineered biocomposites needs to provide construction materials and building products that far exceed current expectations. They need to be lower cost, higher performance, more adaptable, more reliable, lower maintenance, and smarter. Smart materials are able to adapt to changing conditions: for example, a material that increases in porosity when it gets wet so that it dries quicker or a material that senses excess stress or strain and warns the user of the problem. It is also necessary to develop new markets (such as commercial construction, automotive, aerospace) and decrease effects on the environment. These advanced engineered biocomposites will:

- combine wood and natural biofiber for synergistic hybrid materials;
- provide enhanced performance and superior serviceability;
- be more durable, dimensionally stable, moisture proof, and fire resistant;
- possess advanced sensory capabilities for warning users when problems are imminent;

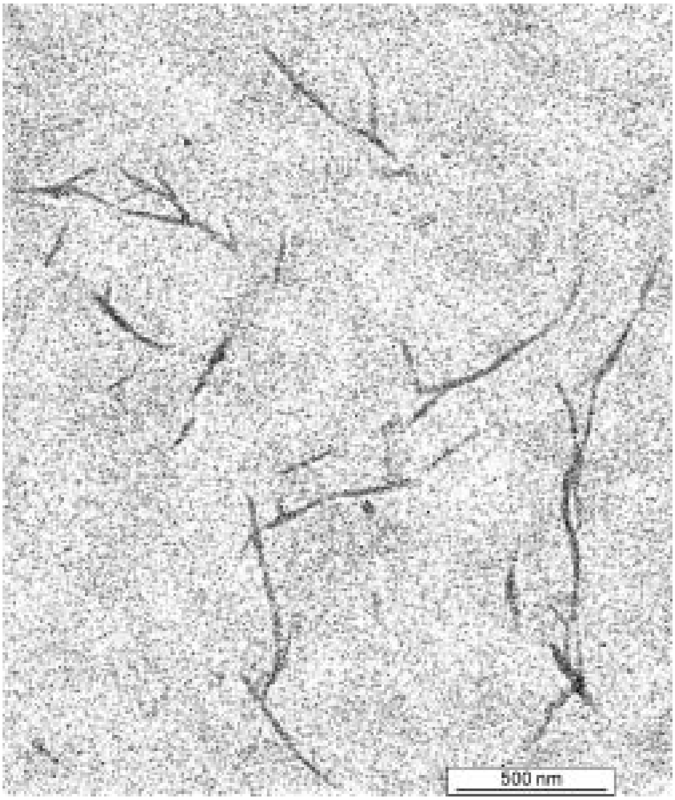


10.3 Concept of the portable, reusable, temporary housing system: (a) using lightweight recyclable biocomposites made from virtually any bio-fiber resource and then used as (b) temporary, reusable structural building systems.[31]

- possess advanced biomemetic capabilities for fixing themselves when problems are imminent;
- be renewable, recyclable, and sustainable;
- decrease environmental impacts from processing and use; and
- have both materials and processes engineered to customize and optimize performance.



10.4 Using wood–plastic extrusion technology (a) to add value to invasive biomass used as lignocellulosic-reinforcement in thermoplastic composites (b).[32]



10.5 Nanocrystalline cellulose-reinforced composites in thermoplastic polypropylene matrix.[34]

To successfully meet these broad goals, it will be critical to collaborate and coordinate multinational, multi-partner research programs. Development of advanced engineered biocomposites will require scientific advances in chemical and materials processing. As was the case in biorefining, governments, academia, industry, and users must work together to develop a shared vision and then coordinate to systematically address a complex series research needs.

10.7.6 Research needs and opportunities

The next generation of bio-based composites gives the wood industry the opportunity for many new markets, but four research needs have been identified:

1. Enhance durability in adverse environmental or critical-use service conditions.
2. Provide higher reliability to meet the special needs of the commercial/non-residential construction market.

3. Minimize environmental life-cycle costs (resource use, energy use, emissions).
4. Address consumer needs for competitively priced products in residential and non-residential/commercial construction, furniture, and transportation systems.

Basic research is needed to increase our understanding of the relationship between performance and the contributions of constituent lignocellulosic materials, ranging from veneer, flakes, particles, fibers, and flour-like materials. We need to combine lignocellulosics with other materials such as Kevlar, polyamides, polyolefin, or fiberglass to produce advanced high-performance materials. This will also include learning to use natural nano-scale reinforcement materials, such as cellulose nanocrystals and microfibrils.

To improve the performance of materials, meet user needs, and promote resource sustainability, a basic understanding will be needed of material applications, their use-environments, and controlling economics. This understanding must identify perceived problems with the performance of current-generation wood-based composites and identify unfulfilled future markets for enhanced products. It must allow us to minimize environmental and life-cycle effects of new and reused bio-based products while also considering economic feasibility for commercial production of bio-based products.

A critical tool to achieve these goals may require using the new science of nanotechnology to manipulate and control materials and processes at the nanoscale. Nanotechnology, if many of its apparent promises can be achieved, may present a tool to improve structural performance and extend serviceability by orders of magnitude. Nanotechnology offers three potential opportunities for development of advanced wood- or lignocellulosic-based biocomposites. First, it is currently leading to new analytical technologies that will provide us a fundamental understanding of material behavior at the nanoscale. Next, it may include the incorporation of nanoparticles into advanced biocomposites to achieve enhanced performance (Fig. 10.5). Finally, it may also lead to modifications of the wood and lignocellulosic raw material surfaces at the nanoscale. This knowledge will then provide tools with which we can begin to understand 'materials–process–performance' relationships. Then we may be able to exploit these three potential opportunities to identify, control, and optimize material and process factors in real time so as to engineer products having highly specified performance characteristics with both economic and environmental advantages.

We must also address our objectives for a sustainable future and advanced product using integrated approaches that simultaneously provide environmental, utilitarian, and economic advantages. It seems that a truly sustainable vision for the use of *integrated biomass technologies* is now evolving. It may include a series of sequential processing approaches including an initial biorefinery stage to obtain ethanol/biodiesel fuels either thermochemically or biochemically, followed by production of biocomposite- or paper-based products from the biorefinery residues, and then production of bio-based electrical energy from biocomposite- or paper-mill residues. Such an integrated resource solution is thought by many to offer the optimum long-term solution to meeting both user needs and sustainable development.

One of our global challenges will be to meet the needs of growing populations with biocomposites from under-utilized, low- or no-value virgin, or waste biomass materials. To accomplish this, we need to work together to advance the fundamental and applied science and technology of manufacturing engineering bio-based composite materials to:

- encourage the use of our ever-changing wood and lignocellulosic resources by providing baseline data required to allow for the optimal use;
- develop highly adaptable manufacturing processes to produce advanced biocomposite products that meet consumer needs while simultaneously empowering resource managers to sustainably manage and improve the forest resource;
- accelerate the on-going development of engineered structural lumber, panel composites and three-dimensional molded and/or extruded composites from small diameter, low-quality timber derived from mixed species and previously unused lignocellulosic fiber sources.

10.7.7 Outlook for advanced biocomposites

Meeting the research needs described above for engineered biocomposite materials that meet user needs and maximize environmental sustainability will also bring economic gains to industry. If this is to be realized, we must commit ourselves to developing the fundamental and applied science and technology necessary to provide improved value, service-life, and utility so the world can use sustainable bio-based materials.

10.8 Advanced structures using biocomposites

The third tenet of *integrated biomass technologies* is advanced structures. The concept of advanced structures is critical to a broader goal of becoming a sustainable global society. Tomorrow's structures need to out-perform and outlast current standards and all while costing less, both economically and environmentally. Many of the materials for advanced structures will probably be advanced biocomposites. But advanced structures will require more than just advanced materials. It will be essential to develop new design approaches and a fuller understanding of the complex relationships of loads, use environment, and both materials and systems performance.

10.8.1 Background

As we move further into the 21st century, the demands and complexity of structures are increasing. In the past, structures were designed based solely on life safety issues. That is no longer the case. Today, structures are designed considering life safety along with functionality, environmental impact, and economics. Performance-based engineering, a design approach that encompasses these considerations, was first used about two decades ago for seismic design of structures and is gaining momentum for engineering design in all materials.

Performance-based engineering implies design, evaluation, and construction of engineered structures and systems that meet, as economically as possible, uncertain future demands of both owner-users and nature. The premises are that performance levels and objectives can be quantified, performance can be predicted analytically, and the cost of improved performance can be evaluated, so that rational trade-offs can be made on the basis of life-cycle cost considerations rather than construction costs alone.

Adoption of performance-based engineering concepts implies major changes in the thinking, practice, and education of designers. Perhaps most important is a shift away from dependence on empirical and experience-based conventions towards a design and assessment process. This implies a shift towards a more scientifically oriented approach with an emphasis on accurate characterization and prediction of structural performance.

Performance-based engineering requires an understanding of structural behavior under a broad spectrum of loading environments that the structure will experience. It then uses those factors to result in a holistic design and assessment process relating accurate prediction of structural performance to realistic descriptions of loads and environments that the structure will experience. This approach is not just for initial design but also emphasizes monitoring the health of the structural system, evaluating performance characteristics, and identifying the need for renovation or new construction.

10.8.2 Recent advances

Our current knowledge of wood properties and structures was developed through independent technical routes; individual structural members were investigated with little consideration of their use in structural systems or interactions with environmental loading. Similarly, excellent studies on various biological agents that attack wood and potential wood preservation systems have yielded baseline information on wood deterioration and wood preservative systems, but little information exists on the potential effect of biodeterioration on structural performance. For the development of a performance-based approach, a coordinated research effort aimed at understanding the interactions of these variables is needed.

Past limitations on testing and systems-analysis prevented in-depth consideration of interacting variables in either laboratory or field environments. The widespread application of personal computers and sophisticated data acquisition and analytical systems now provide the capability to study interactions between a wide number of variables. As such, initial systems performance characteristics and long-term changes in those performance characteristics, especially as they related to durability within the systems, can now be examined.

Another new design criterion will further consider ancillary factors such as portability, reuse and focus on actual required life expectancy.[31]

10.8.3 Research needs and opportunities

Research supporting the development of a performance-based design approach is needed in structural analysis and modeling, durability, structural health monitoring, and life-cycle analysis.

A coordinated research effort aimed at understanding the interactions among various exposure scenarios (mechanical loads, biological agents of deterioration, moisture exposure, fire performance) is now underway to best define performance-based wood design.

Structural analysis and modeling

Structural analysis and modeling uses multidimensional models of entire systems and subsystems, extreme loading conditions, simultaneous structural and environmental loading conditions to predict performance. The studies include fasteners as critical wood design elements (load–deformation response and design criteria, failure criteria, new moment-resisting connections, structural adhesive systems), structural performance characteristics of composites in wet and humid environments, and methods for renovation and upgrade of structures (fasteners and adhesives for structural repair, remedial treatments for fungal and termite deterioration).

Durability

Durability continues to be an important concern for wood- and biomass-based materials and additional research is needed to give baseline information on performance of wood structural systems in response to moisture (properties, moisture design loads, analytical models, moisture transfer, damage accumulation functions); evaluate environmentally acceptable preservatives; and collect baseline information on performance of wood structures in response to fire. Models need to be developed to evaluate the fire performance of advanced structures at the wildland–urban interface. This includes the interaction of the various components and materials used in these advanced structures.

Structural monitoring

We need to develop remote monitoring systems that use sensors to indicate degradation of wood structures applying technologies such as near-infrared spectroscopy, wireless systems, and full-system non-destructive methods. These monitoring systems will evaluate performance characteristics and identify the need for renovation or new construction. This approach forms the foundation of strategies for revitalizing our decaying infrastructure. A performance-based approach provides the appropriate framework for integration of sensing, monitoring, and control systems to monitor and maintain the health of the structure.

Life-cycle considerations

The next generation of advanced structures will need to serve a wider array of uses and user expectations than ever before. Both long-term and short-term costs for building design, materials, and lifetime maintenance will be considered. Material costs will factor both economic and environmental costs. Still another explicit expectation will be usable life expectancy. This expectation will normally be primarily focused on longer life expectancies, but a new opinion now also seems to be arising about shorter life expectancies. In most future structures, designers and engineers will need to develop explicit requirements from users that clearly define issues such as intended life expectancy, future reconfiguration and retrofit options, and end-of-life materials reuse options.

10.8.4 Outlook for advanced structures

Performance-based design will initially have its greatest effect on non-residential wood structures where owner-users can realize its long-term benefits. Innovations and knowledge from development of a performance-based design approach will provide the framework for evaluating and minimizing the environmental footprint of wood-based structures.

The development of a performance-based design approach requires that data acquisition and analysis cannot be limited to measuring just one dependent and one independent variable. Rather it should involve simultaneous, multiple measurements that may link to a single or multiple variables. For example, monitoring the response of a structural subsystem for a single axis of loading and environmental loading might involve load and deformation measurements both in- and out-of-plane of loading, along with simultaneous temperature and moisture measurements to assess environmental loading. This entire set of data would be used to develop a comprehensive multivariate model. Experiments should be conducted at the extremes of the response spectrum so that results can be used to interpolate to common cases, instead of today's more traditional method of extrapolation to extreme events. Economic feasibility studies of advanced structural systems will also be required.

Structural wood design is moving to a performance-based design methodology that encompasses the entire life cycle of a structural system. Performance-based design procedures rely upon data obtained from rigorous scientific studies. Performance-based design will initially have its greatest effect on non-residential wood structures where owner-users can realize its long-term benefits. Innovations and knowledge from development of a performance-based design approach will provide the framework for evaluating and minimizing the environmental footprint of wood-based structures. Finally, advances in this approach will also lead to broader application and improvements for residential structures.

10.9 Summary

Exciting new opportunities exist for biorefining to produce biofuels, bio-based chemical feedstocks, bioenergy, and cellulose nanofibers and for developing advanced biocomposite materials, and for engineering advanced structures. This systematic approach for maximizing performance, resource sustainability, and profitability is called '*integrated biomass technologies*'. Wood and lignocellulosic technologies allow the use of diverse wood and lignocellulosic feedstocks including small-diameter timber, fast plantation-grown timber, agricultural fiber and lignocellulosic residues, invasive species, recycled lumber, and timber removals of hazardous forest-fuels. Another potential advantage provides producers an ability to use, and adapt with, an ever-changing quality level of wood and/or other natural lignocellulosic feedstocks. Still another advantage is the development of advanced bio-based materials and structures with improved performance relative to fire, structural-performance, and service-life. These engineered biocomposite products and advanced structures promote application of bio-based systems in untapped commercial and industrial construction markets. The international research community has recognized this and is currently addressing each of these issues.

From a manufacturing and a global-resource sustainability standpoint, with this evolving fundamental understanding of the relationships between materials, processes, and value/performance properties we will soon be able to recognize the attributes and quality of an array of bio-based materials then adjust our manufacturing and processing systems to produce the highest value-added solution considering an array of social, economic, natural resource, and/or political factors. Thus, as resource properties or availability changes or as economics change, the relative biofuels, biochemicals, biomaterials process streams can be modified to produce the highest value-added solution. We are now developing the technology to produce advanced, high-performance wood- and bio-fuels, -chemicals, and -materials. Then we will be able to employ those technologies as tools to help forest and land managers fund efforts to restore damaged ecosystems and that in turn may further promote sustainable forest management practices.

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11

Market and innovation considerations in development of natural/wood-fiber composites

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11.1 Introduction

Recent years have seen explosive growth in natural, fiber-based composite (NFC) products. Societal leanings toward ‘green’ products and increases in petroleum prices suggest similar increases into the foreseeable future. On a volume basis, the wood products industry dominates this product category with traditional structural and non-structural, wood-based panels. However, new, fiber-based products have largely come from outside this sector. Wood–plastic decking and automotive parts are the most noteworthy examples of new fiber-based products. While most of this book has been technical in nature, this chapter explores NFC products and industry sectors involved in their production from the perspective of marketing and innovation.

First, a background is provided that briefly discusses historical development of NFC products. The types of natural fibers are outlined as are the forces driving increased utilization. The section also covers the main differences between the North American and European marketplaces, especially with respect to wood–plastic composites (WPCs). Industrial organization theory is discussed in order to explain how innovation occurs in new versus mature industries.

The next section discusses approaches to research and development (R&D) in the sector. Research and development is considered from the perspectives of resource or technology push versus market pull. In many cases, products are developed without a market in mind and research shows that this is a risky endeavor. Product development is highly risky in the best situations, but without market-related customer research and knowledge, resource push innovations often result in snazzy new products with no market demand. Following a discussion of resource push, company culture and the ability of firms to maintain high levels of innovativeness are outlined. Finally, future trends are discussed and other sources of information provided.

11.2 Background

What are NFC products? Some categorizations of NFC products include those based on mineral fibers such as asbestos (Bismarck *et al.*, 2005), but here only plant-based fibers are considered. Mohanty *et al.* (2005) place natural fibers into the following categories:

- Straw – rice, wheat, corn stalks, etc.
- Bast –flax, hemp, jute, and kenaf.
- Leaf – sisal, henequen, pineapple, and banana.
- Seed/fruit – cotton, kapok, and coir (from coconut husks).
- Grass – bamboo, switch, elephant.
- Wood.

Natural-fiber composites have been with us for many years (i.e. papyrus), but recently the interest in these products has grown considerably. Historically, NFC products included a handful of wood-based composite panels beginning with plywood, particle-board, medium-density fiberboard, etc. These products are all associated with one industry sector – the wood products industry. However, recent technological advances from a variety of industrial sectors have resulted in a plethora of new product offerings and an infinitely more complex sector that produces NFC products. Today, natural/wood fiber composites are found in settings ranging from traditional panel products to automotive parts to outdoor decks and are based on a wide variety of natural feedstocks. Accordingly, it becomes difficult to fully describe the natural/wood fiber industry. Schneider and Witt (2004) provide an interesting overview of the development and commercialization of WPCs, but most of the new products in the marketplace originate from outside the wood products sector. For example, in 2003, less than a quarter of the companies producing WPCs had roots in the wood products industry (AMI, 2003).

Much of the new product development (NPD) work in this area has come from private and public R&D labs with the motivation originating from a need to deal with nuisance waste streams. For example, as field burning has become less acceptable owing to air quality concerns, new outlets for various types of straw have been necessary. In North America, a relatively new and promising panel product in the marketplace is strawboard. Strawboard is generally a direct substitute for medium-density fiberboard and particle-board. However, utilization of straw is nothing new. In the 1940s, nearly one million tons (910 000 tonnes) of corrugating medium was being produced in the US Midwest from straw, but the last of these mills closed in 1960 because of the high costs of gathering straw and the shift by the paper industry after the Second World War back to hardwoods (Bowyer and Stockman, 2001). Other interesting examples include by-products from the oil palm industry in countries such as Malaysia and from the tequila industry in Mexico. Availability can drive NPD. A good example is development of bamboo-based mat by India's Plywood Industries and Research Institute.

NFC products are most developed in North America and Europe, but the respective approaches are quite different. In North America the largest market is for outdoor decking and wood is the natural fiber that is typically used, whereas in Europe the situation can be described as more technically advanced with the largest market being automotive parts, and agricultural fibers are the norm (Schut, 2005). One reason Europe is more advanced in this area is legislation requiring the recyclability of automobiles and other products.

11.3 A growing interest in natural fibre composite products

The recent high growth rates of NFC products are predicted to continue into the foreseeable future. For example, a Massachusetts-based market research firm, BCC Research, estimates growth rates for WPCs and NFC products in North America to be nearly 10%, up to 2009. The estimate includes a total consumption in 2009 of 1.9 billion pounds (864 000 tonnes) of WPCs and 200 million pounds (91 000 tonnes mill kg) of NFC products (BCC Research, 2005). Other estimates of market growth are even higher (PrincipiaPartners, 2007). According to a UK-based research group, forecasts for Europe are similar with respect to growth rate and expected total production in 2009 will be 290 million pounds (132 000 tonnes) (Hackwell Group, 2006). By far the most noted marketplace for WPCs in North America is the outdoor decking market (Table 11.1).

It has been stated that economics, environmental concerns, and improved properties drive the interest in combining wood and other materials (Youngquist, 1995). Specifically, Youngquist refers to reducing overall costs by substituting lower cost materials, creating products that can use recycled materials and in turn be recycled and designing composites with specific and superior properties for a particular use. Other advantages can include lower weight, availability, ease of recycling, thermal and acoustic insulation, CO_2 neutrality, and lower energy consumption in manufacture (Brosius, 2006). Smith and Wolcott (2006) outline four factors they believe are driving growth in the WPC decking market. First is a favorable value proposition followed by efforts to avoid chemicals (used to treat wood decking) in the environment, homebuilder acceptance of general wood composites, and effective market communications by WPC manufacturers.

Recycling legislation in Europe has been a major driver of the automotive industry pursuing NFC products. Interest from the automotive industry is not totally new. Henry Ford produced a 'biological' car back in 1941 in which 70% of the body was made of a natural fiber composite (Anonymous, 1998). NFC products are finding their way into virtually every interior component of cars and trucks. However, currently they are limited in public transportation because of flammability characteristics (Brosius, 2006).

Table 11.1 Example US companies producing WPC decking products

Company	Example deck brand name(s)	Primary raw materials	Source
CertainTeed Corporation	Boardwalk	Wood flour and polyvinylchloride compound	http://www.certainteed.com/
Correct Building Products, LLC	CorrectDeck	Wood and polypropylene	http://www.correctdeck.com/
Elk Premium Building Products, Inc.	CrossTimbers	Wood and polypropylene	http://www.elkcorp.com
EPOCH Composite Products, Inc.	EverGrain	Wood and polyethylene	http://www.evergrain.com/index.jsp
Fiber Composites, LLC	Fiberon	Wood and polyethylene	http://fiberondecking.com/
Green Tree Composites, LLC polyethylene	Monarch	Wood and high-density	http://www.monarchdeck.com
LDI Composites Company	GeoDeck	Cellulose fiber and polyethylene	http://www.geodeck.com
Louisiana-Pacific Corporation	WeatherBest	Wood flour and polyethylene	http://www.lpcorp.com/deckingrailing/deckingrailing.aspx
Master Mark Plastics, Inc.	Rhino Deck	Wood and polyethylene	http://www.rhinodeck.com/
New Tech (manufactured in China by Meixin Manufacturing)	NewTech	Rice hulls, wood, and other	http://www.newtechwood.com/index.php
TimberTech Limited	Earthwood DockSider	Wood and polyethylene	http://www.timbertech.com/
Trex Company, Inc.	Trex	Wood and recycled polyethylene	http://www.trex.com/
Universal Forest Products, Inc.	Latitudes	Wood and high-density polyethylene	http://www.ufpi.com
Weyerhaeuser Company (manufactured by AERT)	ChoiceDek	Wood and polyethylene	http://choicedek.com/ http://www.aertinc.com/index.asp

The Home Depot sells a brand of WPC decking, Veranda, that is produced by Universal Forest Products, Inc., Fiber Composites, Louisiana-Pacific Corporation, and McFarland Cascade: http://www.verandadeck.com/faq/index.htm.

Table created using web searches and Washington State University web site – http://www.wpcinfo.org/producers/.

According to Elliott-Sink (2005), the following aspects are other reasons for the interest in NFC products:

- NFC products replace petroleum-based components, thereby reducing reliance on foreign oil, often supporting domestic agriculture, and reducing risk of environmental spills, etc.
- NFC products can be more price stable than fully petroleum-based equivalents.
- Biodegradability and recyclability – especially important in Europe and Japan where recyclability of cars is strictly legislated.
- Auto companies are increasingly looking at overall life-cycle costs of their products.

11.4 The industries involved

As described by AMI (2003), WPC manufacturers consist of totally new companies, plastics companies, wood products companies, and recycling companies. Thus, manufacturers come from a variety of sectors. The growth of many NFC products was initially constrained by a lack of familiarity across industry sectors. There was little if any overlap in suppliers, equipment manufacturers or processing technology between wood and plastic industry firms and each have different knowledge and perspectives (Clemons, 2002; Youngquist, 1995). Some wood product companies perceived plastics as a significant threat resulting in what could be described as a hostile outlook towards plastics. On the other hand, the plastics industry was initially unfamiliar with the unique and challenging characteristics of wood and other natural fibers. This resulted in early frustration with using natural fibers as a raw material as well as some product failures.

Smith and Wolcott (2006) describe the diffusion of WPCs among product categories, beginning with non-structural applications such as landscape timbers, picnic tables, and garbage cans – moving on to items such as auto interiors and decking and presently working toward products such as siding, foundations, and industrial decking. The authors focus predominately on the building products sector. In 2005, WPC decking in the United States was manufactured by about 30 firms (Smith and Wolcott, 2006). Anecdotal evidence in the United States suggests a growing interest in WPC products for highway structures and other transportation infrastructure. Some examples of wood–polymer composite manufacturers are given below.

11.4.1 FlexForm Technologies, Inc.

FlexForm Technologies began operations in 1999 and produces nonwoven natural-fiber composite mats and panel products. The company serves a variety of industries including automotive, office interiors, aircraft, recreational vehicles, truck, commercial vehicles, absorbency, modular housing, and packaging. Examples of specific products include automotive door panels, door bolsters, head-liners; interior trim components of non-commercial aircraft; recreational vehicle sidewalls; ceiling tiles; and furniture. The company boasts laboratories with both large and small presses, and contact and forced hot air ovens. These assets are utilized for assisting customers in product development and rapid parts prototyping.

http://www.flexformtech.com/aboutus.php

11.4.2 TeelGRT (Teel Plastics, Inc.)

TeelGRT is a wholly owned subsidiary of Teel Plastics Inc. The company was started in 1996 to commercialize the compounding of natural-fiber composites and it specializes in three market areas. *Construction* includes roofing and shims, *transportation* includes various automotive parts, and *consumer* includes cosmetic packaging, housewares, and furniture. The company boasts an R&D and product testing lab along with staff scientists.

http://www.teel-grt.com/index.php?area=home

11.4.3 Beologic nv

Beologic is a Belgian producer of wood–plastic composites, compounds and conditioned wood-fibres. The company specializes in supplying raw materials for the WPC industry. Its two main product lines are Beoline® and Beofibre®. Beofibre® is granules filled with wood-fibres (25–85%) in a plastic matrix. Customers can specify aspects such as color, technical properties, and composition. Beofibre® is conditioned wood-fiber; fiber length and moisture content can be specified by the customer.

http://www.beologic.com/beologic.php?lang=EN

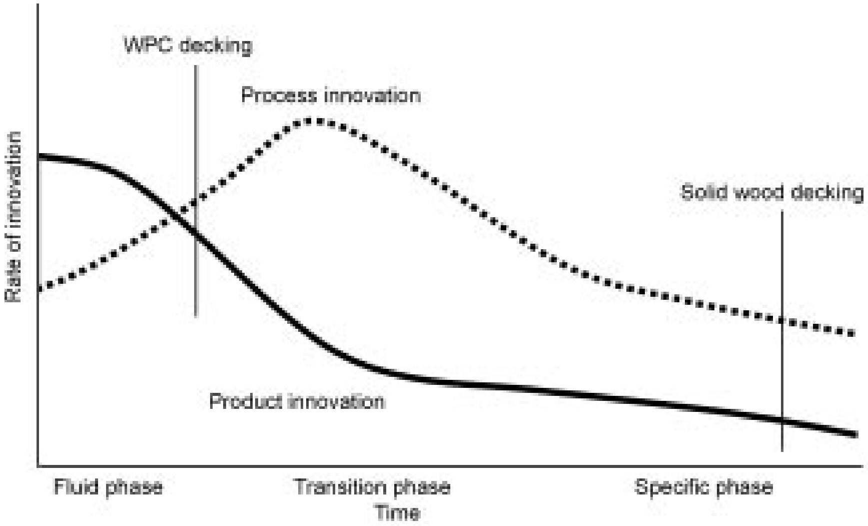
11.4.4 Trex Company

Trex is the leading producer of WPC decking in the US market. The company was originally part of Mobil Corporation which in 1992 purchased the technology and assets used to create Trex. These new assets formed the Composite Products Division of Mobil which in turn was bought out from the company by four Mobil executives in 1996. Trex became a public company in 1999. Net sales were US$294 million in 2005. At the end of 2005, the company sold its products through 92 wholesale distribution facilities which in turn supplied over 3200 retail locations. The company claims annual brand promotion expenditures of approximately US$19 million and claims to be successful in establishing a brand in a market sector that is generally not characterized by brand identification. Trex has manufacturing facilities in Virginia, Nevada, and Mississippi and has 35% ownership in a Spanish joint venture firm, Denplax SA.

http://www.trex.com/

11.5 Innovation across the life cycle

The proliferation of new products in sectors such as decking follows industrial organization theory that suggests innovation differs across industry life cycles. According to Utterback (1994), innovation activity is highest during early stages of the life cycle and declines as industries mature. Also, product innovation is higher in early stages while process innovation grows in importance in later stages (Fig. 11.1). He identifies three distinct stages in the evolution of innovation, a fluid phase, transition phase, and specific phase.



11.1 Industry evolution and corresponding innovation focus (adapted from Utterback, 1994).

In the fluid phase there is significant experimentation with product design among competitors. Thus, the rate of product innovation is quite high, while little concentration is placed on process innovation. This is characteristic of the rapid product evolution in the WPC decking sector where products have gone from a very basic 'board' to products of various designs and colors. At some point in the industry evolution the focus changes from product to process innovation or the transition phase. Some indicators suggest this is taking place today. The consulting firm PrincipiaPartners (2007) describes the WPC decking market as shifting to, 'increasingly focus on how products are formulated and manufactured in order to lower product costs', suggesting the sector is beginning to enter the transition phase (Fig. 11.1). That is not to say that NPD has ceased. Recent years have seen significant developments in offerings from WPC decking manufacturers including decking that mimics high-value tropical hardwoods. In the final, or specific phase, industries are focused on costs, volume and capacity. In this phase both types of innovation occur in small incremental steps (Utterback, 1994) and continues until some external shock such as technological change or new competition (Tushman and Nadler, 1986) occurs that brings a new wave of product innovation.

11.6 The challenges of research and development

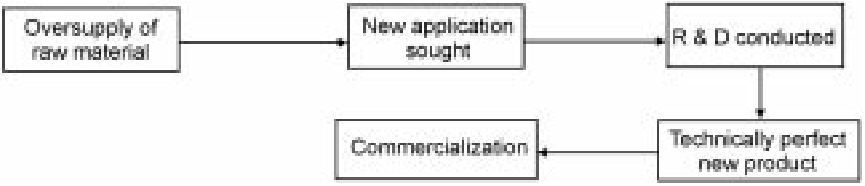
Differences in industry innovation were described previously according to the common evolutionary pattern. Another important factor impacting innovation is industry as well as company culture. The wood products industry is known to be mature and traditional. On the other hand, industries such as plastics have a reputation for innovation and new product development. This difference in industry culture can be partially shown in the differences in how industry sectors invest in R&D. As a percentage of sales, US wood, plastic, and chemical companies invest 1%, 2%, and 6%, respectively (NSF, 2007).

The traditional model of innovation and R&D is a linear model beginning with scientists in a corporate facility. The model of Thomas Edison's Menlo laboratory of the late 1800s was followed by many companies. Edison's company, eventually named General Electric Company, churned out numerous new products from its R&D laboratory under this model as did many other large companies. However, this model has come into question of late as companies have failed to find a strong connection between R&D investment and business success (Radjou and Wolff, 2006). The corporate world is increasingly focused on innovation in business models in addition to product innovation and is asking the R&D function to become more market focused, collaborative, and adaptive (Radjou and Wolff, 2006).

Research and development statistics provide an incomplete picture of successful innovation. If R&D is not implemented effectively it can be a poor investment. As suggested above, many wood product companies are reorganizing their approach to R&D in an effort to create a closer link to the marketplace and avoid the pitfalls of R&D push (Hansen *et al.*, 2007; Smith and Wolcott, 2006). By closely aligning R&D efforts with specific customer needs, the goal is to shift the paradigm from one of R&D push to market pull. In a general assessment of plant/crop-based renewable resources, experts claimed that improved approaches to NPD are needed (Anonymous, 1999), suggesting that improvements are needed regardless of sector.

11.7 Research and development push

Historically in the forest industry, many innovations have occurred via a resource push mechanism rather than market pull (Bull and Ferguson, 2006). What this means is the creation of products is motivated primarily by resource issues without the marketplace in mind, a road that often leads to failure (Fig. 11.2). Use of hybrid poplar in the US Pacific Northwest is a good example of this. Originally planted for use in pulp mills, global surpluses of paper chips made hybrid poplar plantations for pulp chips unviable. Companies were then faced with a raw material with no use. At least one company invested significant resources in developing solid wood products from the hybrid poplar despite the fact that it was ill-suited for many such applications. Other examples of this come from waste streams from other production processes (e.g., tequila and palm oil). Local economic development efforts have often resulted in products that effectively utilize local resources, but do not necessarily find a fit in the marketplace.



11.2 Innovation based on resource push (adapted from Bull, 2005).

Many new NFC products are the outcome of ‘pure’ R&D efforts and can also be described as ‘push’ development efforts. What is often motivating NPD is that natural fibers are readily available, cheaper than alternatives, or in some cases governments are interested in using these fibers as a way of eliminating them from waste streams or making their mother industries more competitive (Bowyer and Stockman, 2001). For example, the USDA Forest Service Forest Products Laboratory has studied many kinds of panel products produced from waste materials such as paper and rubber.

Two examples of a technological development which then had to find a market are described below.

11.7.1 Technology in search of a market I

The Commonwealth Scientific Industrial Research Organization in Australia developed the Scrimber process. The process forms a high-strength, engineered product using small-diameter trees that are crushed into strands. The strands are combined with adhesive and formed to desired shapes in a specialized steam-injection hot press.

In the 1980s a plant was built in Australia, but it experienced numerous problems and was eventually abandoned. A few years later, Georgia Pacific Corporation further explored feasibility in the United States, but it too eventually dropped the project. Most recently, Mississippi State University was selected as a site for a demonstration plant in the US South. Operations at the plant began in 2003. Currently, full-scale commercialization is planned with a plant to be sited near Meridian, Mississippi by Shuqualak Lumber Company. The process is now known as the TimTek process. Despite its long history and current momentum, the process has yet to be considered a commercial success.

http://www.nafi.com.au/timbertalk/index.html#results
http://www.cfr.msstate.edu/timtek/news.html
http://www.scrimtec.com/

11.7.2 Technology in search of a market II

After 7 years of R&D effort and numerous patents, in 1994 Andersen introduced Fibrex – a composite combining the desirable characteristics of wood with the low maintenance of vinyl. The company especially promotes the fact that Fibrex saves raw materials by utilizing waste wood-fiber from its own operations. Fibrex is a blend of wood-fiber and a specially formulated thermoplastic polymer. Today Fibrex is a large set of materials, each of which is customized for a particular window or door part. The company claims that the strength of Fibrex material allows narrower sash and frames and allows more glass area than competitors. Since Fibrex does not require finishing it is deemed to be low maintenance. The product has been a success in the marketplace and the company uses Fibrex in several product lines.

http://www.andersenwindows.com/
http://www.rbaohio.com/rep_windows/fiberx.aspx

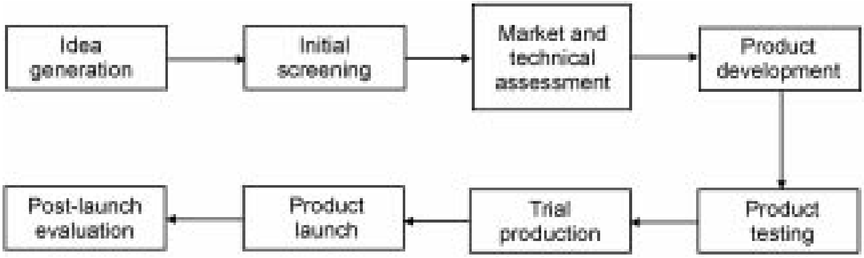
11.8 Market pull

Finally, there is market pull where products originate with the motivation of filling unmet customer or consumer needs and raw material decisions are made based on what is required to meet the need rather than what new or cheaper raw material might be used.

Modern NPD practices typically have a specific structure and follow a common pattern starting with idea generation and ending with product launch and evaluation (Fig. 11.3). Leading companies practice a formal NPD process that has key decision points for moving forward with development or killing the project. What most separates best and worst performers in NPD is how this process is implemented (Cooper *et al.*, 2004b).

For the overall NFC sector to move forward effectively it needs well-implemented innovation and NPD that is focused on customer needs. This is, in fact, one of the weakest NPD areas across industries as identified by Cooper *et al.* (2004b). They also suggest gaining insights directly from the customer are a characteristic of best NPD performing companies. In other words, the most successful companies are adept at gaining deep insights into customer needs and transferring those to the benefits offered by new products.

As outlined above, industry cultures differ. The wood products industry is not known for its expertise in NPD. In fact, it has been documented that firms in the sector generally do not utilize structured NPD processes (Hansen, 2006). As mentioned earlier, mature industries tend to focus on process innovation and cost reduction. When firms from other sectors, with more effective NPD, begin to compete with traditional industry companies, the latter are at a disadvantage. While it may be, for example, that some window and door manufacturers have a strong connection to the final consumer and are conducting their NPD in concert with final consumer knowledge, there is an array of companies that simply are not doing a good job with their NPD processes. Some of this stems directly from culture – a lack of focus on the need to develop new products in order to retain long-term viability. In other cases, the culture may be there, but there is insufficient investment in proper innovation management and new product development processes.



11.3 Generic steps in new product development.

11.9 Innovation management

The success of NPD (Cooper *et al.*, 2004b) and other forms of innovation within a firm is partially tied to culture (Crespell and Hansen, 2008). Culture is the 'norms, values, and beliefs that reinforce behaviors' within a firm (Hult *et al.*, 2004). Creating an innovation strategy has been identified as a best practice in guiding NPD (Cooper *et al.*, 2004a). This strategy, along with strong leadership, contributes to an innovative organizational culture. Developing a culture of innovativeness can be especially challenging for larger firms operating in mature industries. This is one reason it is common to see spin-offs of small units from larger companies (e.g., Trex and Mobil Corp.). It is easier to navigate the challenges of commercialization without the bureaucracy and history of the larger parent company.

Managerial attitude toward change has long been identified as influencing organizational innovation (Damanpour, 1991). Bull and Ferguson (2006) found that flexible management was important for successful commercialization of innovations and that a company culture supportive of collective learning was an important core competency. Managers often describe aspects of company culture that are not conducive to innovativeness (Hansen *et al.*, 2007). Other studies of manager perceptions have found similar results (AIC, 2004). Ultimately, successful innovation depends on a variety of factors including proactive management, selection of an appropriate business structure, a learning organization (again part of culture), and strategic communication and networking.

11.10 Future trends

In discussing future composites with grade school children, a former Oregon State University colleague, Dr Philip Humphrey, often held up a human femur bone and explained how one day NFC products would be possible in which fibers are oriented three dimensionally, thus providing the final product with very special properties. He envisioned structural NFC products that could be used in ultra-low-weight automobiles and even aircraft! Who knows whether this future will become reality. However, the following issues may have important impacts on the development of NFC products.

Nanotechnology presents myriad opportunities for improving NFC products. Addition of low levels of nanoscale fillers can increase strength and stiffness. The application of nanotechnology may lead to faster and more efficient drying of natural fibers, reducing overall production costs (Anonymous, 2005). Various nanotechnology-based coatings can serve to increase water resistance, reduce biodegradation and volatile organic compound (VOC) emissions, and enhance pest resistance, and will likely be used to increase surface hardness, wear resistance and even flame resistance (Roughly, 2005). Nanocrystalline cellulose is being explored for a variety of uses since it is stronger than steel and stiffer than aluminum (Simonsen *et al.*, 2003). Cellulose nanocrystals and nanofibrils are being explored for a wide range of applications including reinforcing agents in a variety of plastics (Simonsen *et al.*, 2003), membranes in the fuel ethanol process (J. Simonsen, 2007, personal communication), medical implants and other tissue engineering products (Joseph *et al.*, 2003; J. Simonsen, 2007, personal communication), barrier films for toxic industrial chemicals (Simonsen *et al.*, 2007a), and as a component of liquid crystal displays in televisions, cell phones, and computer monitors (Simonsen *et al.*, 2007a, b). This new field presents major opportunities for the use of NFC products in applications that are impossible with conventional NFC materials.

As technology improves to provide enhanced material and product characteristics, NFC products will become more diverse and enter markets as yet unexplored. Already, WPCs are found in a myriad of outdoor applications. The future will see increased use in structural applications and in products such as furniture, sporting goods, and other consumer products (Brosius, 2006).

Companies are increasingly relying upon positive environmental performance to differentiate themselves from the competition. Those companies that genuinely integrate sustainable development concepts into their business strategies are well positioned to capitalize on their efforts within markets that value environmental performance. There are many societal trends suggesting a positive future for ‘green’ companies. Recycling standards in Europe and Japan are driving the use of NFC products. Government legislation and corporate purchasing policies are also important drivers in creating markets for green products. Green building according to standards such as those developed by the US Green Building Council (Leadership in Energy and Environmental Design) is also driving interest in green products. While all of these factors are creating market potential for green products, final consumers still represent a small, direct demand for green products. Research on the topic of environmental certification of wood products suggests that only a small proportion of final consumers will pay more for an environmentally certified and labeled product, though a majority will choose a labeled product at equal cost (Anderson and Hansen, 2004). It can be expected that final consumers will continue to evolve towards an appreciation of environmentally preferable products. Life-cycle analysis and environmental ‘grading’ of products will likely develop to help consumers make intelligent, environmentally oriented buying decisions. Given the nature of NFC products, all of these factors should contribute to their increased demand.

The recent explosion of interest in biofuels presents a potential snag for future development of NFC products. A major factor in the incorporation of natural fibers has been the relative low cost of those fibers. As petroleum prices continue to climb, natural fiber feedstock prices will likely follow. In a related example, interest in corn-based ethanol has already dramatically boosted corn prices in North America. This development has had the unintended effect of increasing tortilla prices in Mexico, impacting the country's poorer population. This illustrates how the economics of NFC products can be affected by macroeconomic factors.

Finally, development of NFCs is in its infancy and the possibilities seem endless. Various experts are estimating high growth rates for the rest of this decade. While prognostication of market growth into the distant future is ill-advised, this appears to be a product category poised for long-term growth.

11.11 Sources of further information and advice

Consulting companies

- Applied Market Information, Ltd.
  http://www.amiplastics.com
- Business Communications Company, Inc.
  http://www.bccresearch.com
- NetComposites
  http://www.netcomposites.com
- Principia Partners
  http://www.principiaconsulting.com

Industry associations

- PlasticsResource.com
  http://www.plasticsresource.com/s_plasticsresource/doc.asp?TRACKID=&CID=40&DID=422
- TRplastic.com
  http://www.trhubnet.com/plastics/associations.nsf/queryassociations!Openform
- American Chemistry Council – Plastics Division (USA)
  http://www.americanchemistry.com/plastics/
- Association of Plastics Manufacturers (Europe)
  http://www.plasticseurope.org/Content/Default.asp?
- Deck Industry Association (USA)
  http://www.deckindustry.org/info_form2.htm
- North American Deck and Railing Association
  http://www.nadra.org/
- Timber Decking Association (UK)
  http://www.tda.org.uk/

Trade journals

- *Plastics Technology*
  http://www.ptonline.com

- *High Performance Composites & Composites Technology*
  http://www.compositesworld.com
- *Plastics Additives & Compounding*
  http://www.addcomp.com
- *Plastics News International Magazine*
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- *Professional Deckbuilder Magazine*
  http://www.deckmagazine.com/

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Part III

Performance of natural-fibre composites

12

Mechanical testing of natural-fiber composites

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12.1 Introduction

Natural fibers are important because of the renewed interest in their use in the development of low-cost 'eco-friendly' natural-fiber composites. Indeed, the mechanical properties of natural fibers containing cellulose in composite materials[1–3] are the subject of current international research efforts. This is especially important if such fibers are residues of agro industrial processes and if their raw properties are acceptable for composites, making their purification to pure cellulose unnecessary. Examples of such natural fibers are residues from the processing of pineapple,[4] banana,[5] rice,[6] coconut,[7] and sugar cane.[8] From society's point of view and owing to the pressure of environmental groups, leading to new environmental regulations, the production of natural-fiber composites has gained great attention, since it is recognized that natural fibers are cheap, readily available, and renewable. Natural cellulosic fiber–polypropylene composites are being used in the automobile industry, and their use is growing.[9]

The experimental characterization of composite materials has been an elusive topic, because it has been a continuously evolving one. The advent and widely expanding use of composite materials in more demanding applications such as highly loaded structures have forced a continuous revision of the subject of mechanical testing. This has resulted in the development of new test methods and the existing techniques continuously verified and re-examined. The principal difficulty arising in the testing of composites has also arisen when testing natural-fiber reinforced composites (NFRC) because of the inherent variability of the geometrical, physical, and mechanical properties of this type of fiber.

Research practice has far exceeded the test methods specified in standards for these new materials. The results found in the literature for the characterization of NFRCs have mainly relied on test protocols developed for metals, wood, polymers, and advanced fibrous composites. Issues such as the non-homogeneity and anisotropy of unidirectional, laminated, and multiply oriented reinforcement are also present in the newly developed NFRC. For this class of materials the usual terms of tensile, compression, shear, and bending tests have to be specified in terms of the direction of the load, and, in the case of continuous unidirectional fiber reinforced composites, the axes of symmetry of the material.

In the case of NFRC, the material anisotropy and microstructural peculiarities raise a number of issues that need to be considered. Then, the selection of the loading scheme for which the material characteristics are best related to the experimentally determinable values, selection of the analytical apparatus for experimental data processing, and estimation of the range of validity are of principal significance.

In this chapter, a review of the mechanical characterization of a natural-fiber reinforced thermoplastic–polymer matrix composite under testing modes such as tensile, compressive, flexural, and shear is performed. For this purpose, a model system consisting of high-density polyethylene (HDPE) reinforced with henequen fibers (*Agave fourcroydes*) was selected. Several studies have been conducted in the past few years for this fiber–matrix system and a detailed experimental program has been conducted to measure fiber–matrix adhesion, to determine interfacial chemistry and material properties, as well as the fiber-matrix interfacial failure model.[10,11]

12.2 Materials and experimental procedures

HDPE (Petrothene) extrusion grade was supplied by Quantum Chemical Inc. A melt flow index of 0.33 g/10 min was determined using ASTM standard D-1238-79 at 190 °C and a weight of 2160 g. A density of 0.96 g/cm^3 was determined using ASTM standard D-792-86 and benzene as an immersion liquid. The melting point (135 °C) was determined in a DSC-7 Perkin Elmer calorimeter. Henequen fibers with an average diameter of 180 μm and an average length of 6 mm, supplied by Desfibradora Yucateca, SA (Desfiyusa Co.) of Mérida, Yucatán, México, were used.

Sodium hydroxide and xylene, reagent grade from Técnica Química SA, were used for the various surface treatments. As a coupling agent, vinyltris (2-methoxy-ethoxy) silane (Silane A-172) from Union Carbide was used. Dicumyl peroxide from Polyscience was used as a catalyst to the reaction between the silane coupling agent and the polymer.

12.2.1 Fiber surface treatments

The nomenclature for the different henequen fiber surface treatments used is as follows: FIB refers to composites made with henequen fibers without any surface treatment; FIBNAPRE refers to composites made with henequen fibers treated with an aqueous NaOH solution and then pre-impregnated with dissolved HDPE; FIBNASIL refers to composites made with henequen fibers treated with an aqueous NaOH solution and then with a silane coupling agent.

12.2.2 Treatment with NaOH

The fibers were treated with a NaOH aqueous solution (2% w/v) for 1 h at 25 ºC, and then washed with distilled water until the water no longer indicated any alkalinity reaction. Subsequently, the fibers were dried at 60 ºC for 24 h.

12.2.3 Treatment with a silane coupling agent

A 1% of the silane coupling agent and 0.5% w/w dicumyl peroxide (Polyscience), weight percentage with respect to the fiber, were dissolved for their hydrolysis in a mixture of methanol–water (90/10 w/w) at 25 ºC. The pH of the solution was adjusted to 3.5 with acetic acid while continuously stirring for 10 minutes. Then, the fibers were immersed in the solution and left for 1 h under agitation and then dried at 60 ºC for 24 h and at 120 ºC for 2 h.

12.2.4 Surface pre-impregnation with a polyethylene diluted solution

The henequen fibers were pre-impregnated with a 1.5% w/w HDPE/xylene solution as follows: HDPE in powder form was dissolved in xylene at 110 ºC in a Kettle reactor by continuously stirring it. The fibers were placed in a stainless-steel basket and carefully immersed in the hot solution and stirred continuously for 1 h. Then, the basket was removed and the lumps of fibers were transferred to a flat tray and kept in an oven at 60 ºC for 24 h to allow evaporation of the solvent. The lumps of impregnated fibers were dispersed before blending them with the matrix.

12.2.5 Composites processing

A 20% v/v fiber content HDPE–henequen fiber composite was chosen in order to determine the effect of the different fiber surface treatments on its mechanical properties. The fibers were incorporated into the HDPE matrix, at 180 ºC using a Brabender Plasticorder intensive mixer, model PL330. The mixing process was performed as follows: first, one-half of the HDPE was placed inside the mixing chamber for about 1 min at 30 rpm; then the fibers were added over a period of 3 min and then the other half of the HDPE was added and the mixing speed was increased to 60 rpm for 5 min. The resulting material was compression molded at a pressure of 1 ton using a Carver laboratory press at a temperature of 180 ºC. The specimens for the mechanical test were obtained from these laminates according to ASTM standards.

12.2.6 Specimen conditioning and test conditions

The behavior of a specimen of a fiber reinforced composite in testing can be determined by its past history to a considerable extent. In the case of NFRC, the specimen preserves a ‘memory’ not only of the production method and the storage time, but of the conditions directly before the tests. Therefore, the reproducibility of the manufacturing conditions and of the environmental conditioning before tests and during testing must be ensured. In brief, time, temperature, and relative humidity should be recorded before and during the tests.

12.3 Mechanical testing

12.3.1 Tensile properties

Procedures

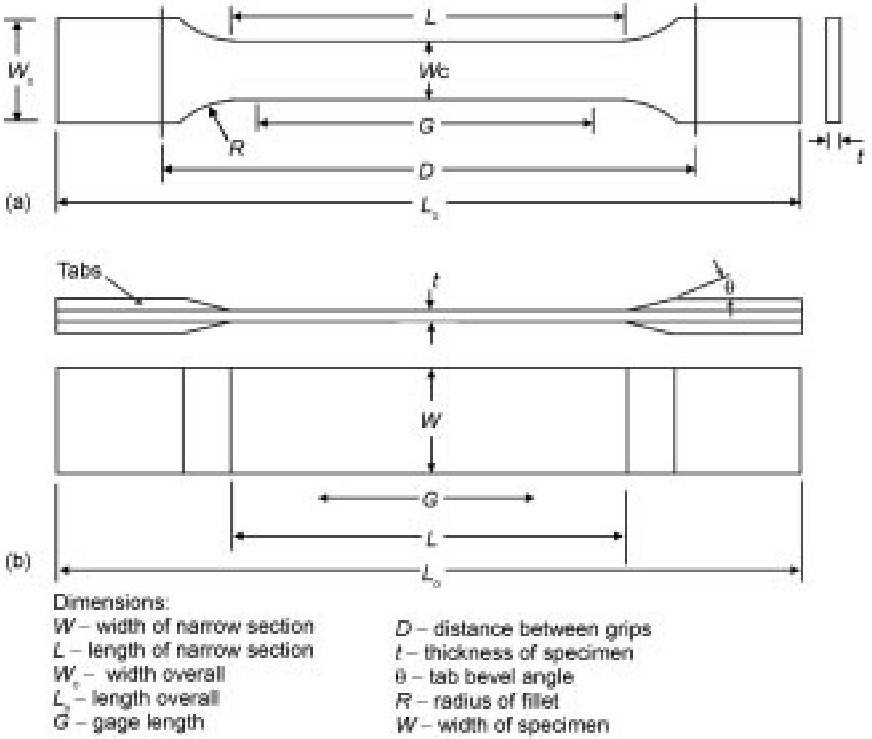
Uniaxial tension is the most widespread and most studied mechanical test for composites. The popularity of uniaxial tension as a test method is explained mainly by simplicity of accomplishment as ease of processing and analysis of test results. The characteristics obtained in uniaxial tension are both for material specification and for estimation of load-carrying capacity.

Despite its apparent simplicity, the tension test is subject to a series of problems due to the structure and properties of the fibrous polymeric composites. Then, the main difficulty of performing an acceptable tensile test typically increases as the orthotropy of the material increases, i.e. as the ratio of the axial stiffness (or strength) to the transverse stiffness (or strength) increases.

Proper introduction of the applied force to the test specimen is one primary concern. Mechanical clamping grips or pneumatically actuated grips are perhaps the most commonly used. The tensile force is introduced via shear at the clamp–specimen interface. This shear force is equal to the clamping force times the effective coefficient of friction at the interface. Care should be taken to avoid the roughness of the grips to penetrate the sample and produce premature specimen failure. The typical test-sample dimension for this type of test has been standardized in ASTM D638 and ASTM D3039[12,13] as shown in Fig. 12.1. In this case, the cross-head speed used for the type IV tensile specimens was 5 mm/min.

The elastic properties are determined from the stress–strain curve. The initial slope is equal to the elastic stiffness or modulus in the direction of the applied load:

$$E_1 = \frac{\Delta\sigma_1}{\Delta\epsilon_1}$$



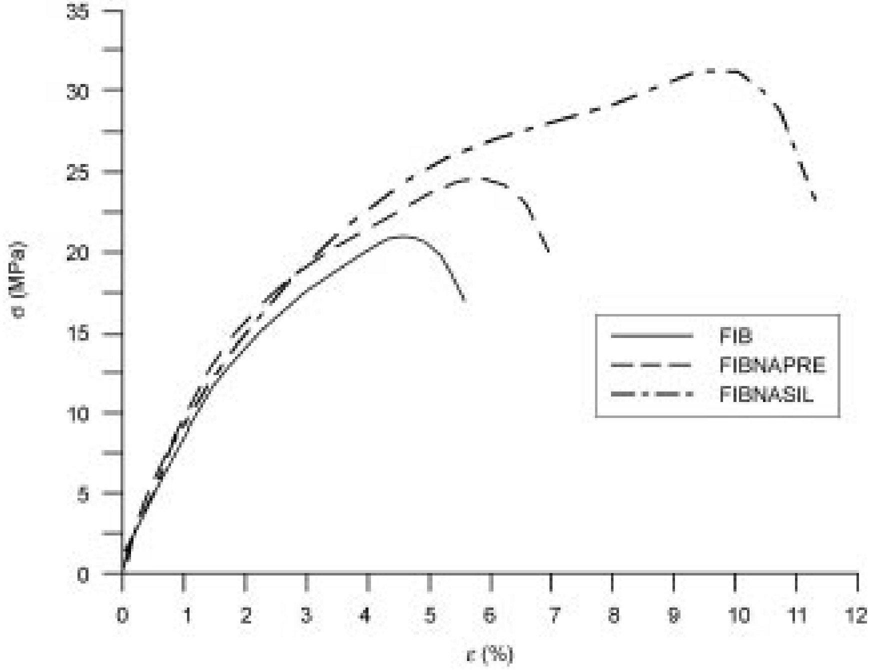
12.1 Typical tensile test specimen geometries: (a) dogbone shape sample according to ASTM standard D638; (b) straight-sided specimen according to ASTM Standard D3039.

If the material is orthotropic, then a second test should be performed with specimens fabricated at 90° with respect to the first material direction of symmetry to obtain the second stiffness value E_2. If the longitudinal and transverse strains ϵ_1 and ϵ_2 can be measured in these two material directions while performing the test, either by means of a biaxial extensometer or with strain gage rosettes, then the main Poisson ratio ν_{12} can be determined from the negative ratio $(-\epsilon_2/\epsilon_1)$.

The longitudinal and transverse tensile strengths, σ_1 and σ_2 are defined as the ultimate values of stress for the 0° and 90° tensile tests respectively. The ultimate strains ϵ_1 and ϵ_2 are the strains corresponding to σ_1 and σ_2. A representative example of stress versus strain curve for the henequen–HDPE composites is shown in Fig. 12.2.

Tensile test results

The tensile tests properties results for the short fiber henequen–HDPE composite are shown in Table 12.1. No noticeable effect on the elastic modulus was



12.2 Representative curves of tensile stress versus strain for henequen–HDPE composites.

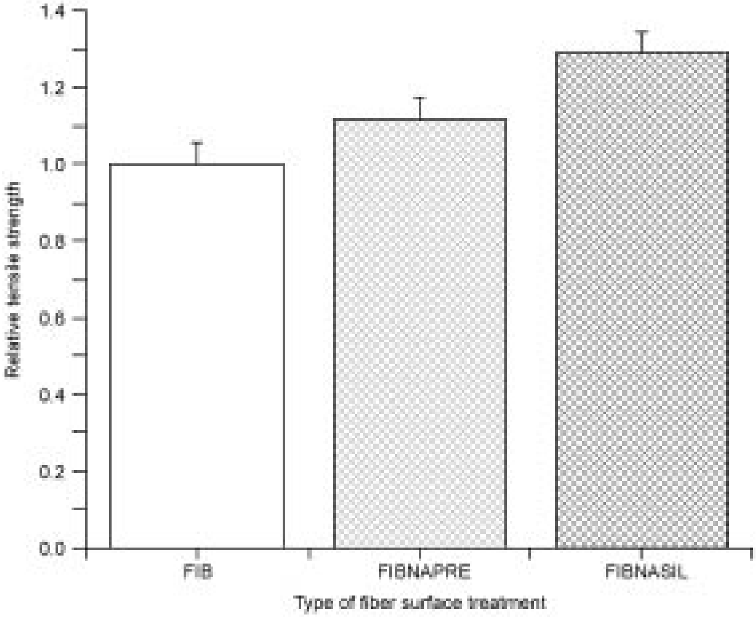
noticed as a result of the different interface interactions between the HDPE and the henequen fibers (see Table 12.1). It is well known that the fiber reinforcing effect is most efficient along the fiber axis orientation. However, the processing technique will dictate the final fiber orientation distribution, one of the most important characteristics that will determine the composite mechanical properties. The anisotropy expected from an injection-molded part is not the same as that found in extrusion- or compression-molded parts. Furthermore, the mathematical prediction of a composite stiffness is well established for common fiber orientation distributions, i.e. when the fibers are oriented parallel to the test direction; when the fibers are oriented in a transverse direction, perpendicular to

Table 12.1 Tensile properties of a short fiber henequen–HDPE composite for three different surface treatments

Type of fiber surface treatment	Tensile strength (MPa)	Elastic modulus (MPa)	Ultimate strain (%)
FIB	22.63 ± 1.06	855.01 ± 59.87	5.29 ± 0.76
FIBNAPRE	24.40 ± 1.9	910.18 ± 61.23	5.66 ± 0.64
FIBNASIL	29.14 ± 1.72	835.20 ± 58.65	9.01 ± 1.17

the test direction and when the fibers are randomly oriented. The formulas developed for these different microstructures have been developed for engineering fibers, which, because of the high stiffness, will remain straight after processing, unlike natural fibers, that do not remain straight after processing because their high flexibility. It has been shown that the mercerization of natural fibers greatly improves their resin pick-up or wettability, contributing to a 21% rise in the mechanical properties of the composite.[14] It is believed that this alkaline treatment results in an improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking, hence promoting more resin/fiber interpenetration at the interface.

The tensile strength of the HDPE–henequen fibers composite relative to the tensile strength of the composite made with untreated fibers (FIB) is shown in Fig. 12.3. When the fiber surface was modified with an aqueous NaOH solution followed by a resin pre-impregnation process (FIBNAPRE), a marginal improvement of the tensile strength of the composite of approximately 11% with respect to the untreated fiber composite was observed. Thus, the fiber-surface modification with the alkaline solution followed by a pre-impregnation process resulted in a better fiber–matrix interaction, that is, a better fiber–matrix mechanical interlocking. However, when the same alkaline surface-modified fiber was treated with a silane coupling agent (FIBNASIL), a 30% increase in the relative tensile strength was observed. This increment in the tensile strength



12.3 Relative tensile strength for a HDPE/henequen fibers (80:20 v/v) composites for three different fiber surface treatments.

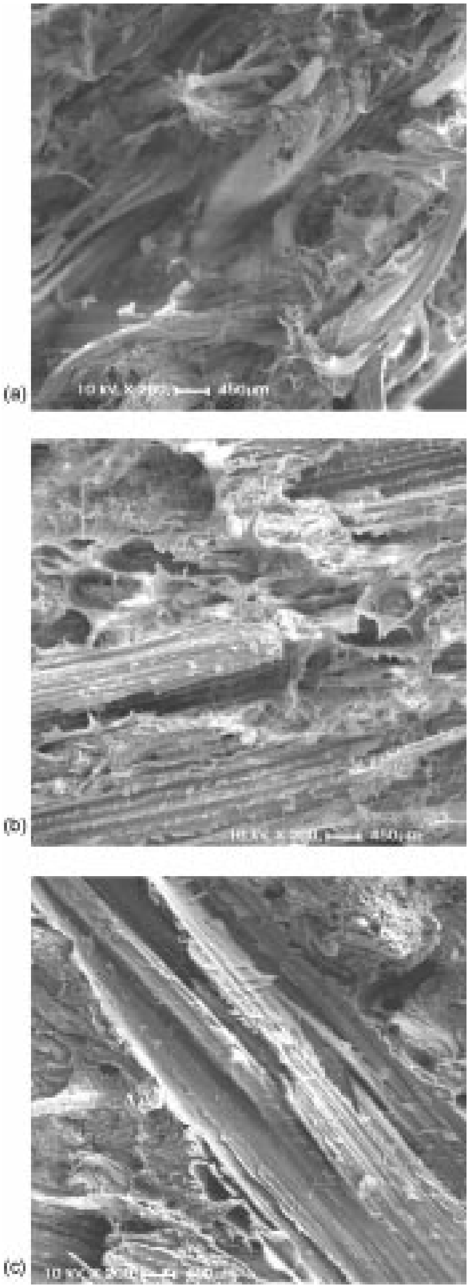
is attributed to chemical interactions between the exposed cellulose fibers and the HDPE.

Tensile failure modes

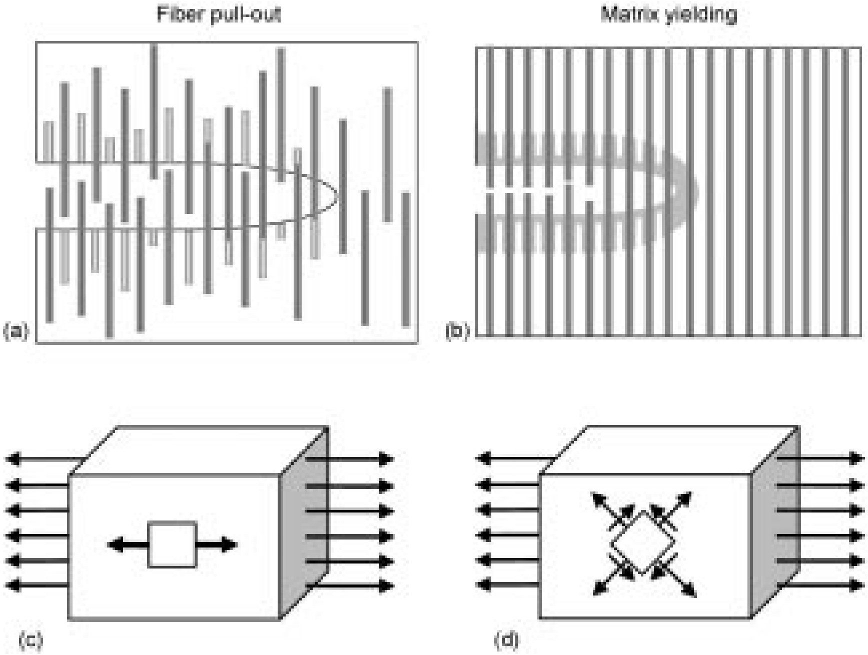
Figure 12.4 shows representative photomicrographs of fracture surfaces of samples subjected to tensile stresses, for the untreated, and those treated with a NaOH aqueous-dilute solution and a matrix pre-impregnation or a silane-coupling agent. The surfaces of the untreated fibers (FIB) are completely free of any matrix material. This is an indication of fiber–matrix interfacial failure followed by extensive fiber failure and the ensuing fiber pull-out off the matrix. Furthermore, the matrix shows considerable tearing. The fibers subjected to the alkaline aqueous solution plus matrix pre-impregnation also show interfacial failure but, in this case, there is no indication of fiber pull-out but, rather, it shows massive failure of both fibers and matrix. The failure mode observed on the fibers indicates fiber splitting and tearing and this is attributed to a better interaction with the matrix, but still such interaction is a frictional or mechanical interlocking type. There were also traces of matrix material adhering to the fibers, again indicating a closer contact between the fiber and the matrix, and, therefore, a better wetting of the fibers. It is believed that the matrix solution was able to fully penetrate the fiber and upon failure of the laminate, it showed tearing and shearing. When the fibers were silane treated, the failure surface indicates a massive matrix failure and the fibers are completely coated with the matrix, and there are no indications of fiber pull-out off the matrix.

It can be said from these failure modes that the increase of the tensile strength of the composite is an effect of the fiber–matrix interface increases. It can also be said that a low fiber–matrix adhesion results in a failure mode dominated by fiber pull-out and matrix failure. As the interfacial shear strength (IFSS) increased, the failure mode is more like matrix tearing and flow and fiber tearing. The feeble resistance of short fiber composites to stresses, especially those oriented transverse to the fibers, is due mainly to the relatively low strength of the matrix. This is especially so with polymer matrices, where low moduli can also contribute to low properties. Furthermore, when the fiber–matrix interface is weak, the interface can dominate the properties of the composite if loads are applied in a transverse direction to the fibers. In this case, for HDPE, with strength of 25.0 MPa, the effect of the interface strength is seen to have an effect and that an upper bound for the composite tensile strength is imposed by the properties of the matrix.

Failure of the tensile test sample is assumed to occur in a plane transverse to the applied load. However, observation of the failure surfaces and the micro-photographs indicates that for increasing degree of adhesion between fiber and matrix, the failure mode changes from fiber pull-out and matrix yielding and/or tearing to a shear-type failure as depicted in Fig. 12.5(a) and 12.5(b). Also, for



12.4 Photomicrographs of fracture surfaces of a HDPE/henequen–fiber (80:20 v/v) composite subjected to tensile stresses: (a) FIB, untreated henequen fibers; (b) FIBNAPRE fibers treated with aquous NaOH solution and a pre-impregnation with dilute resin solution; and (c) FIBNASIL, fibers treated with NaOH aqueous solution silane and a coupling agent solution.

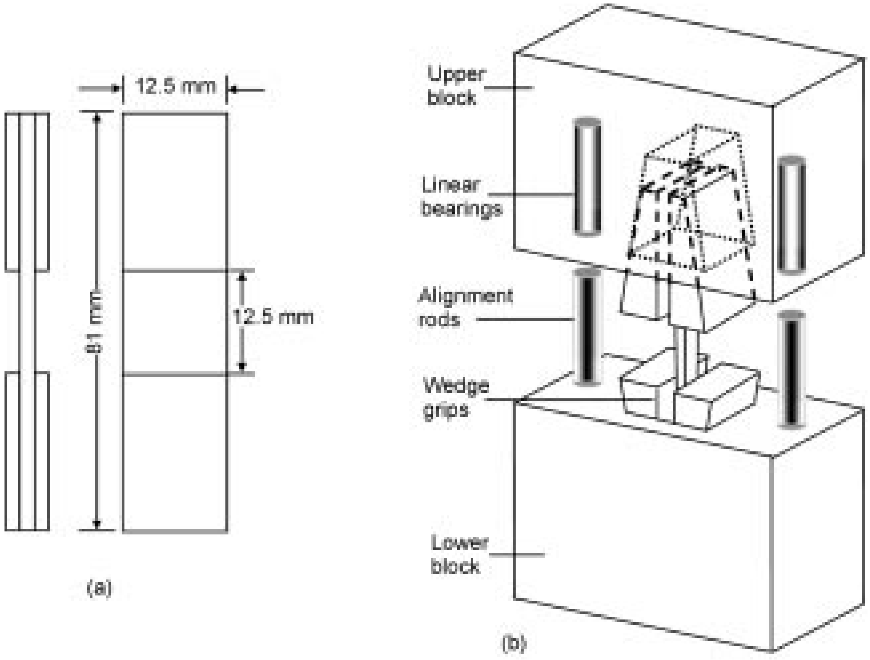


12.5 (a) Fracture of a composite with low fiber–matrix adhesion showing fiber pull-out; (b) fracture of a composite with high fiber–matrix adhesion showing matrix yielding and fiber failure; (c) tensile stress at normal planes; and (d) equivalent stresses at 45° with respect to load direction for a specimen subjected to normal tensile loads.

low stiffness materials, yielding of the matrix together with fiber splitting are indicative that the shear stress component is also responsible for failure. This is understandable if it is considered that for a plane located at some angle to the tensile load direction there are also shear stress components as shown in Fig. 12.5. As depicted in Fig. 12.5(c) and 12.5(d), the equivalent stress of a tensile stress for a plane rotated 45° with respect to the direction of loading is represented by shear and normal stress components. Shear-induced failure is very strongly influenced by the matrix and then it can be said that shear-induced failure is matrix dominated, with some possible contribution from fiber failures when these cross the crack plane.

12.3.2 Compressive properties

Compression testing of fibrous polymeric composites is a widespread form of testing. The apparent simplicity of loading, measurement of the load and deformation, and the simplicity of the analytical apparatus are attractive. Nowadays there are a few standards (ASTM D 695 and ASTM D 3410[15,16]) to determine compression properties of polymers and composites. In general, all



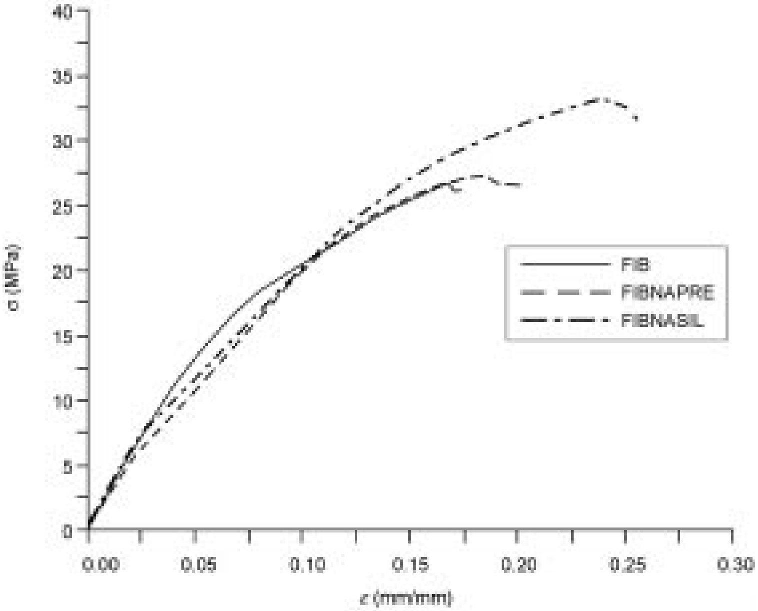
12.6 Typical test sample dimensions and fixture for compressive properties.

the basic relations concerning tensile testing of fibrous polymeric composites are retained in compression, with due consideration taken of the direction of deformation. At the same time, tension and compression differ qualitatively more than the respective tests of isotropic materials.

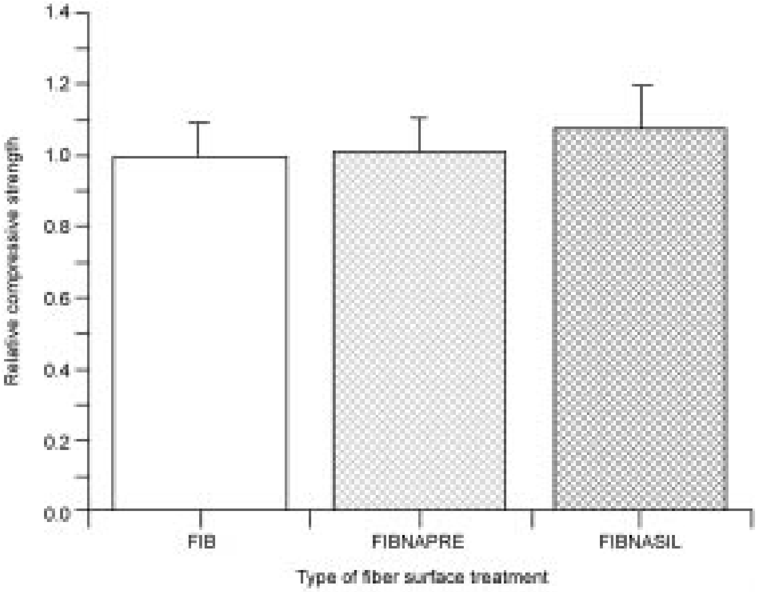
In this case, compression tests were performed using an Instron Universal Testing Machine Model 1125, equipped with a 500 kg load cell, after conditioning at 25 °C according to the standard ASTM 3410. Figure 12.6 shows typical test sample dimensions according to the developments of the Illinois Institute of Technology Research Institute (IITRI) incorporated to ASTM D 3410 standard.

Figure 12.7 shows representative stress–strain curves from the compression tests. The compressive tests properties results for the short fiber henequen–HDPE composite are shown in Table 12.2. Figure 12.8 shows relative compressive strength values for the henequen–HDPE fibers.

The elastic properties are also determined from the stress–strain curve using the same analytical expressions used in tensile testing. The initial slope is equal to the elastic stiffness or modulus in the direction of the applied load. Depending on the anisotropy of the material, then tests in two orthogonal directions have to be performed. The mechanical properties to be determined from these tests are the longitudinal and transverse moduli, E_1 and E_2, the ultimate strains ϵ_1 and ϵ_2 and the compressive strengths σ_{1c} and σ_{2c}.



12.7 Representative stress–strain curves from the compression tests for a HDPE–henequen fiber (80:20 v/v) composite.



12.8 Relative compressive strength for a HDPE–henequen fiber (80:20 v/v) composite for three different fiber surface treatments.

Table 12.2 Compressive properties of a short fiber henequen–HDPE composite for three different surface treatments

Type of fiber surface treatment	Compressive strength (MPa)
FIB	30.00 ± 2.70
FIBNAPRE	30.41 ± 2.71
FIBNASIL	30.41 ± 2.72

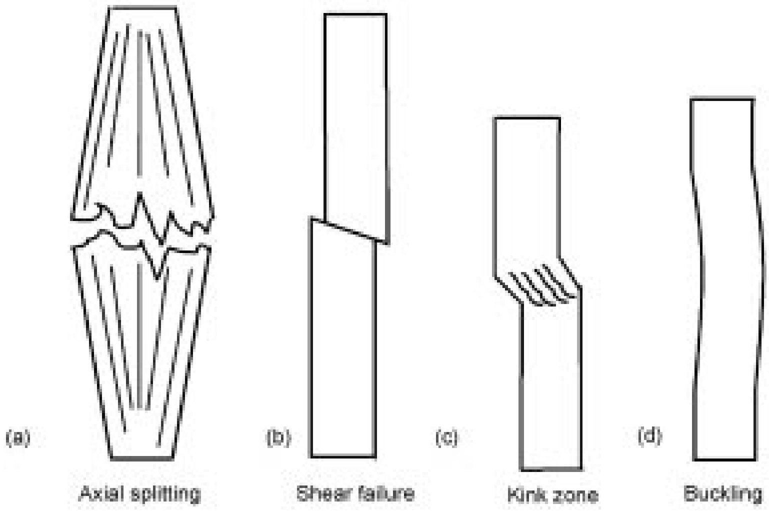
Peculiarities of the deformation in compression

In general, a compression stress–strain curve of fibrous polymeric composite material is non-linear. However, in loading in the direction of reinforcement, the stress–strain curve is practically a straight line (with the usual measurement errors) from the start of the loading up to failure of the specimen. Sometimes, characteristic breaks are also observed in the stress–strain curve just as in tensile tests. If such a break appears shortly before failure of the material, it is explained by a loss of stability of part of the reinforcing material.

Three basic failure modes of specimens are usually observed.[17] For low-modulus matrix materials, local buckling, that is, initial waviness of the reinforcing fibers, markedly affects the strength of the material under compression. In testing medium-stiffness matrix composites, transverse rupture of the material is due to the difference between the Poisson ratios of the material components and to non-uniform distribution of transverse strains over the specimen length leading to local buckling of the fibers. The critical load will be determined by the characteristics of the already partly distorted material. The third failure mode for rigid matrix materials, the composite fails in compression (shearing of the fibers at an angle of 45°) without any buckling of the fibers. These three failure modes are the principal ones, but they can be accompanied by a series of other phenomena such as inelastic and non-linear behavior of the fibers and especially of the matrix, etc., thus making very difficult to establish the failure mode (see Fig. 12.9). Figure 12.10 shows photographs of the failure mode of the specimens. The main failure mode observed was local buckling.

12.3.3 Flexural properties

As mentioned above, pure, uniform tension, compression, and shear loading must be applied individually to establish the fundamental strength and stiffness properties of a composites material. A flexure test, i.e. bending of a beam, typically induces tensile, compressive and shear stresses simultaneously. Thus it is not a practical means of determining the fundamental properties of a composite material.[18,19] However, owing to their simplicity, bending (flexural) tests of bars with a straight axis are very widespread. In bending, the modulus of



12.9 Basic failure modes of specimens subjected to axial compressive loads.

elasticity E_1^b, and the strength according to normal stress σ_1^{bu} and in a configuration of a short beam, the shear strength τ_{12}^{bu} can be determined. Figure 12.11 shows a schematic of the sample geometry and loading configuration.

The flexural tests were performed using an Instron Universal Testing Machine Model 1125, equipped with a 500 kg load cell, after conditioning at 25 ºC according to the ASTM standard D790, a three-point bending configuration and specimens with nominal dimensions of 50 × 25 × 2 mm^3, a span of 32 mm and a cross-head of 1 mm/min were used.

The tensile and compressive stresses at the surfaces of the beam at any location where the ending moment is a maximum can be calculated from simple beam theory[20] as:

$$\sigma_{\max} = \frac{M_{\max}(h/2)}{I}$$

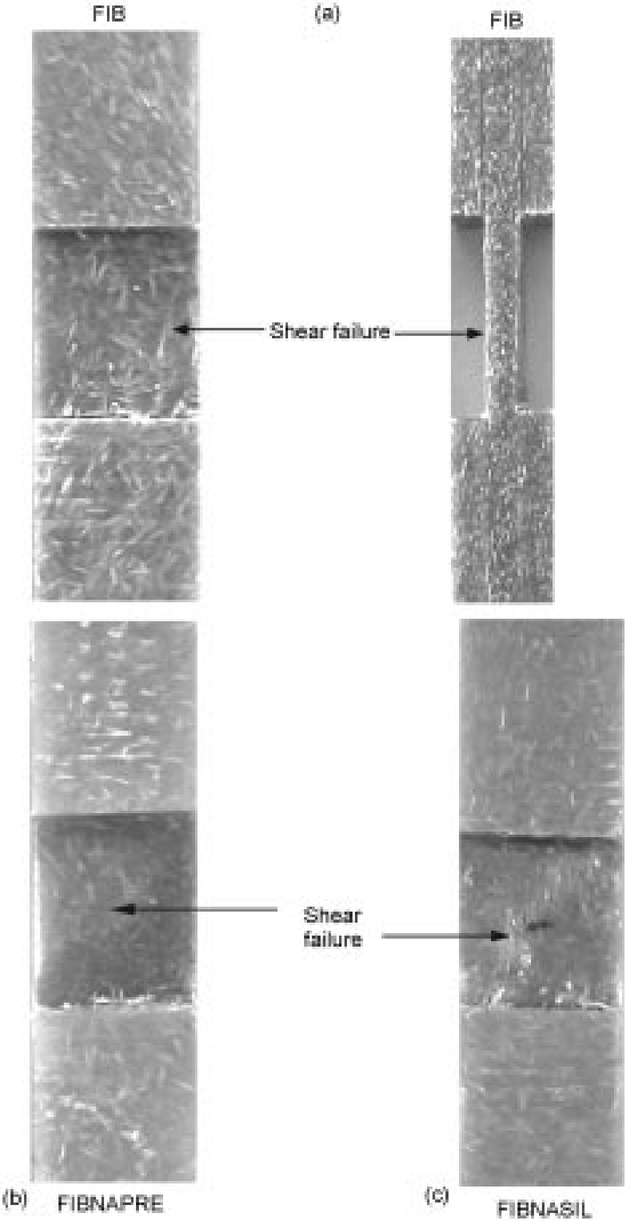
where $M_{\max}$ is the maximum bending moment, h is the thickness of the beam, and $I = wh^3/12$ is the moment of inertia of a beam of rectangular cross-section of width equal to w.

For the three-point bending configuration, the maximum bending moment at the midlength of the beam is given by $M_{\max} = PL/4$, then

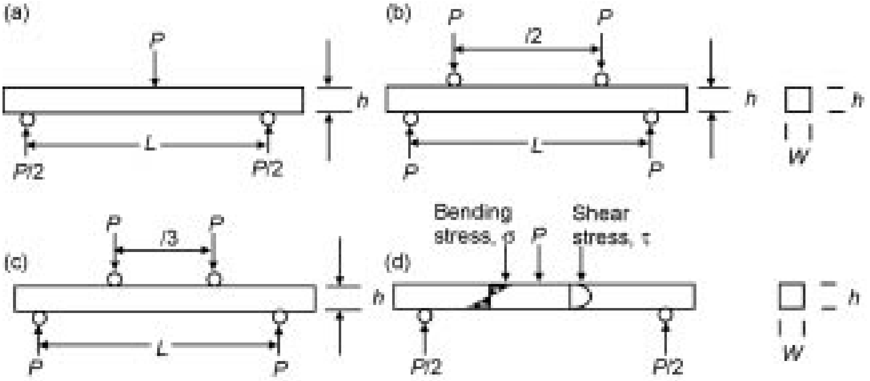
$$\sigma_{\max} = \frac{3PL}{2wh^2}$$

The flexural modulus is calculated from a plot of load, P vs. center deflection, δ, as:

$$E_f = \frac{L^3}{4wh^3}\frac{\Delta P}{\Delta \delta}$$



12.10 Photographs of compression failure for HDPE–henequen fiber (80:20 v/v) (a) FIB, untreated henequen fibers; (b) FIBNAPRE fibers treated with aqueous NaOH solution and a pre-impregnation with dilute resin solution; and (c) FIBNASIL, fibers treated with NaOH aqueous solution silane and a coupling agent solution.



12.11 Schematic of flexure test loading configurations: (a) three-point loading; (b) quarter-point loading; (c) third-point loading; and (d) stresses in the beam subjected to three-point flexure.

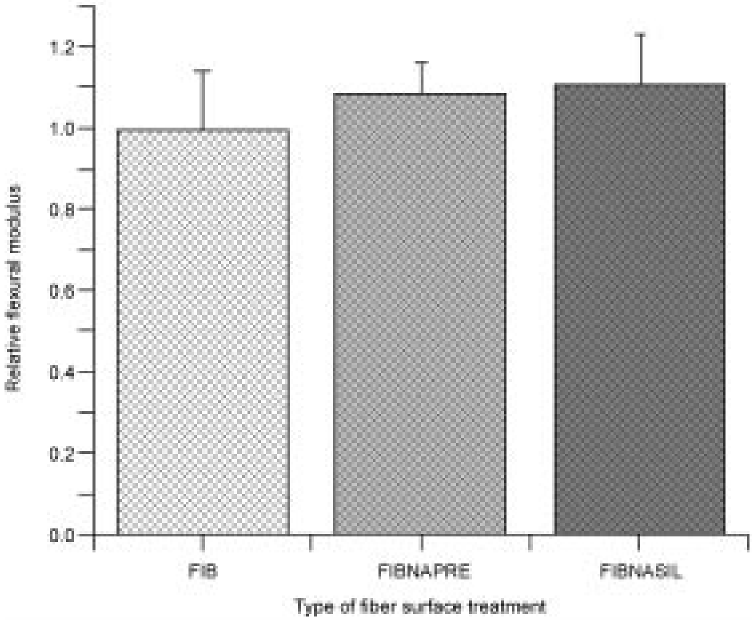
This relation, however, assumes that the shear deformation is negligible.

Flexural behavior

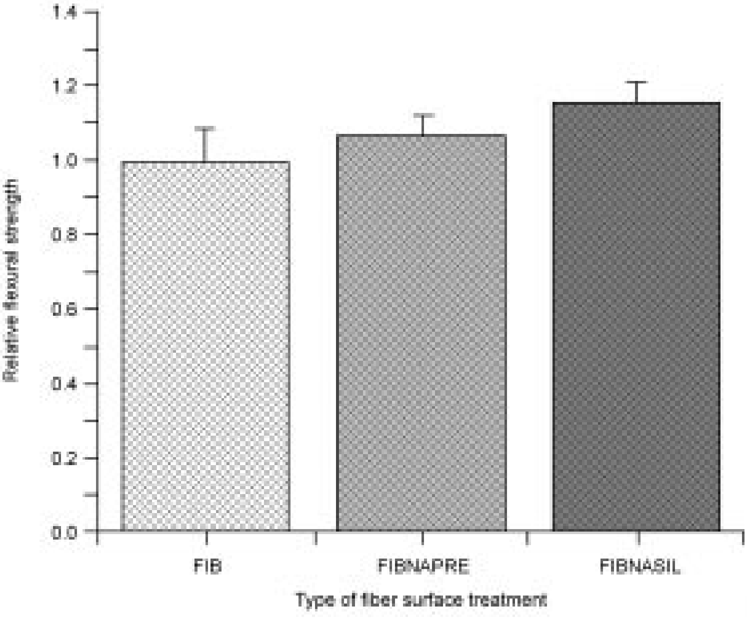
The flexural tests properties results for the short fiber henequen–HDPE composite are shown in Table 12.3 and the relative flexural modulus and strength of the HDPE–henequen fiber composites plotted again as a function of the different fiber surface treatments are shown in Figs 12.12 and 12.13 respectively. The observations made earlier for the tensile strength on the effect of fiber–matrix adhesion are also seen clearly here. The fiber surface treatments had a marginal effect on the flexural modulus, similar to the observations made for the tensile properties. The flexural strength improved by approximately a 3% just by modifying the topography of the fiber by an alkaline aqueous solution. The increment of interfacial area of contact was beneficial to the flexural strength (see Fig. 12.13). Such relative increase was doubled when the fibers were pre-impregnated with the matrix–liquid solution even when the fiber had no surface modification by any alkaline treatment. When these two surface treatments are combined, an additional increase is observed for the flexural strength. This indicates that better contact and

Table 12.3 Flexural properties of a short fiber henequen–HDPE composite for three different surface treatments

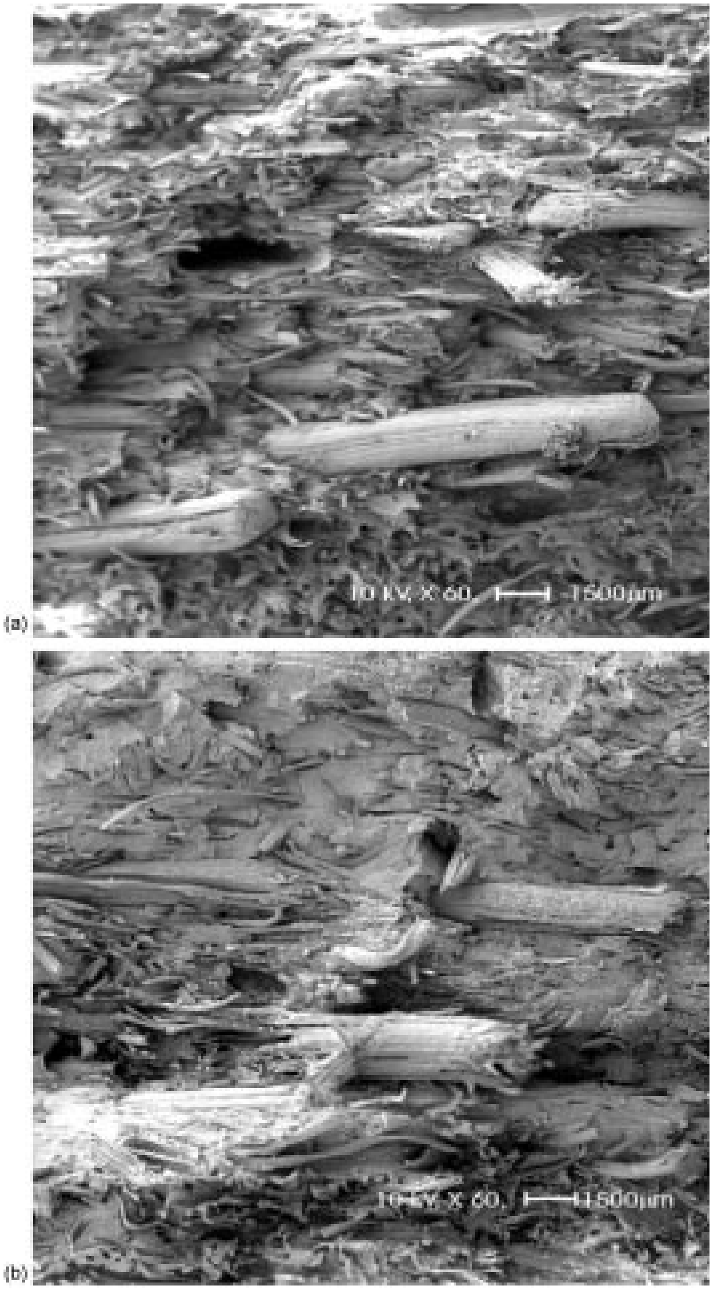
Type of fiber surface treatment	Flexural strength (MPa)	Flexural modulus (MPa)
FIB	39.02 ± 3.32	1902.25 ± 381.27
FIBNAPRE	41.85 ± 2.13	2071.22 ± 139.84
FIBNASIL	45.45 ± 1.93	2114.60 ± 364.20



12.12 Relative flexural modulus for three HDPE–henequen fibers (80:20 v/v) composites for three different fiber surface treatments.



12.13 Relative flexural strength for three HDPE–henequen fibers (80:20 v/v) composites for three different fiber surface treatments.



12.14 Photomicrographs of fracture surfaces of a HDPE–henequen fiber (80:20 v/v) composite subjected to flexural stresses: (a) FIB, untreated henequen fibers; (b) FIBNAPRE fibers treated with aqueous NaOH solution and a pre-impregnation with dilute resin solution; and (c) FIBNASIL, fibers treated with NaOH aqueous solution silane and a coupling agent solution.

the increase in area of contact between the fiber and the matrix are improving the level of adhesion, probably by the incorporation of a mechanical component of adhesion for the matrix–fiber interfacial strength. When the fiber is treated with the coupling agent, a larger increase in the flexural strength is also observed (13% approximately). When the chemical and the mechanical components of the adhesion are combined, a larger increase of strength is observed (20%).[10,11]

Flexural strength and failure modes

The failure modes are discussed to further clarify the relationship between fiber–matrix adhesion and the flexural strength. The specimens for FIB (Fig. 12.14(a)) shows no trace of matrix material on both between and around the fibers. The fiber treated with NaOH and pre-impregnated with the matrix (Fig. 12.14(b)) show traces of polymer still adhering into and around the fiber. The fiber failure mode even shows the cellulose microfibrils still surround by the polymer. When the fiber was treated with NaOH and the coupling agent, the failure mode changed to matrix failure and the fibers are still held by the matrix (Fig. 12.14(c)). A considerable amount of fiber tearing was also noticed. Similar observations about the failure micro-mechanisms, the influence of fiber–matrix interaction, and direction of the stress component made for tensile failure can also be said about the flexure results.

12.14 Continued

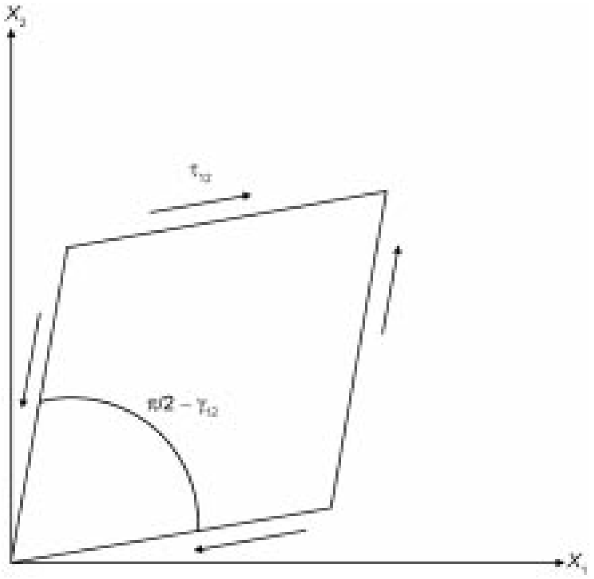
12.3.4 Shear properties

Polymeric composites with a fibrous structure have a typical shortcoming – their low shear resistance – especially in planes where the properties are determined by the matrix and the interfacial shear strength (IFSS). Low shear resistance refers to both low shear modulus and low shear strength. The main difficulty in determining shear properties of a material is to provide pure shear in the specimen and thereby assure sufficient precision of the method and the processing of experimental results. Figure 12.15 defines the in-plane shear stress τ_{12} and shear strain γ_{12}.

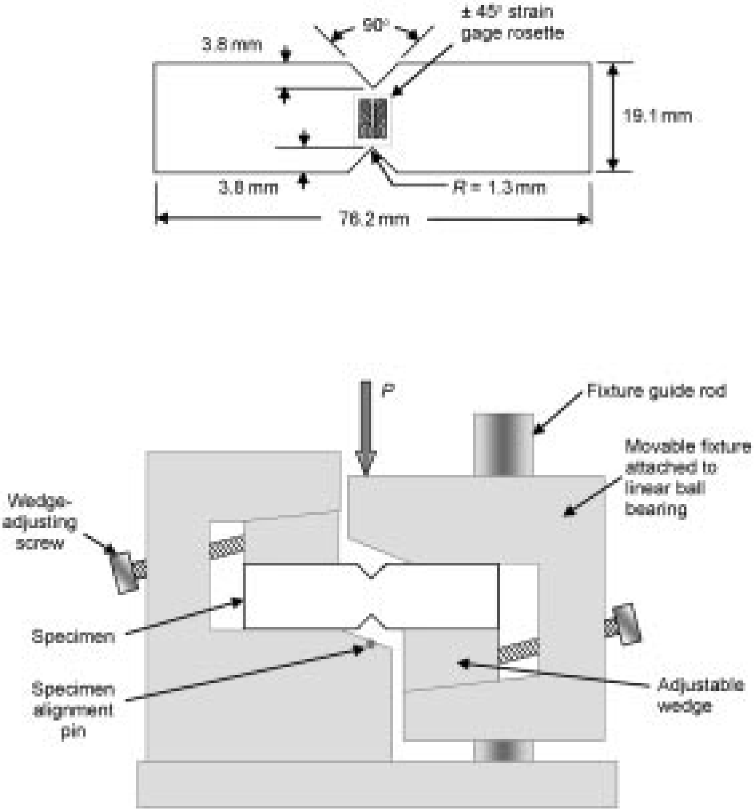
The Iosipescu shear test method is a popular shear test. The configuration and specimens are shown in Fig. 12.16. This test method is described in ASTM D-5379 standard[21] using a Wyoming Shear Test Fixture adapted to a universal testing machine. In this case the tests were performed after conditioning at 25 °C. The Iosipescu shear test specimens were cut from the laminates obtained previously, and the dimensions of specimens were 76 mm in length, 19 mm in width, and 2 mm thick; the distance between the two 90 notches was 12 mm. The cross-speed used was 0.5 mm/min. The average shear stress across the notched section of the specimen is calculated using the simple formula

$$\tau_{12} = \frac{P}{A}$$

where P is the applied force and A is the cross-sectional area of the specimen between the notches.



12.15 Definition of the in-plane shear stress τ_{12} and shear strain γ_{12}.



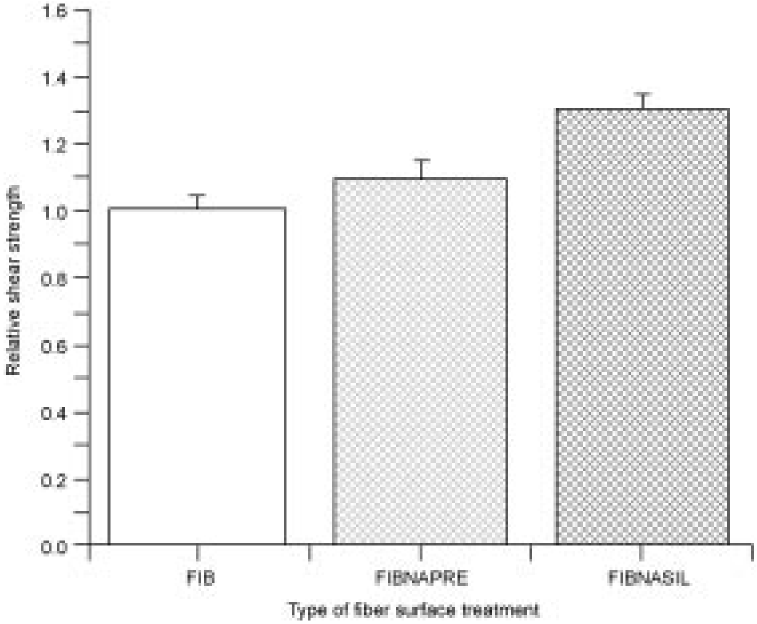
12.16 Configuration and specimen for the shear test method as described in ASTM D-5379 standard using a Wyoming shear test fixture.

Shear strength and failure modes

The shear test properties results for the short fiber henequen–HDPE composite are shown in Table 12.4 and the relative shear strength of the HDPE–henequen fiber composites plotted again as a function of the different fiber surface treatments is shown in Fig. 12.17. Similar observations made earlier for both the

Table 12.4 Shear properties of a short fiber henequen–HDPE composite for three different surface treatments

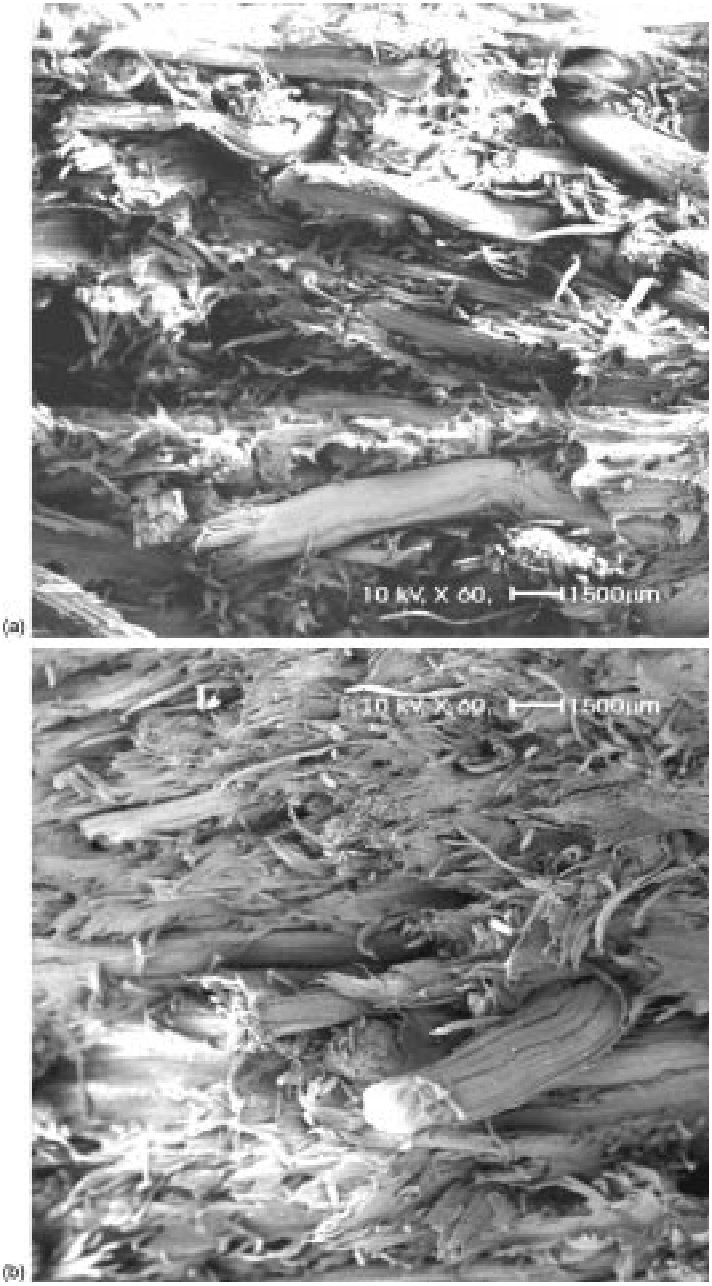
Type of fiber surface treatment	Shear strength (MPa)
FIB	14.39 ± 0.61
FIBNAPRE	15.81 ± 0.80
FIBNASIL	18.88 ± 0.41



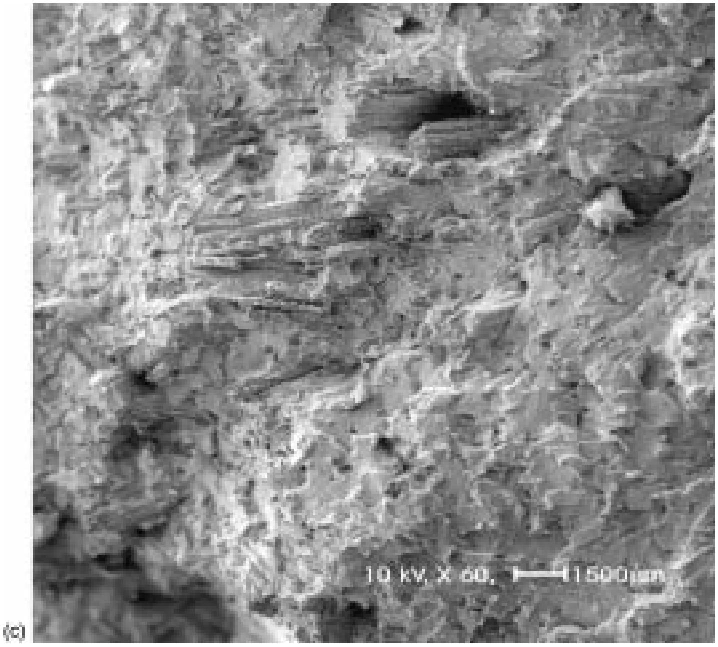
12.17 The relative shear strength of three HDPE–henequen fiber (80:20 v/v) composites for three different fiber surface treatments.

tensile and flexural strength on the effect of fiber–matrix adhesion are evident here. However, the effect of increased fiber surface area of contact with the matrix seems to have a larger effect on the shear strength. Fiber pre-impregnation by itself has no great contribution to the shear strength. The largest increase in shear strength is observed for the fiber treated with both the aqueous alkaline solution and the silane coupling agent. From previous observations of the tensile and flexural properties for this fiber surface treatment combination, increments of approximately 20% and 30% respectively were obtained. In the case of the shear strength, such increase is of the order of 25%.

Observations of failure surface of Iosipescu shear test samples further clarifies the importance of fiber adhesion on shear strength results. Figure 12.18 shows a series of scanning electron microscope (SEM) photographs for the composite for 20% v/v fiber content and tested under shear loads. In Fig. 12.18(a), the untreated fibers appear to be free of any matrix material adhering to them, thus indicating poor fiber–matrix adhesion. In Fig. 12.18(b) the fibers treated with the aqueous NaOH solution and then are pre-impregnated, more tearing of the fibers can be observed, together with some cavities left by the pulled-out fibers. Despite this, there is some fiber pull-out but the fiber is coated with the matrix polymer. Another feature of this fiber treatment is on the matrix failure mode, because appreciable shear yielding rather than tearing is observed. It can be inferred that mechanical interlocking and friction are responsible for



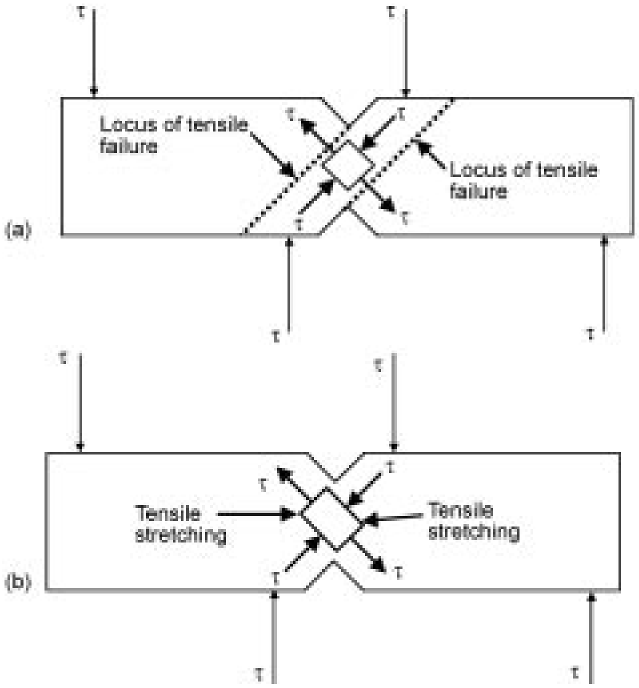
12.18 Photomicrographs of fracture surfaces of a HDPE–henequen fiber (80:20 v/v) composite subjected to shear stresses: (a) FIB, untreated henequen fibers; (b) FIBNAPRE fibers treated with aqueous NaOH solution and a pre-impregnation with dilute resin solution; and (c) FIBNASIL, fibers treated with NaOH aqueous solution silane and a coupling agent solution.



12.18 Continued

the observed composite strength increment. Figure 12.18(c) shows the failure surface for the composite with fibers treated with the aqueous NaOH solution and the silane coupling agent. It can be observed that the fibers are still coated with the matrix and that the matrix failed by shear yield flow and tearing from the fiber. If the matrix failure mode of the untreated fiber composite is compared with the pre-impregnated fiber composite, it can be seen that it changes from tearing mode to shear yielding. Then, from these matrix failure modes, it can be said that there exists a higher force transfer capability at the fiber–matrix interface in the composites with fibers treated by pre-impregnation and a silane coupling agent. It should be pointed out that the matrix properties are an upper bound for the composite strength, especiallly when the fiber–matrix adhesion is strong. In this case, such upper bound is given by the yield strength of the matrix.

Again, the degree of fiber–matrix adhesion is seen to have an influence on the failure modes observed under shear. Also, as depicted in Fig. 12.19, even when the plane joining the notches in the sample is subjected to a pure shear load, in a plane located at an angle of 45°, the stress components are represented by tensile and compressive stresses.[22] That is, even though shear strains can be generated, true shear failure does not occur. In the case of brittle polymers, tensile failure would occur in a plane located at 45° (Fig. 12.19(a)). In the case of ductile polymers, the resulting deformation is stretching at the same plane oriented at



12.19 Iosipescu test on neat polymers: (a) brittle polymers break at 45°, while (b) ductile polymers stretch at 45°.

45° (Fig. 12.19(b)). When the last loading mode prevails, on the specimen failure surface is a notable fine leaf-like structure in the polymer, called shear hackle. This develops through the joining up of cavities produced by the tensile component of the shear stress, as shown in Fig. 12.19. The process requires some opening of the failure crack, so it is not pure shear. We therefore have shear-induced failure, but no true shear strength for a composite, as for the polymers themselves. Shear-induced failure is very strongly influenced by the matrix, as shown in Fig. 12.19. From the Iosipescu test some of the difference between the apparent matrix shear strength and that of the composite may be due to fibers crossing the fracture plane. These fibers may be broken or torn in the test, and examples of such broken fibers are evident in Fig. 12.18(c). We conclude that shear-induced failure is matrix dominated, with some possible contribution from fiber failures, when these cross the crack plane. There is, however, no such thing as a composite shear strength. The failure stress depends very strongly on the influence of the fibers, and the goemetric details of the test in relation to the fibre geometry.

12.4 Conclusions

An extensive study has been conducted on a model system consisting of high-density polyethylene reinforced with henequen fibers (*Agave fourcroydes*). Several studies were conducted in the past few years for this fiber–matrix system, and detailed information of the fiber–matrix adhesion, the interfacial chemistry and average material properties, as well as the fiber–matrix interfacial failure model, was gathered.

A mechanical testing program that included loading modes in tension, compression, flexion, and shear was reviewed and the most important aspects of each test mode were revised. What became evident was that the difficulty in establishing a pure loading mode to obtain a particular answer was enhanced by the complexity of the material's microstructure, failure modes of both fiber and matrix and the interfacial fiber–matrix conditions, and the geometry of the sample. Also, despite the fact that there is a variety of methods of experimental determination of the elastic constants, there is no economical method of testing of all types of polymeric fiber reinforced composites for simultaneous determination of the elastic constants as well as the strength values. Furthermore, specimen shape and dimensions depend greatly on the purpose of the test.

From these test methods, however, it is possible to establish the structure–property relationship between the fiber–matrix adhesion levels and the strength and failure modes for each loading mode. In order to detect the major failure modes, representative fracture surfaces of the specimens must be examined using a scanning electron microscope.

12.5 References

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13

Mechanical performance of thermoplastic matrix natural-fibre composites

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13.1 Introduction

Ecological concerns and the depletion of fossil energy resources have motivated pursuit of alternative ‘green’ materials. This has promoted natural-fibre composites to the priority lists of many companies in both industrial and developing countries. Although natural materials have been around for millennia, the current development stage is fundamentally different from traditional usage. Natural-fibre composites are being considered as high-tech materials meant to replace conventional (synthetic) composites in high-performance applications. There are a number of advantages that natural fibres can offer compared with synthetic materials. To name just a few: natural fibres are sustainable; they are biodegradable and environmentally friendly; these fibres are lighter than synthetic reinforcement thus presenting indirect energy savings (for example, lighter cars use less fuel). However, there are also shortcomings, specifically, a large variability of properties related to location and time of harvest, processing conditions, etc., and sensitivity to the ambient conditions (temperature and moisture). In order to produce high-quality fibres, a multi-step manufacturing process is required that contributes to the cost of high-performance natural fibres. Although biodegradability is a major advantage of natural fibres, it can also turn into a drawback in certain situations because uncontrolled degradation of material is undesirable.

This chapter is intended to review the mechanical properties of thermoplastic natural-fibre composites and grade their performance with respect to their synthetic counterparts.

13.1.1 Common types of thermoplastic matrix natural-fibre composites and their applications

Thermoplastic natural-fibre (NF) composites can be classified by the polymer used as a matrix as well as by the type of the fibre reinforcing the polymer.

Nearly all thermoplastics are recyclable, and some also biodegradable. Generally speaking, polymers that are obtained from natural sources (for example, lignin and starch) are biodegradable. Most of the synthetic polymers are only recyclable, although some of them might be biodegradable (for instance, polyglycolic acid, PGA).

Since we are dealing with natural reinforcement, it is biodegradable by definition, and fibres should be classified by their origin. We will consider plant fibres only, even though there are a number of fibres of animal origin as well as mineral fibres. Some of the most commonly used plant fibres to produce composites are flax, hemp, jute, sisal, kenaf, abaca, banana and, of course, wood. Although these fibres originate from different plants, there is a very important common attribute, which actually makes these reinforcements so good in terms of mechanical performance – high cellulose content.

The way reinforcement is arranged and introduced into the polymer can also be used to classify NF composites. For example, fibres can be chopped or arranged in mats to produce randomly oriented composites; fibres can be arranged in bundles to manufacture woven or stitched fabrics for unidirectional and multi-axial laminates, etc. However, in this chapter we are mostly going to focus on the classification of materials by the type of fibre used in composite.

Polypropylene (PP) is probably the most commonly used plastic to produce thermoplastic natural-fibre composites (NFC). Other synthetic plastics, such as polyethylene (PE), polystyrene (PS) and polyamides (PA) are also common in NFCs. In recent years, natural resins as well as other biodegradable polymers, are more often considered as a matrix for the NFC due to the environmental advantage they offer, even though some of these polymers are rather expensive. These environmentally friendly materials include the following polymers: lignin, starch, poly(lactic acid) (PLA), poly(β-hydroxybutyrate) (PHB), polyhydroxyalkanoate (PHA), polycaprolactone (PCL), poly(glycolic acid) (PGA), poly(vinyl alcohol) (PVOH), etc.[1] Latest information on development of entirely bio-based composites can be found on EC IP FP6 project 'BIOCOMP' home page at www.biocomp.eu.com.

Currently, the main areas of application of thermoplastic NFCs are packaging, transportation and building industries. The packaging industry requires materials that possess specific properties, but that can also be easily discarded after use. Composites produced from natural constituents are extremely well suited for these applications. Transportation industry, especially automotive, needs light, high-performance materials which can be fully recycled (or simply disposed of) after service life. NFCs potentially are able to fulfil most of these requirements. However, until very recently the automotive industry has been using NFCs mostly in non-structural applications, such as miscellaneous interior panels (dashboard, door panels, etc.).[2,3] This is related to the drawbacks of NFCs which will be discussed later in this chapter. However, there is ongoing development of a new class of NFC which can be used in load-carrying applications; good examples of such work can be found on the webpage of the European research project 'ECOFINA' (EC IP FP5 project), www.ecofina.org.

In the building industry, NFCs are mostly employed as low-cost insulation (thermal and acoustic) materials made out of industrial scrap (for instance, wood flour from sawmills). It should be noted that one of the success stories, at least in the United States, concerning these materials is NFC decking. However, even the building industry is beginning to look for ways to employ these materials in structural components. For instance, NFCs are considered for the strengthening of concrete, similarly to glass and carbon fibre composites, although use of thermoset resins is dominating there.

13.1.2 Brief overview of mechanical properties of thermoplastic matrix natural-fibre composites

The tensile properties of some of the PP-based NFCs along with glass fibre reinforced PP are presented in Table 13.1. Note that direct comparison of these properties is probably unfair because fibre geometry (and possibly orientation) differs for these materials; besides, some of the fibres were specially treated to improve adhesion between matrix and filament. Nevertheless, these results clearly demonstrate the potential of NFCs, especially when specific properties are considered.

Tensile, flexural and compressive properties of NFCs are rather competitive compared with glass fibre composites, especially if comparison of specific properties is made. However, long-term performance (particularly creep), highly non-linear behaviour, low impact strength and extreme sensitivity to temperature and moisture are weak points of these materials in terms of mechanical performance. More detailed discussion of mechanical properties of NFCs is presented in this chapter.

Table 13.1 Properties of NFC with PP matrix[1,5]

Property/fibres	Glass	Wood flour	Sisal	Flax	Jute	Kenaf
Fibre content (wt%)	40	40	40	40	30	50
Tensile strength (MPa)	100	19	55	67	36	65
Tensile modulus (GPa)	6.0	2.5	4.8	6.7	4.6	8.3
Fiber density (g/cm^3)	2.54	1.40	1.45	1.50	1.40	1.40
Composite density (g/cm^3)*	1.21	1.05	1.06	1.07	1.01	1.10
Specific strength (MPa/(g/cm^3))	82	18	52	63	36	59
Specific modulus (GPa/(g/cm^3))	4.9	2.4	4.5	6.3	4.6	7.6

* Calculated by using rule-of-mixture from densities of fibres and PP (0.9 g/cm^3).

13.1.3 Advantages and drawbacks of thermoplastic matrix natural-fibre composites compared with synthetic short fibre composites

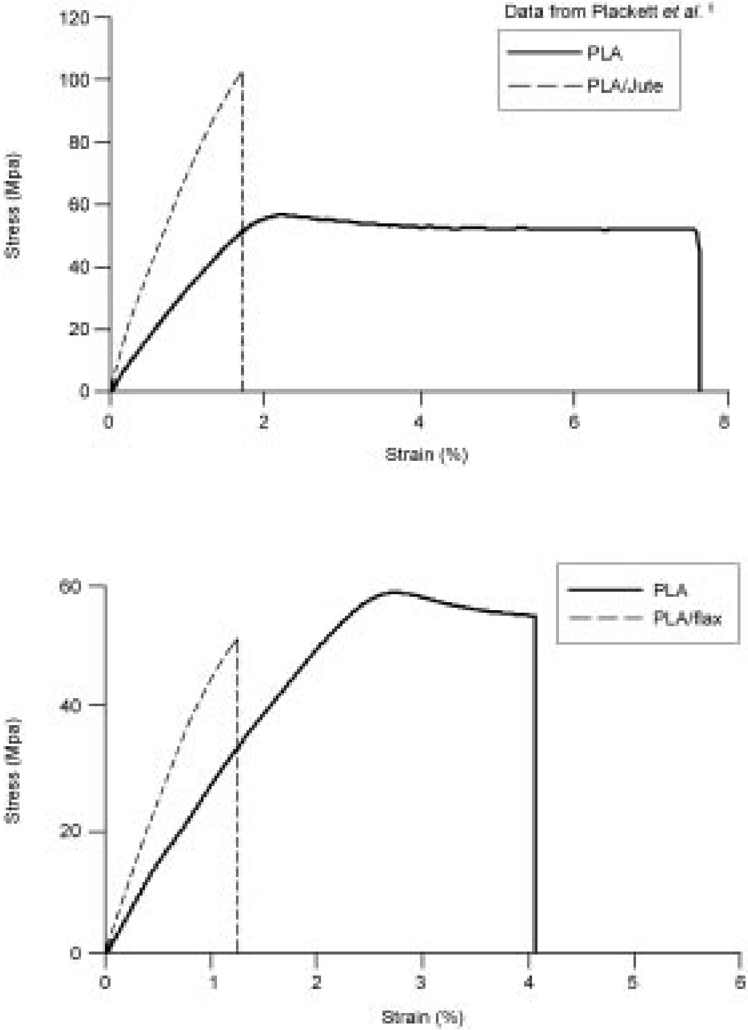
A brief summary of pros and cons regarding NFC is given in Table 13.2. It is seen that there are still a number of problems that have to be solved before NFCs become fully competitive with synthetic fibre composites. On the other hand, many of those weaknesses can (and will) be overcome with the development of more advanced processing of NF and their composites. Moreover, environmental friendliness and sustainability of these materials might outweigh some, if not all, of the drawbacks.[4] However, absolute environmental superiority of NFs compared with synthetic fibres is still questionable, because improvement of the properties of NFs and their composites require more processing steps, which in their turn consume more energy. Therefore, it is essential to continue with careful life-cycle assessment of these materials in order to retain the main advantage (low environmental impact) in the process of developing high-performance NFCs.

Table 13.2 Advantages and disadvantages of thermoplastic NFCs

Pros	Cons
Sustainable	Could be more expensive if fully bio-based and biodegradable
Fully recyclable	Extremely sensitive to moisture and temperature Geometrically unstable at high temperature and moisture content
Biodegradable (if proper matrix is used)	Uncontrolled biodegradation can occur
Good specific properties	High variability of properties
Light, non-abrasive	Non-linear mechanical behaviour Poor long-term performance Low impact strength

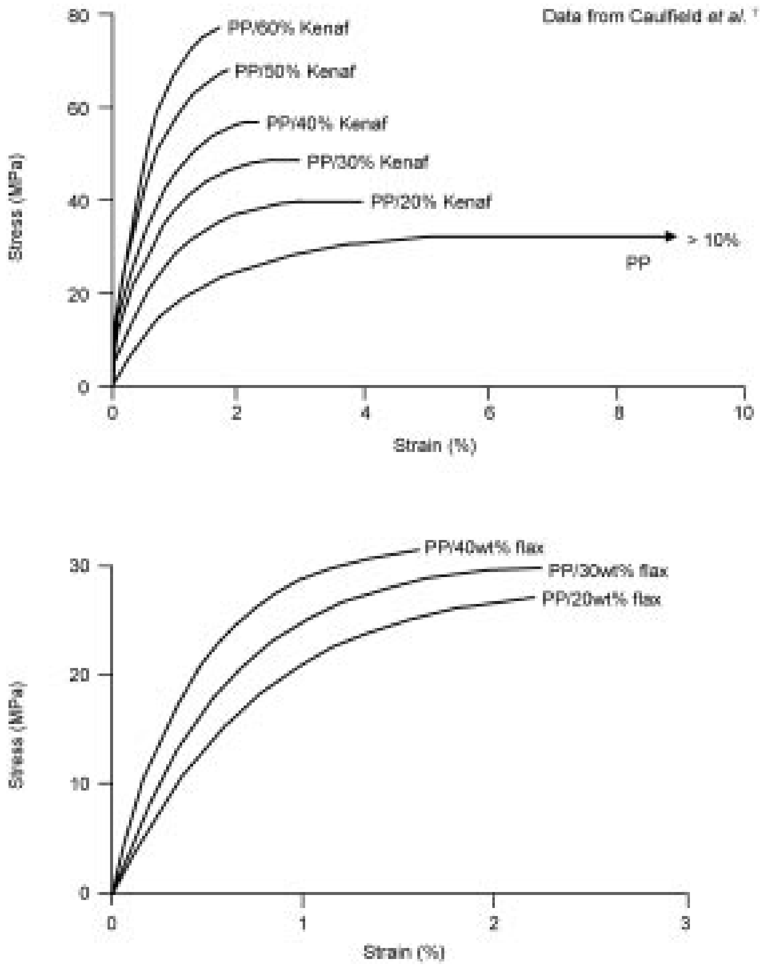
13.2 Stress–strain response in tension

Normally, thermoplastic polymers have rather high strain at failure compared with synthetic or natural fibres. However, the addition of fibres to plastics often results in more brittle failure, especially when short fibres are used as reinforcement. An example of such behaviour is presented in Fig. 13.1. It is seen that elastic modulus of the composite is higher than that of the neat polymer, which is expected. On the other hand, strength of the composite (as well as strain at failure) is sometimes lower than strength of the neat resin. This is related to



13.1 Stress–strain curves of neat thermoplastic and NFC.

microstructure of the material that is determined by manufacturing procedure and constituents. For example, poor wetting of fibres by polymer results in material with defects, such as voids and fibre agglomerates, which promote premature failure. Data in Fig. 13.2 for PP/kenaf and PP/flax fibre composites clearly show that, with the increase of fibre content, the material becomes stiffer and stronger but, at the same time, strain at failure is significantly reduced compared with neat polymer (PP can sustain much higher strains than 10%).



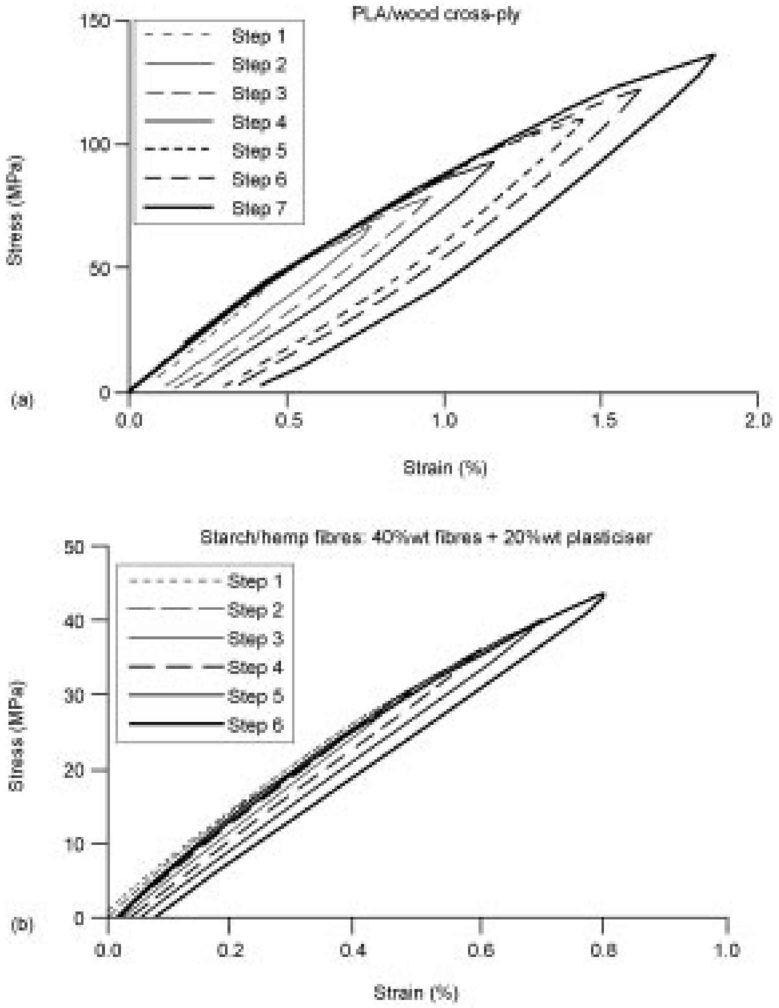
13.2 Stress–strain curves for PP/kenaf and PP/flax fibre composites at different fibre contents.

13.2.1 Elastic limit and non-linear behaviour

The tensile response of neat thermoplastic polymers as well as NFCs starts to deviate from linearity at rather small strains (see, e.g., Figs 13.1 and 13.2), linear behaviour being observed at strains lower than 1%. The limit of linearity, of course, depends on properties of the constituents and the microstructure of composite, but it is fairly safe to state that the linearity of the stress–strain curve for randomly oriented composites extends to strain levels of about 0.5% for most NFCs with a non-linear thermoplastic matrix. However, this might not be true for composites with fibres well oriented in the loading direction.

Apparent non-linear behaviour is demonstrated in Fig. 13.3 where multiple loading–unloading cycles for a PLA/wood-fibres cross-ply laminate and a starch/hemp fibre injection moulded composite are presented. These graphs show that there is a visible non-linear response (hysteresis loop) even at the first loading cycle, which reaches a strain of 0.3–0.4%.

Although non-linearity is observed rather early for these materials, irreversible plastic deformation might occur at a much later stage. In many instances, after a specimen has been loaded to a low strain level and then unloaded, apparent residual strains are seen, e.g. Fig. 13.3, as the stress–strain curve does



13.3 (a) Multiple loading–unloading cycles of PLA/wood-fibre cross-ply laminate and (b) starch/hemp fibre injection moulded composite.

not return to its origin upon unloading. However, if the specimen is left unloaded and unconstrained (one of the grips is opened) for a sufficiently long time (at least five times longer than the previous loading cycle), these residual strains are completely recovered. This implies that the material behaves in a visco-elastic manner.

13.2.2 Properties–microstructure relation

The thermomechanical performance of composite material is defined by the mechanical properties of constituents and by the microstructure. The morphology is characterised by two main parameters: fibre length and fibre orientation. The influence of these parameters on Young's modulus and strength can be evaluated by a rule-of-mixture type of expression. Young's modulus is expressed as follows:

$$E = \eta_{lE}\eta_{oE}E_f V_f + E_m(1 - V_f) \qquad 13.1$$

where E_m and E_f are matrix and fibre Young's modulus respectively; V_f is volume fraction of fibres; η_{lE} is fibre length efficiency factor; and η_{oE} is orientation efficiency factor. Both length and orientation efficiency factors can be calculated if fibre length and orientation distributions in the composite are known. Tensile strength is given by:

$$\sigma_{uc} = \eta_{ls}\eta_{os}\sigma_{uf} V_f + (1 - V_f)\sigma_m \qquad 13.2$$

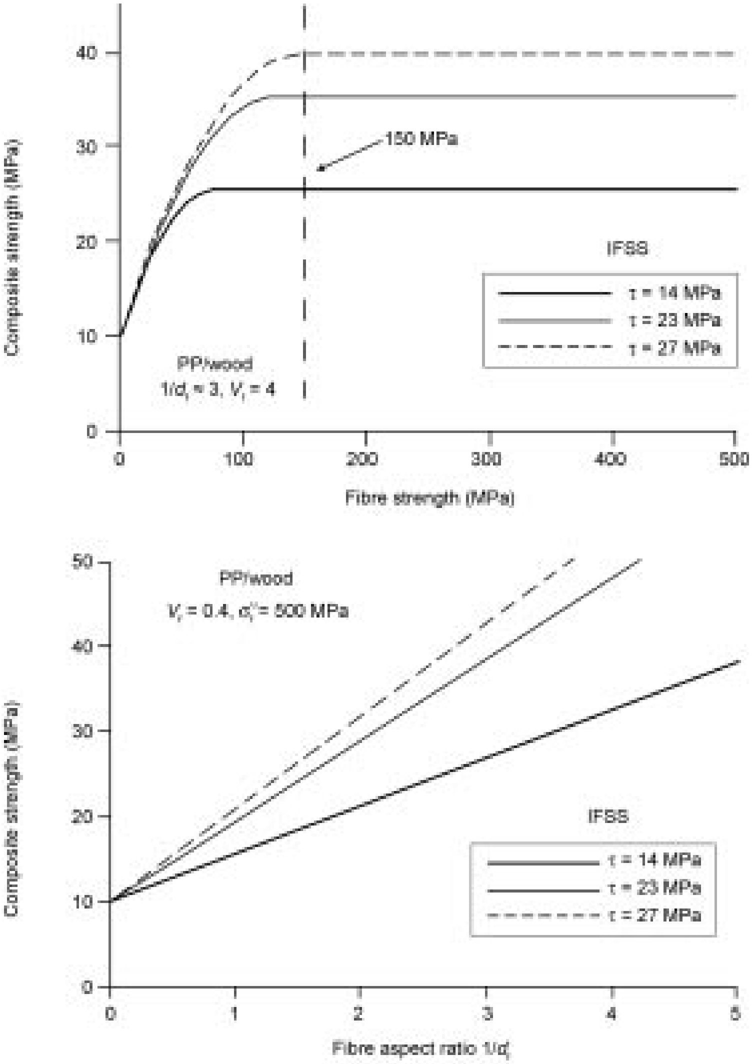
where σ_m and σ_f are matrix and fibre strength respectively; η_{ls} is the fibre length efficiency factor; and η_{os} is the orientation efficiency factor for calculation of strength. In this case, the length efficiency factor is related to the critical (or ineffective) fibre length which is defined by interfacial strength, fibre strength and fibre geometry:

$$\eta_{ls} = \begin{cases} 1 - l_c/2l & l \geq l_c \\ l/2l_c & l < l_c \end{cases} \qquad 13.3$$

It is important to realise that the fibre critical length l_c is defined by a combination of such parameters as fibre strength σ_{uf}, fibre radius r_f and the strength of fibre–matrix interface τ and is given by:

$$l_c = \frac{\sigma_{uf} r_f}{\tau} \qquad 13.4$$

This means that in order to efficiently utilise fibre properties, one should either have fibres longer than the critical fibre length or improve the interfacial shear strength (IFSS) to a level that would significantly reduce the critical fibre length. An example of the dependence of composite strength on fibre strength and fibre aspect ratio at different IFSS values is shown in Fig. 13.4 (results by Nyström *et al.*[8]). The calculations presented in Fig. 13.4 were performed for very short



13.4 Dependence of composite strength on fibre strength and fibre aspect ratio.

fibres (wood powder). It is fairly obvious that fibre strength becomes relatively unimportant for this material because the maximum fibre strength that can be utilised in this material system is only 150 MPa, although the actual fibre strength exceeds 500 MPa. Moreover, the composite strength linearly increases with fibre aspect ratio (for $l < l_c$) and IFSS, resulting in significant strength enhancement. Thus one can conclude that fibre length (or rather fibre aspect ratio) and IFSS are the most important parameters when it comes to the mechanical properties of short fibre randomly oriented composite material.

Another crucial parameter which has not been discussed yet is fibre orientation, but at this point it can be considered that most of the thermoplastic composites have either 2D or 3D randomly oriented fibres unless specially developed manufacturing procedure (for example, as presented by Nair *et al.*[9]) is employed to control fibre orientation. However, these procedures are used on the laboratory scale and cannot be considered mainstream manufacturing methods.

Microstructure characteristics and the effect of processing on morphology

Composites based on thermoplastic polymers are manufactured mainly by extrusion (by different methods) followed by injection or compression moulding. Fibres are chopped during the process, and therefore composites contain short fibres (a few millimetres at most). Fibre orientation in the composite material is three dimensional, but not necessarily isotropic (that depends on production specifics characterised by injection process, shape of mould, etc.). Besides, natural-fibre mat thermoplastic composite plates with different fibre contents can be manufactured using the film-stacking method. Thermoplastic pultrusion is also applied for a continuous manufacturing process. Only compounding and injection moulding processes will be briefly discussed below.

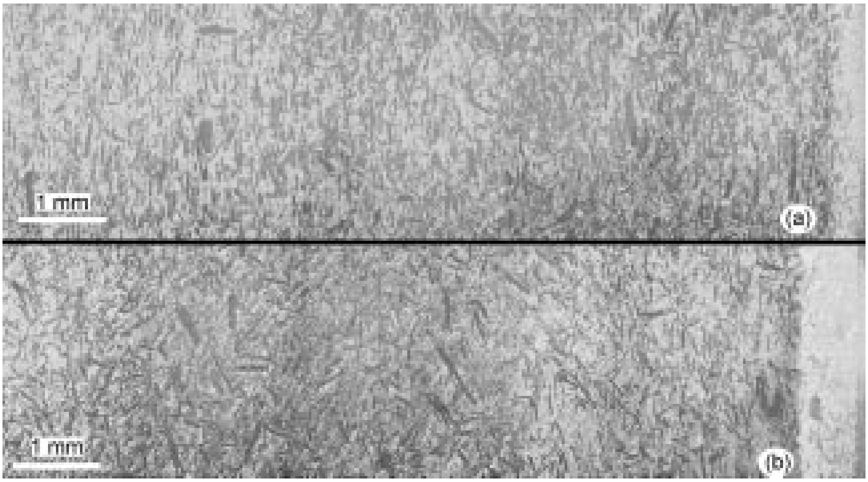
There are a number of devices available for compounding such as dedicated mixers, for instance Brabender, and different types of extruders. Extruders are equipped either with a single screw or with twin screws. In the case of twin screws, they can co-rotate or counter-rotate. The screw can be shaped just for transportation like an Archimedes screw, it can be conical to build up pressure or of even thickness, equipped with kneading and dispersing elements to improve blending. The length to diameter ratio of the screw as well as the free space for the material differs among screws, leading to different residence times. The mentioned characteristics of manufacturing equipment along with processing conditions affect the microstructure of the composite compound. It has been shown[10] that the principal parameters to be considered for optimisation of the processing procedure with respect to composite morphology include screw speed, the number of dispersing elements, mass flow and granule length. Optimisation of the compounding step has been mostly performed with respect to the fibre length since it was shown[8] to be the crucial parameter regarding the mechanical performance of composites. Low screw speed preserves fibre length better, but this effect is more pronounced when the extrudate is cut into longer granules.[10] Using many dispersing elements makes the fibre length more homogeneous, but the average length becomes shorter. However, if the screw speed is high, this detrimental effect is less pronounced. The effect of mass flow on the average and maximum length of fibre seems to be negligible.

The injection moulding machine is characterised by its clamp size and injection capacity. Clamp force ranges from a couple of tonnes to several thousand tonnes. The most frequently used machines typically possess a clamp force around 300 tonnes.[11] The injection capacity ranges from a few grams to hundreds of kilograms. Most of the heat that melts granules evolves from friction between granules, and between the barrel and the screw. Size of the screw often gradually increases. The parameters studied by Nyström[10] for optimisation of injection moulding process with respect to composite morphology are cylinder temperature, screw speed, injection speed and back-pressure. It was concluded[10] that injection moulding that followed the compounding stage reduced fibre length even more. However, mechanical properties were not affected by this as much as expected. This is probably because injection moulding also affects other properties of composite material, such as fibre orientation, crystallinity of matrix and mechanical properties of fibres (e.g., via degradation of fibres due to high temperature). The only clearly identified significant effect turned out to be high cylinder temperature which has a negative effect on strength if the injection speed is low.

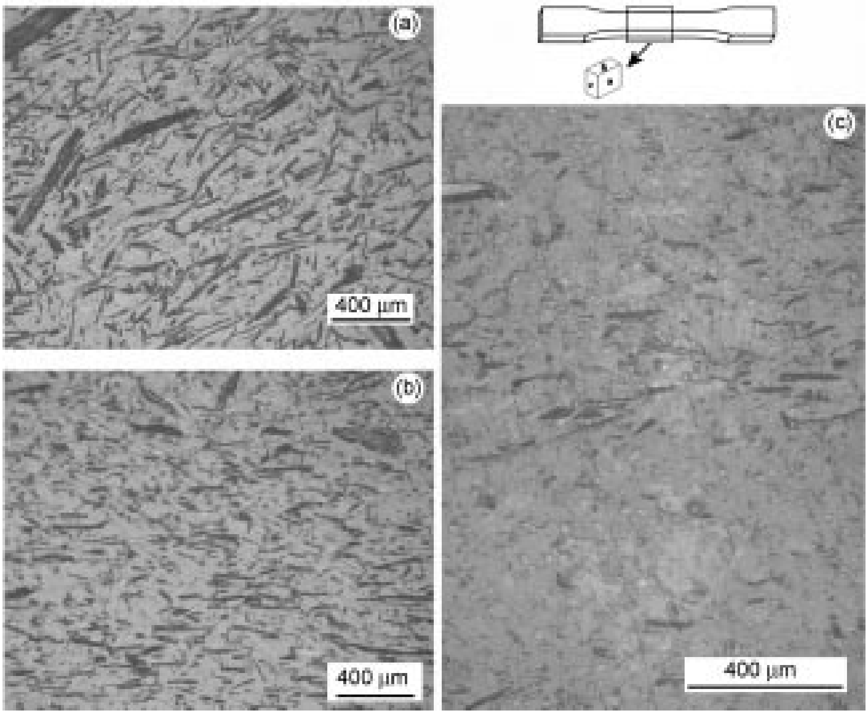
Some additional notes can be made concerning the manufacturing of thermoplastic composites and the influence of processing parameters on material morphology:

- The mechanical properties are not only defined by fibre length and orientation, although these are probably the most affected by the specific processing method and most important parameters. Voids, residual stresses, degradation of the matrix[12] and degree of crystallisation are some of the matrix/processing-related features that also influence the final composite properties.
- In addition to the manufacturing equipment, the rheological properties of the matrix affect fibre breakage, since a more viscous polymer leads to higher friction. Therefore, use of additives (such as adhesion promoters, for example) which might reduce viscosity of the polymer, can result in better fibre length preservation and reduce agglomeration of fibres.
- As there is a danger of thermal degradation of fibres, NFC processing temperature as well as time of exposure to high temperature are limited, as detailed, for example, for flax fibres by Van de Velde and Baetens.[13]

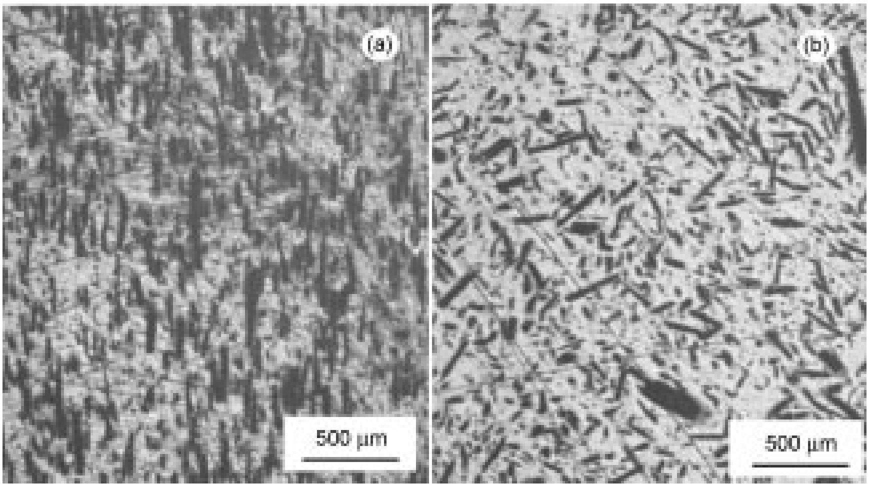
A random 2D or 3D fibre orientation is usually assumed for short fibre NFC, which is most often a reasonable hypothesis. However, owing to the manufacturing procedure, a preferential fibre orientation might be induced. The example of induced fibre orientation in a PP/flax composite produced by injection moulding[10] and extrusion[14] is shown in Figs 13.5 and 13.6, respectively. The micrograph in Fig. 13.5 demonstrates that fibre orientation can be rather inhomogeneous within the same specimen. The image in Fig. 13.5(a) is taken from the surface of sample, whereas the image in Fig. 13.5(b) is produced away from the surface (the sample was polished), approximately in the middle of specimen. Similar phenomena are seen in Fig. 13.7 for an injection moulded PP/flax composite;[8] however, in this case, images are made at the same depth but from different sides of the sample: Fig. 13.7(a) is from the side opposite to the



13.5 Micrograph of an injection moulded flax/PP NFC specimen (view from the top) at different depth: (a) surface; (b) middle.



13.6 Top (a), edge (b), and cross-section (c) micrographs of an extruded flax/PP matrix NFC specimen.



13.7 Micrograph of an injection moulded flax/PP NFC specimen: (a) side opposite to the inlet; (b) the same side where inlet is located.

inlet, whereas Fig. 13.7(b) is from the same side as the inlet. It is obvious that in one case (Fig. 13.7(a)) the fibres are well aligned and in the other case a random distribution is observed. This, naturally, leads to variation of material characteristics and complicates prediction of the mechanical properties of these composite materials.

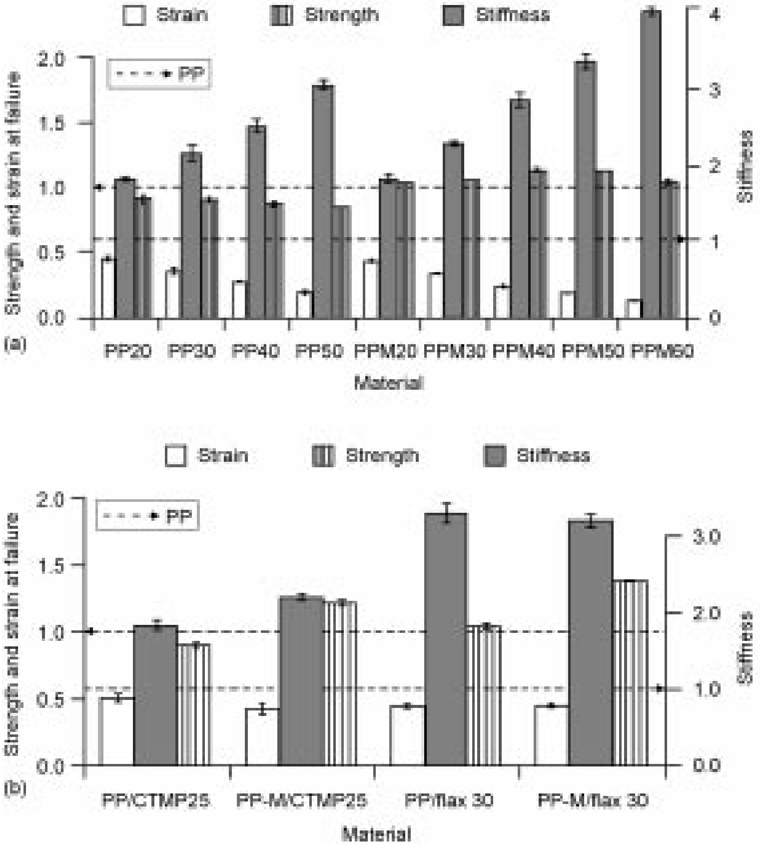
Elastic properties

The elastic modulus of a polymer is usually significantly improved by addition of NF, whereas strength and strain at failure are often reduced or only marginally improved unless well-aligned fibres with high aspect ratio are used.

Normalised (with respect to the properties of matrix) mechanical properties for different NFC are presented in Fig. 13.8. Figure 13.8(a) shows the results for PP/wood powder and PPM/wood fibre composites with different fibre content (20–60 wt%), where PPM stands for plastic with adhesion promoter. Figure 13.8(b) shows data for 25 wt% of chemi-thermomechanical pulp/PP (PP/CTMP25 and PPM/CTMP25) and 30 wt% flax fibres/PP composite (polymer with 'PPM' and without 'PP' adhesion promoter is used). These results show that even if very short fibres are used, such as wood powder (aspect ratio ≈ 3), there is still a very significant increase of elastic modulus and only minor, at best, improvement of strength and strain at failure is achieved.

Effect of microstructure imperfections on tensile strength

One of the most common reasons for premature failure of the material is the presence of different kinds of defects. Such defects are, for example, voids, dry reinforcement and fibre agglomeration. Fibre agglomeration in a composite

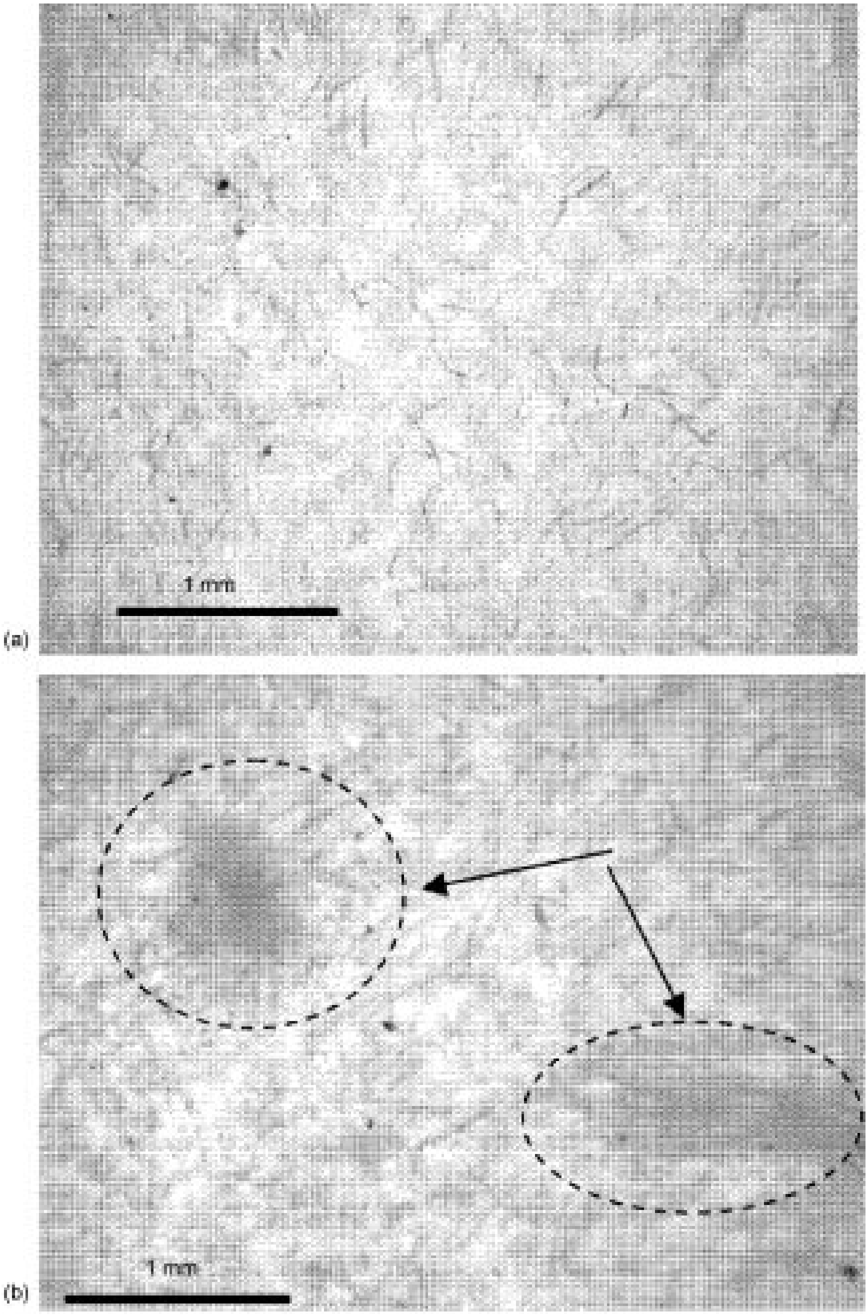


13.8 Normalised mechanical properties of (a) PP/wood powder (PP20–PP50 and PPM20-PPM60) and (b) PP/chemi-thermomechanical pulp (PP/CTMP25 and PPM/CTMP25) and PP/flax fibres (PP/flax and PPM/flax) composite. The number in notation corresponds to the fibre content.

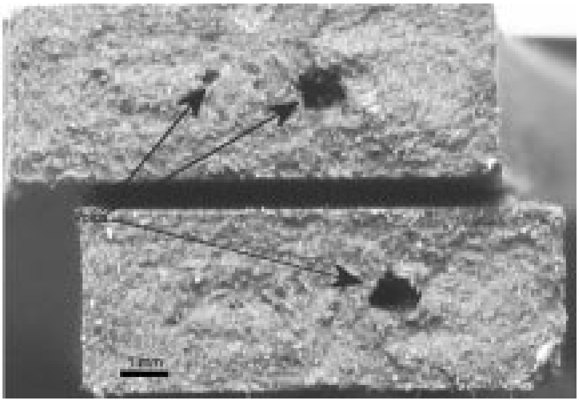
without adhesion promoter is seen in the image of Fig. 13.9(b). The sites of agglomeration are sources of stress concentrations and potential failure initiation. The same effect, with even more severe consequences, is caused by the presence of voids which are formed during the manufacturing. An example of these kinds of defect is shown in Fig. 13.10.

13.2.3 Failure scenario in tension

Generally, four failure events can be identified during the tensile loading of short fibre composites: yielding and cracking of matrix, fibre debonding, fibre pull-out and fibre fracture (see Fig. 13.11). Usually fibres are misoriented in short fibre composites, and therefore a combination of the mentioned failure modes is seen in composite fracture.

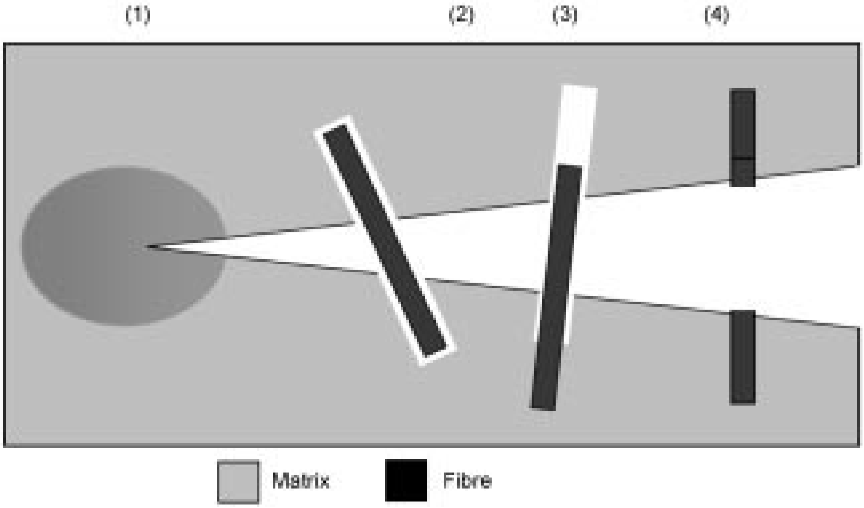


13.9 Injection moulded PP/chemi-thermomechanical pulp with (a) and without (b) adhesion promoter.

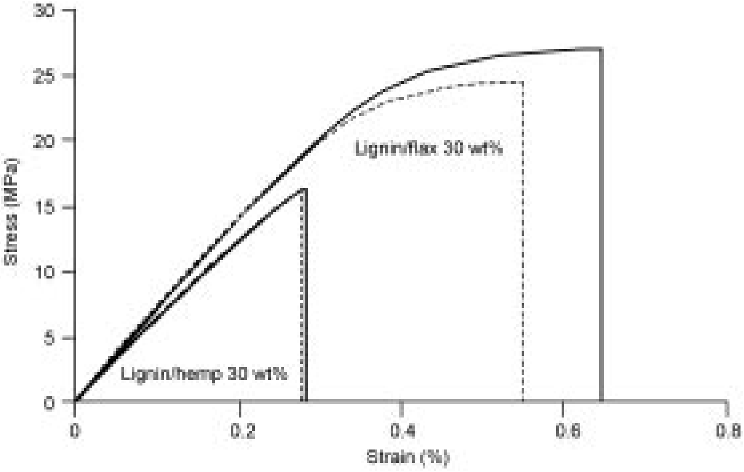


13.10 Injection moulded lignin/hemp fibre composite.

To enhance the composite toughness, it is advantageous if all the mentioned failure events accompany crack propagation. For example, if failure is initiated by a defect, and a crack starts to develop, it would be impeded by fibres oriented perpendicularly to the crack plane. In this case, if the interface is very strong, fibre fracture is likely to occur and the crack will continue to propagate until the final failure of specimen. On the other hand, if energy can be additionally dissipated by fibre debonding and subsequent pull-out, the damage becomes more distributed and the final failure of composite is delayed. However, if fibres are too short then energy dissipated by fibre debonding and pull-out cannot



13.11 Failure events observed in short fibre composites during tensile loading: yielding of matrix (1), fibre debonding (2), fibre debonding and pull-out (3), fibre fracture (4).

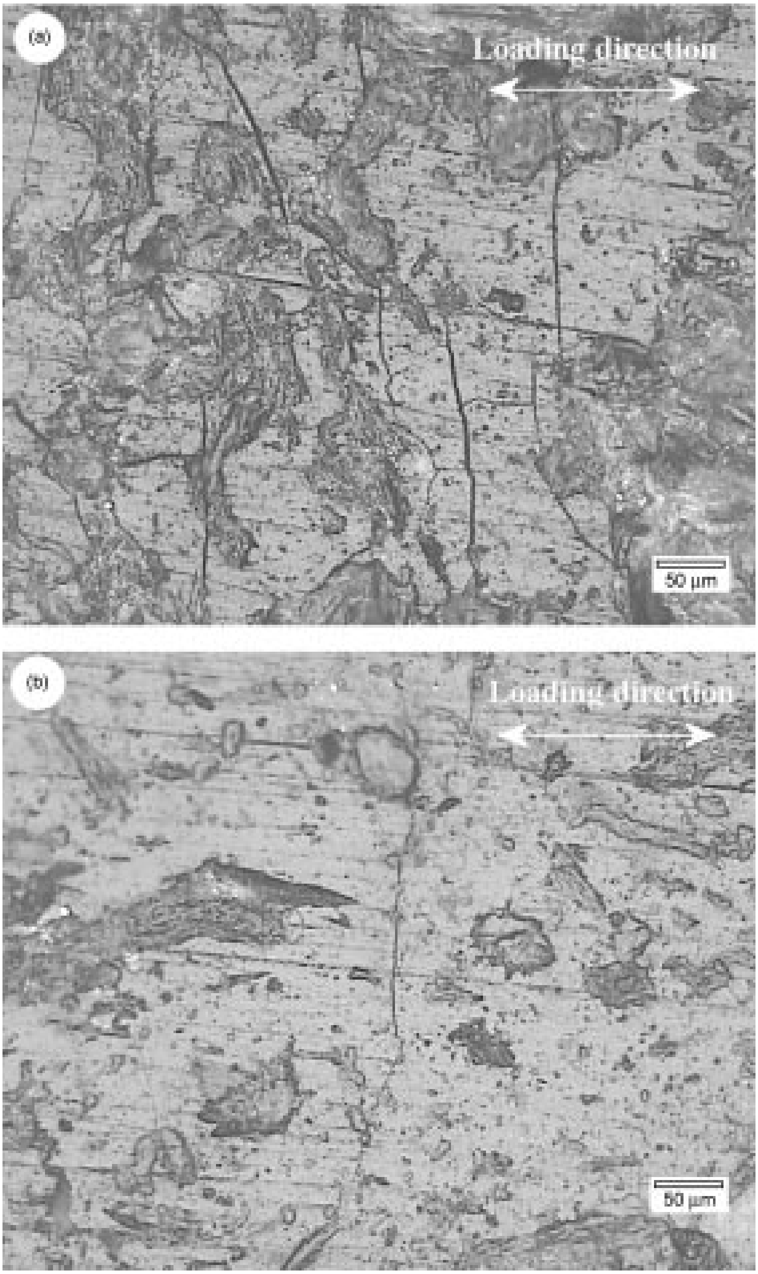


13.12 Stress–strain curves of lignin/hemp and lignin/flax injection moulded composite.

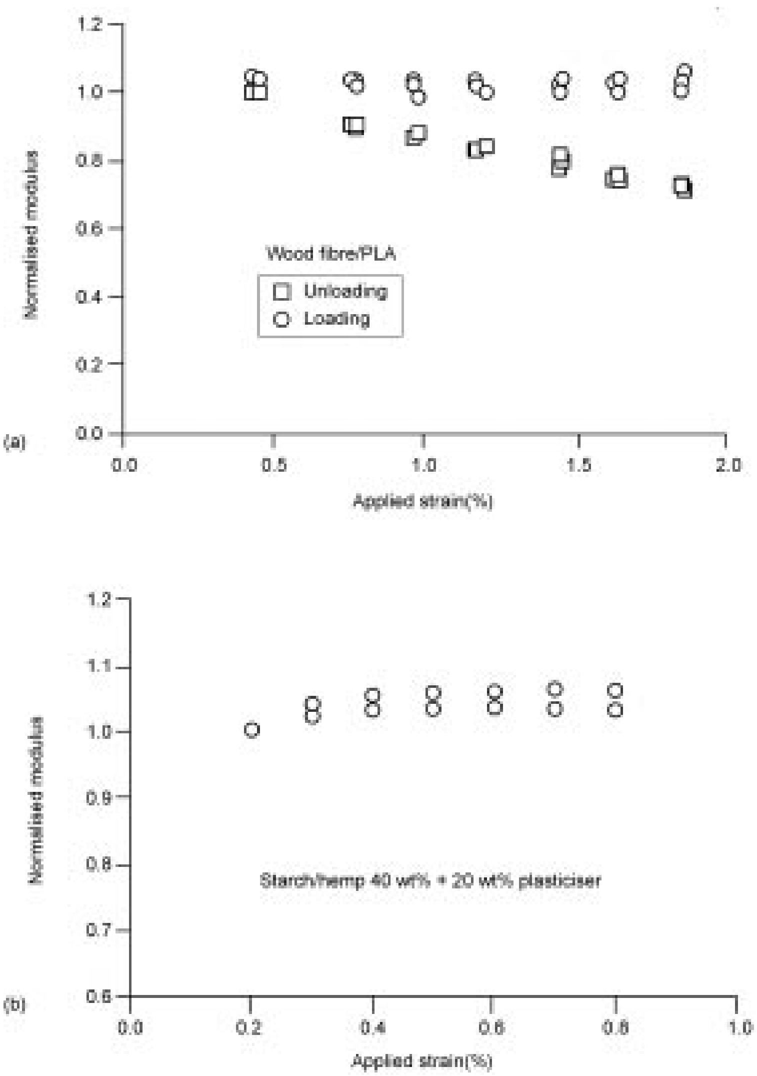
significantly influence damage propagation and final failure. An example of such behaviour is demonstrated by the stress–stress curves for brittle and more ductile failure of composites with 30 wt% of fibres and lignin matrix presented in Fig. 13.12. It should be noted that the matrix and manufacturing technique (injection moulding) is the same for both materials but fibre type and length differ. The initial length of flax fibres is higher than that of hemp, which results in higher strength and toughness. Micrographs of specimens after failure (view from the edge) are presented in Fig. 13.13. It is obvious that in the case of flax composite, damage is much more dispersed (Fig. 13.13(a)), whereas there are fewer cracks in hemp composites (Fig. 13.13(b)) but they are running through larger volume of material and cause premature brittle-like failure (as seen in Fig. 13.12).

13.2.4 Damage development and degradation of mechanical properties

One of the principal indications of damage accumulation in composites is the reduction of elastic properties during the service life of the component. The damage accumulation could be also partially responsible for hysteresis loops, shown in Fig. 13.3, due to opening and closure of cracks and debondings/delaminations in the material. However, non-linear behaviour shown in Figs 13.3 and 13.12 (for flax composites) is not always the result of damage. For example, a decrease of elastic modulus as a function of maximum applied strain is shown in Fig. 13.14(a), where elastic modulus is normalised with respect to the modulus of undamaged laminate. These are results for the same laminate as in Fig. 13.3(a). The apparent modulus is obtained in two ways: from the loading



13.13 Micrographs (view from the edge) of lignin/flax (a) and lignin/hemp (b) injection moulded composite after failure.



13.14 Normalised elastic modulus as a function of applied strain for cross-ply PLA/wood fibre composite laminate (a) and injection moulded starch/hemp composite.

part of the stress–strain curve within the strain interval of 0.25–0.45% and from the unloading stress–strain curve within the same corresponding stress interval. Note that for linear elastic material, the modulus should not depend on the way it is measured, and both methods would produce the same elastic modulus value. The loading–unloading is performed according to the curves shown in Fig. 13.3 but between each loading step the specimen is left unloaded for a time interval five times longer than previous loading cycle. The results in Fig. 13.14(a) show that the modulus measured from the loading step does not change with increasing applied strain, whereas the modulus obtained from the unloading part of the curve shows linear decay with increasing strain. This indicates that there is no irreversible damage such as cracks and only visco-elastic effects are observed. Thus, the effect on the apparent modulus is visible on the unloading curve but after recovery, the material exhibits the same response to loading as before. This is also very obvious from the stress–strain curves in the Fig. 13.3, where the loading curves coincide but the unloading curves are markedly different.

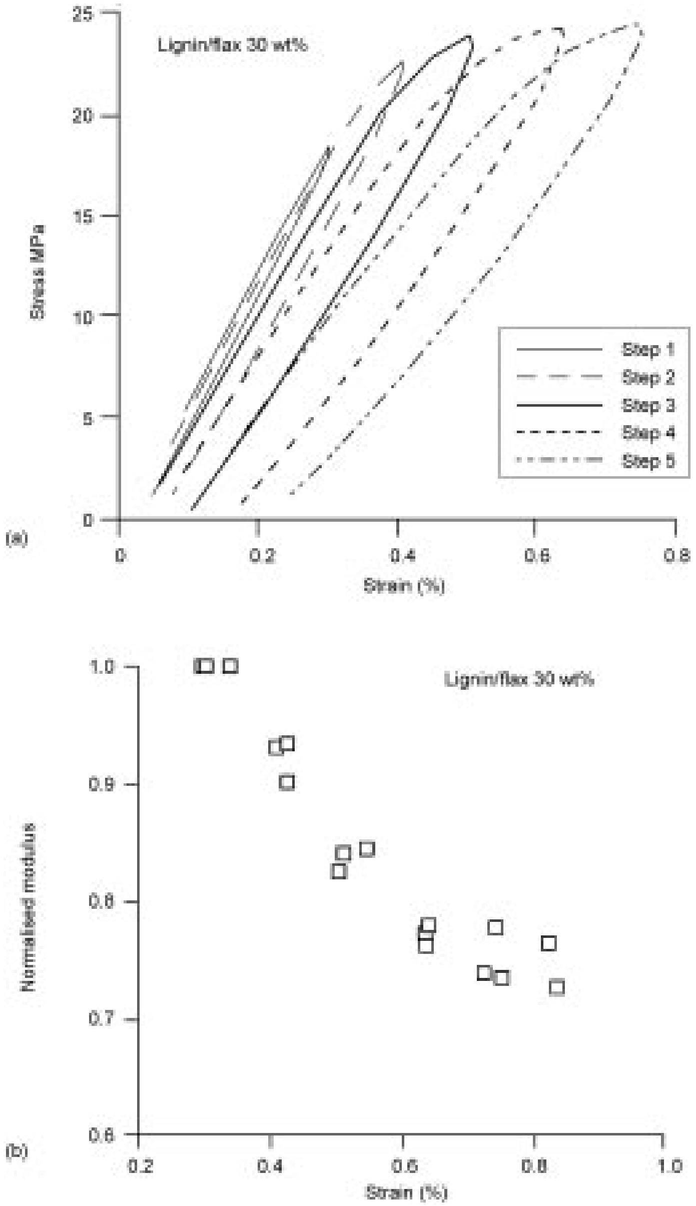
Similar behaviour is registered for injection moulded starch/hemp composites with 40 wt% fibres and 20% plasticiser. Loading–unloading cycles for this material are shown in Fig. 13.3(b) and the normalised elastic modulus as a function of applied strain is shown in Fig. 13.14(b) (the modulus is also measured from the loading part of the curve). It can be noted that the modulus increases slightly with strain for this material, which can be attributed to the development of plastic strains and possible re-orientation of fibres along the loading direction.

However, in the case of lignin/flax injection moulded composites the loading part of the stress–strain curve for each subsequent loading step differs from the previous one (see Fig. 13.15(a)). This is also reflected in significant degradation of elastic modulus with applied strain (see Fig. 13.15(b)). In this case there is definite damage accumulation during the loading (see Fig. 13.13(a)). Different damage tolerance of NFCs with different matrices can be obviously attributed to the toughness and viscoelastic properties of resin. It seems that if the matrix material is very tough and exhibits highly viscoelastic behaviour, damage in composites is suppressed and instead of debonding (or delamination) and cracks, plastic deformation of the matrix occurs. For example, lignin is rather brittle compared with starch-P (starch with plasticiser) and PLA, and in NFCs with this matrix, visible damage has been observed. In other composites, with PLA and starch-P matrix, only accumulation of plastic deformation is observed and no significant reduction of elastic modulus is found.

13.3 Shear and compression

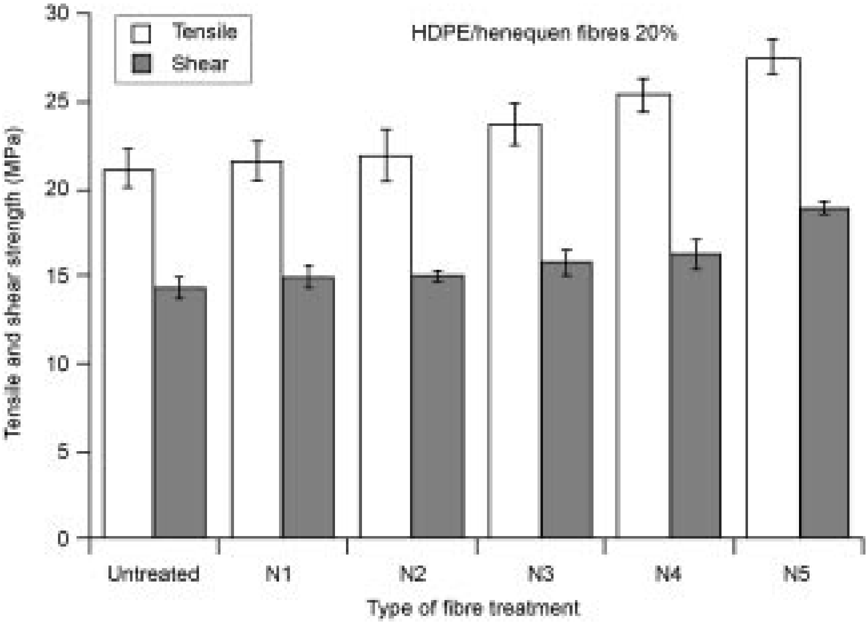
Shear and compressive properties of NFCs have received less attention than tensile response. The actual experimental results presented in this section are therefore relatively limited.

If the material is isotropic, and NFCs reinforced with short fibres often can be considered as such, then shear modulus can be expressed through the tensile modulus and Poisson ratio, but shear strength cannot be so easily estimated. It is reasonable to assume that the shear response of short fibre NFC is mostly governed by the properties of the polymer matrix. Clearly, the reinforcement modifies the matrix response to some extent. For example, tensile and shear



13.15 Multiple loading-unloading cycles (a) of lignin/flax injection moulded specimen and resulting modulus degradation (b).

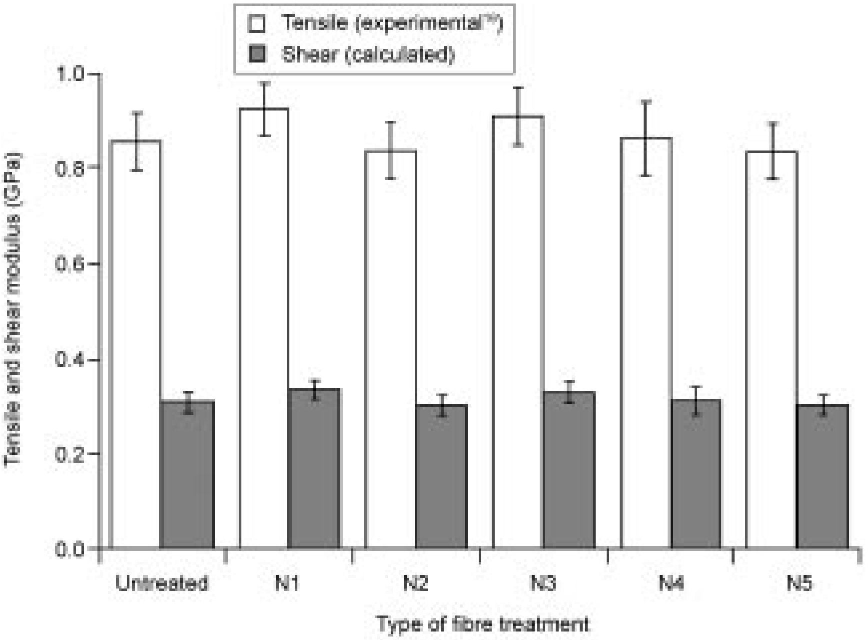
strength of high-density polyethylene (HDPE)/henequen fibres (20 vol%; fibre length 6 mm) with different fibre treatments[15] are presented in Fig. 13.16 (types of fiber treatment: N1 – NaOH solution; N2 – pre-impregnation with HDPE; N3 – NaOH solution and pre-impregnation with HDPE; N4 – silane coupling agent;



13.16 Tensile and shear strength for HDPE/henequen fibres (20% by volume) with different fibre treatments.[15]

N5 – NaOH solution and silane coupling agent; for more details on fibre treatment, see Herrera-Franco and Valadez-González[15]). It is seen that shear strength varies with fibre treatment in exactly the same manner as tensile strength, although the actual values are lower. This suggests that there is some influence of fibre properties on shear strength, although the effect seems to be rather limited. The tensile strength of the same matrix (HDPE) is reported to be around 25 MPa,[16] which means that only one of the treatments (Fig. 13.16, treatment N5) yields higher values of tensile strength (an increase of approximately 10% compared with HDPE) than the matrix. Since shear strength follows the same trend as tensile strength with respect to the fibre treatment, one can conclude that the presence of reinforcement in NFCs will not increase the shear strength unless interfacial adhesion is significantly improved. Similar values for shear strength of long fibre HDPE/henequen fibre composites (the same materials as shown previously[15]) with silane-treated fibres and without any treatment are presented by Herrera-Franco and Valadez-González[17] (for specimens tested by the Iosipescu method in the transverse direction). Untreated fibre composites have a shear strength of approximately 9 MPa, whereas fibre treatment increases the shear strength values up to 13.5 MPa.

Since shear modulus measurements for the considered HDPE/henequen composite are not available, a rough estimation can be performed (assuming that the composite material is isotropic, i.e. the orientation of the short fibres in the

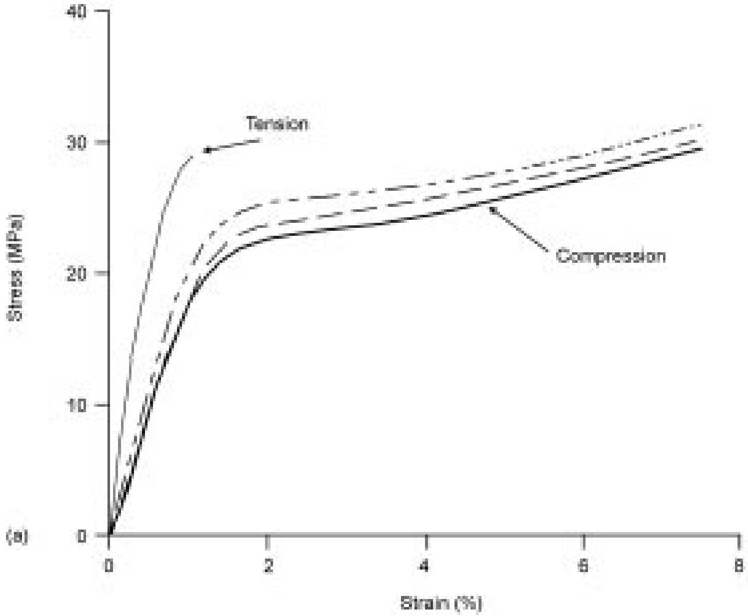


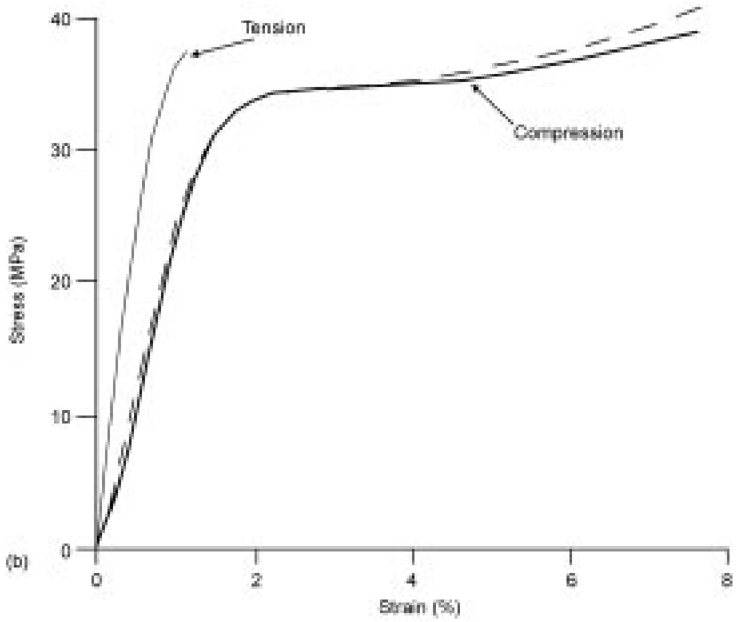
13.17 Measured tensile[15] and calculated shear modulus for HDPE/henequen fibres (20% by volume) with different fibre treatments.

composite is random). The shear modulus is related to the tensile modulus and Poisson ratio as follows: $G = E/2(1 + \nu)$. The Poisson ratio of HDPE is within the interval of $\nu = 0.41$–0.43 according to the Cambridge Engineering Selector database; and so the average value of 0.42 has been used. The Poisson ratio of henequen fibre is assumed to be 0.33.[17] This would lead, by the rule of mixtures, to a composite Poisson ratio of approximately 0.38. The measured tensile modulus[15] and the estimated shear modulus for HDPE/henequen composite (with different fibre treatments, see Herrera-Franco and Valadez-González[15] for details) is presented in Fig. 13.17. The tensile modulus for this thermoplastic is 0.792 GPa,[17] whereas the shear modulus for HDPE is within the interval of 0.22–0.38 GPa (values from Cambridge Engineering Selector database). These results show that the addition of reinforcement has very limited (almost negligible) effect on the stiffness of HDPE, regardless of fibre treatment.

Stress–strain curves from tension and compression tests of a starch/hemp fibre 40 wt% composite with different contents of plasticiser are shown in Fig. 13.18. These results indicate that the tensile modulus is significantly higher than the compressive modulus. The measured values are as follows:

- for 32.5 wt% plasticiser, tensile modulus is 4.32 GPa and compressive 2.07 GPa;
- for 30 wt% plasticiser, tensile modulus is 5.23 GPa and compressive 2.18 GPa.





13.18 Tensile and compressive stress–strain curve for starch/hemp fibre (40 wt%) composite with different amount of plasticiser: (a) 32.5 wt%; (b) 30 wt%.

From the elasticity point of view there should be no difference between modulus measured in tension and compression within the elastic limits (modulus was measured at low strain values <0.35%). However, one should be careful with these results because an extensometer was used in the tensile tests so that strain was measured fairly accurately, whereas it was impossible to use an extensometer in the compression tests and strain was calculated from the displacement of the cross-head of the testing machine; therefore, strain (and modulus) measured in compression has to be corrected for the compliance of the test setup. It seems unlikely, though, that such a correction will change the results by more than a factor of two.

Compressive strength seems to be rather high for these composites: yield stress (which can be used as a practical compressive stress limit) is only slightly lower (by 10–20%) than the stress at failure in tension. This is similar to composites with well-aligned reinforcement, where the compressive strength under loading in the reinforcement direction is usually lower than the tensile strength. It is commonly assumed that most often compressive failure in composites occurs by plastic micro-buckling which is initiated by misalignment of reinforcement with respect to the loading direction (angles of misalignment in the order of 2–5°). In such a situation the shear yield stress of matrix becomes one of the most important factors that define the compressive strength of composite. However, there are some results that show relatively high compressive strength for HDPE/wood flour 50 wt% of approximately 41 MPa,[18] which is significantly higher than the flexural strength (approximately 27 MPa) of the same composite and values for a similar composition (HDPE/sawdust 50 wt%), for which flexural strength was 22 MPa and tensile strength only 9 MPa.[19] One of the possible explanations for the compressive strength of HDPE/wood flour composite being higher than the tensile strength could be the fact that, strictly speaking, wood flour cannot be considered as fibre, due to its small aspect ratio. Moreover, at high filler content one can expect formation of agglomerates, which makes this material even more similar to a composite reinforced with particles. It is known that the tensile strength of particulate composites often is lower than the strength of matrix material, especially if adhesion between matrix and fillers is low. On the other hand, it can be argued that the interfacial strength becomes less important in compression and thus rigid particles increase compressive strength of composite. Note that this speculation is based on results from different sources and it is rather difficult to ensure that tensile and compression tests are performed at the same conditions. For example, it is known that HDPE is sensitive to strain rate[20] and higher strain rates in compression might lead to higher strength compared with tensile results. In order to conclusively reveal the peculiarities of performance of thermoplastic NFCs in shear and compression, more experimental data are required.

13.4 Flexural properties

Flexural and tensile properties of different thermoplastic (mostly PP, which seems to be the most frequently used thermoplastic in combination with natural fibres) NFCs are presented in Table 13.3. Properties of a PP/glass fibre composite are also given for comparison. These results lead to rather similar conclusions as the data presented in Table 13.1 for the tensile properties of NFCs with a PP matrix. The flexural properties of NFC are slightly lower (especially strength) than those of the glass fibre composite. However, if specific properties are considered, the comparison again would be in favour of NFC.

The normalised tensile and flexural strength and modulus of PP/flax fibre composite with different fibre content (and different type and amount of coupling agents) are presented in Figs 13.19 and 13.20, respectively.[21] Data are normalised with respect to the values for neat PP: tensile strength 32.4 MPa, flexural strength 36.9 MPa, tensile modulus 0.90 GPa, flexural modulus 1.29 GPa. These results show that flexural properties of the NFCs follow the trend for tensile properties almost exactly (see discussion concerning tensile properties in Section 13.2). This suggests that fracture micro-mechanisms that occur in the materials under flexural loading are similar to those observed in tension. It is also in agreement with the observation that, in many instances, failure in bending tests starts on the side of the specimen experiencing tension.

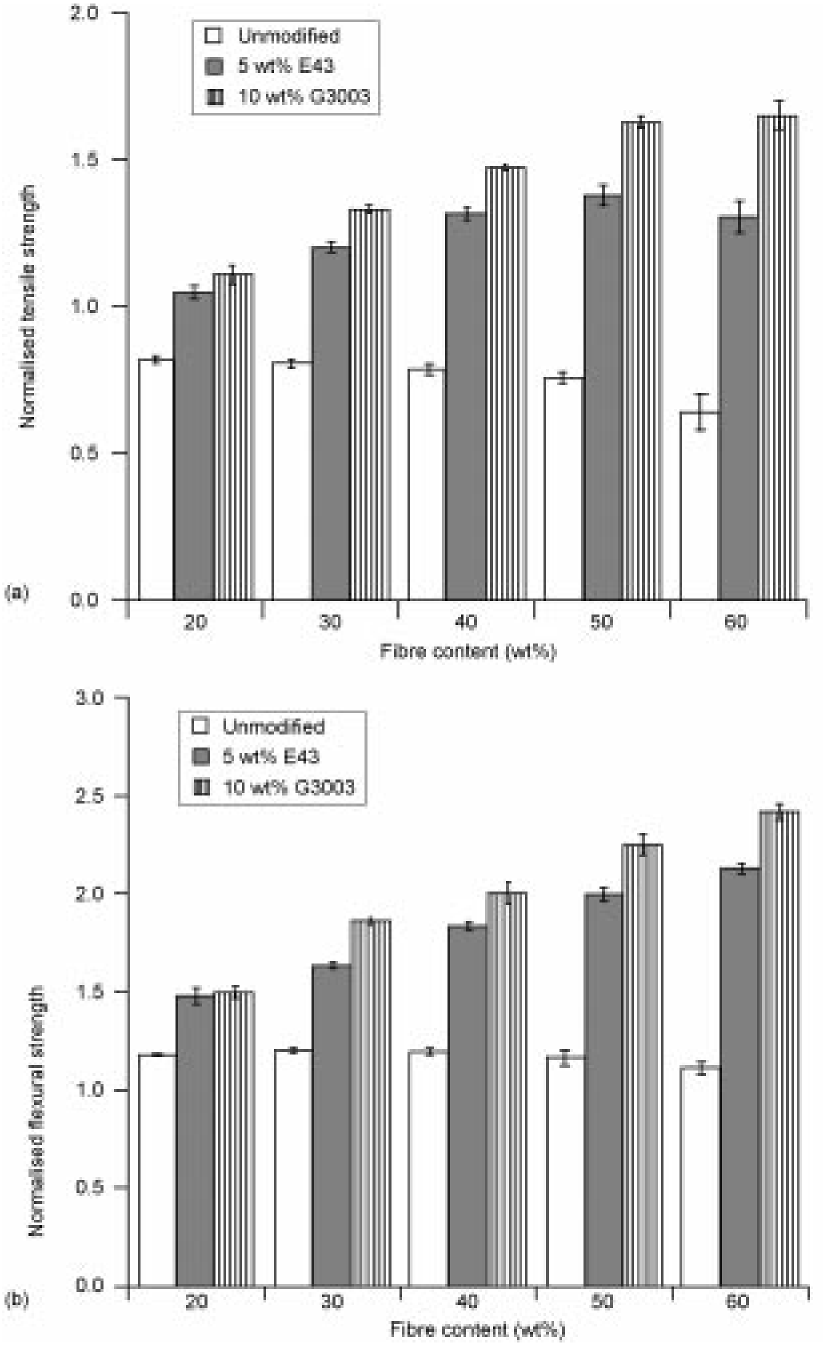
Another example of similiar behaviour of NCFs in tensile and flexural tests is shown in Figs 13.21 and 13.22 for PP/flax and PP/jute composites respectively (fibre content 30wt% in both materials).[22] Data presented in Figs 13.21 and 13.22 show how the tensile and flexural strengths of NFCs is affected by the addition of a coupling agent which is meant to improve fibre–matrix adhesion. Results presented in those graphs are normalised with respect to the data for composite without coupling agent.

Analysis of the results presented in Table 13.3 and Figs 13.19 and 13.20 indicates that flexural properties of NFCs are consistently higher than tensile properties. It can be argued that the flexural properties of neat resin are also higher than tensile properties (for example PP/flax composite presented in Figs 13.19 and 13.20). However, this difference is much smaller than the differences observed for NFCs (actually PP/glass fibre composite also shows similar behaviour; see Table 13.3). Such differences in strength values can be explained by the volume effect: the larger the volume of material tested, the lower the strength (and vice versa). In the case of a bending test only a small part of the specimen is under maximum stress and thus measured flexural strength is higher. However, this argument does not work for stiffness (flexural stiffness for neat PP is also higher than tensile modulus[21]). In order to explain differences in stiffness, the actual strain rate in bending and tensile tests should be compared because there is a possibility that strain rate at the tensile side of the specimen in

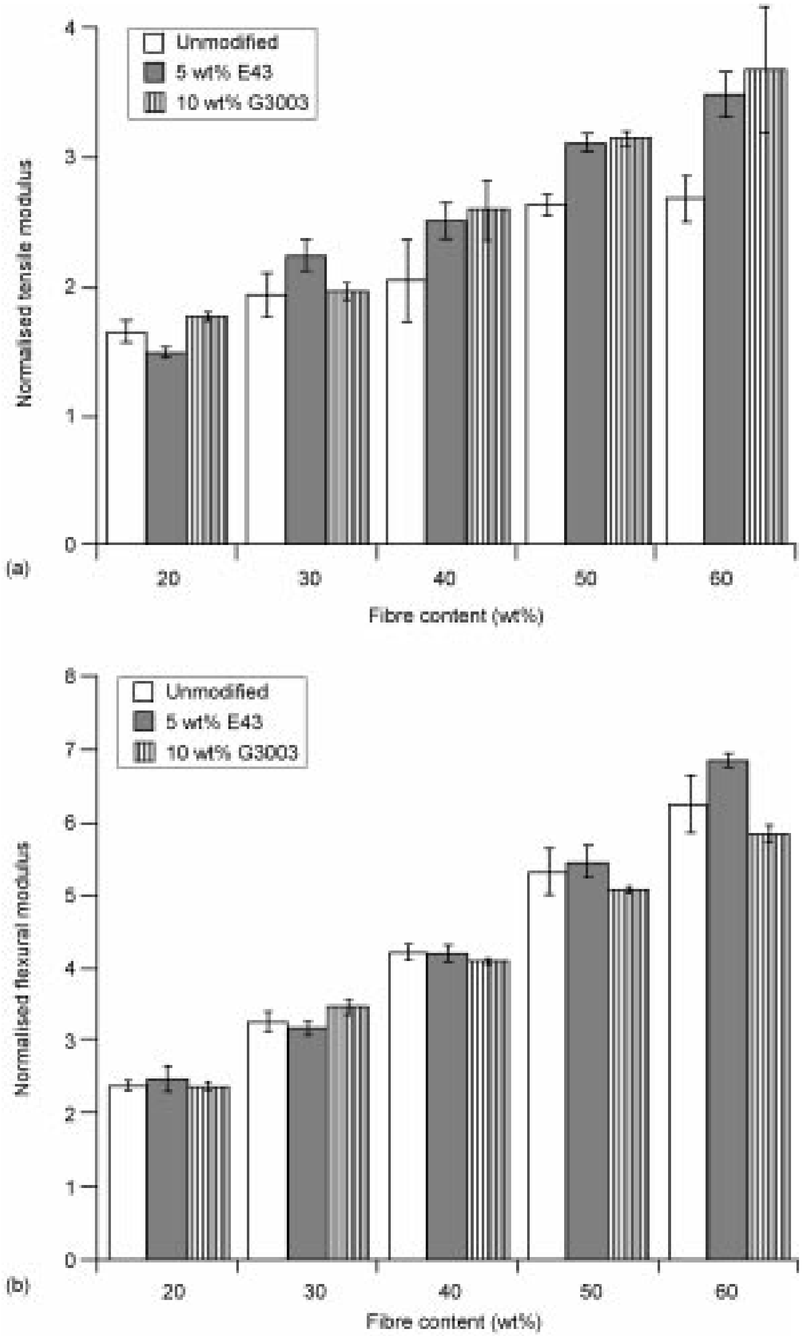
Table 13.3 Flexural and tensile properties of different thermoplastic short fibre NFCs

Property	Composite										
	PP/ glass[27]	PP/ flax[21]	PP/ flax[22]	PP/ sisal[23]	PP/ jute[22]	PP/ wood[24]	HDPE/ RH*[25]	MBY#/ sisal[26]	PP/ hemp[27]	PP/ kenaf[28]	PP/ bagasse[28]
Fiber content (wt%)	30	30	30	30	30	30	65	15	30	30	30
Flexural strength (MPa)	88.1	44.3	49.3	49.0	52.4	60.0	33.5	N/A	58.9	N/A	N/A
Flexural modulus (GPa)	4.70	4.21	N/A	N/A	N/A	N/A	2.90	2.75	3.80	5.00	2.65
Tensile strength (MPa)	57.4	26.0	33.2	N/A	34.1	35.0	13.5	16.8	32.9	N/A	N/A
Tensile modulus (GPa)	3.20	1.74	N/A	N/A	N/A	N/A	2.39	2.20	2.60	N/A	N/A

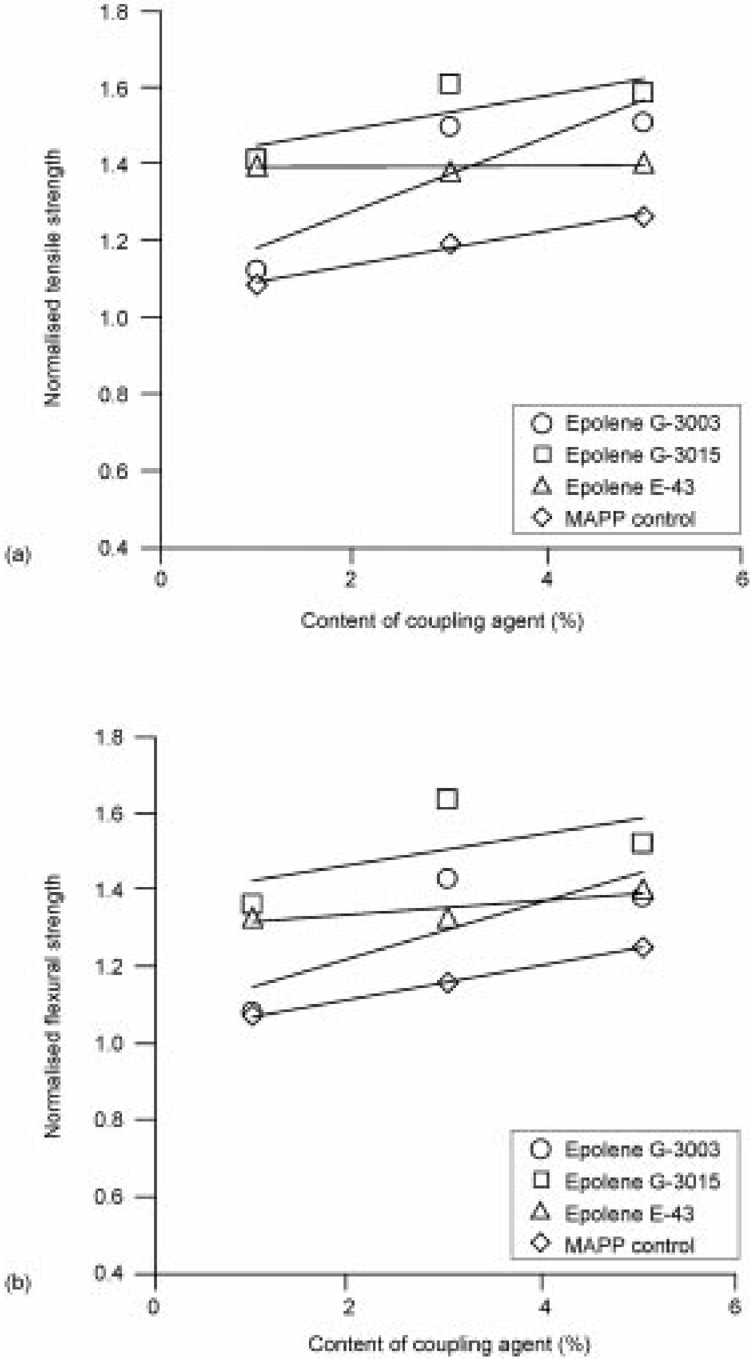
* RH, Rice husk; # MBY, MaterBi-Y (commercially available biobased polymer).



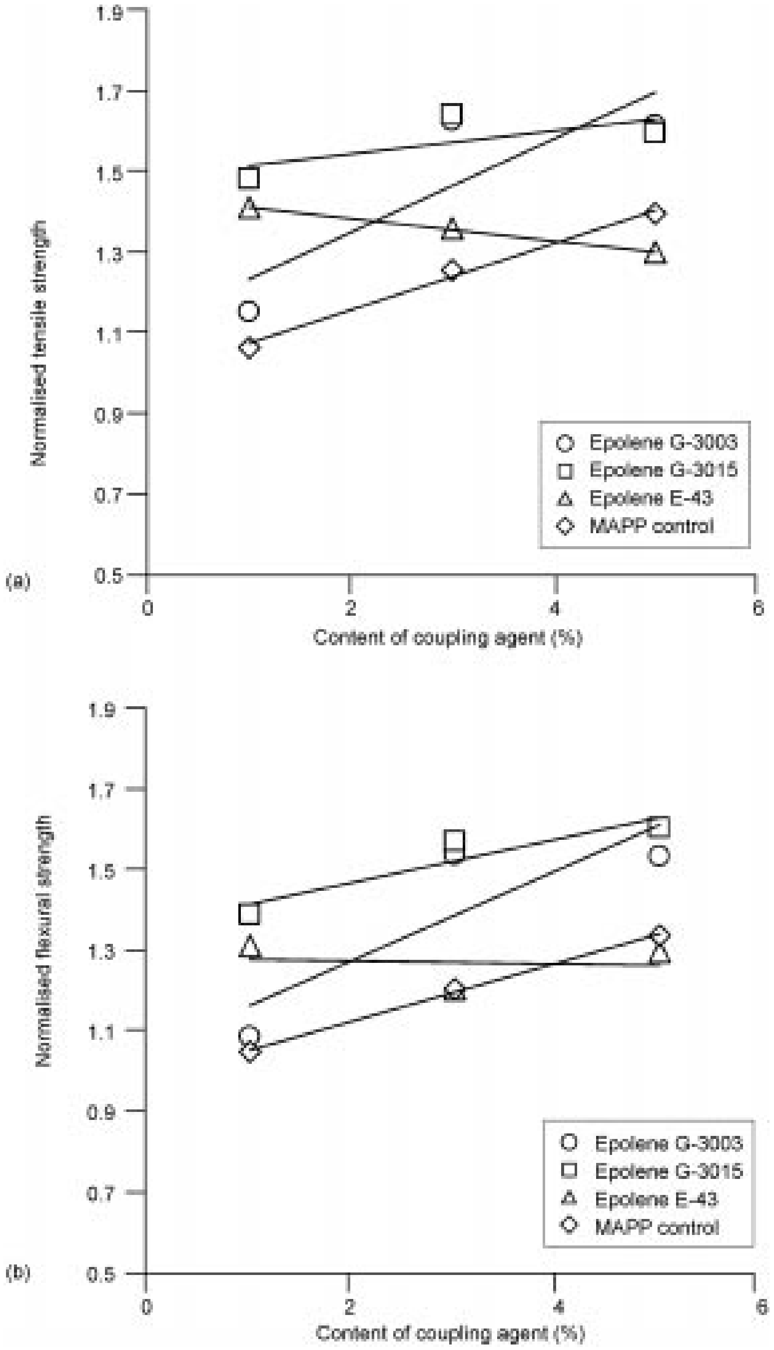
13.19 Tensile (a) and flexural (b) strength of PP/flax fibre composite with different fibre content.[21] Values are normalised with respect to the properties of PP.



13.20 Tensile (a) and flexural (b) modulus of PP/flax fibre composite with different fibre content.[21] Values are normalised with respect to the properties of PP.



13.21 Tensile (a) and flexural (b) strength of PP/flax 30 wt% composite with different type and amount of coupling agent.[22]



13.22 Tensile (a) and flexural (b) strength of PP/jute 30 wt% composite with different type and amount of coupling agent.[22]

a bending test is higher than the strain rate in a tensile test. It is well known that thermoplastics properties are strain rate dependent.

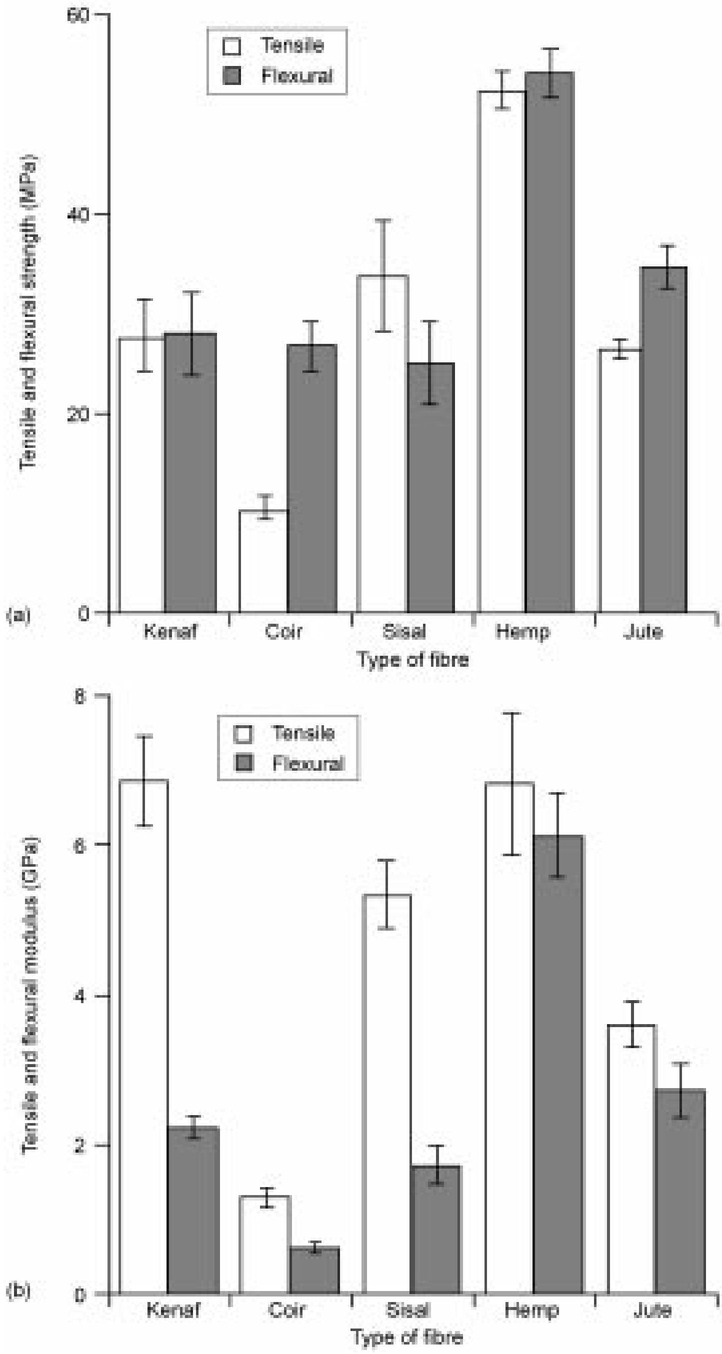
Another argument that has yet to be mentioned in this discussion is stress distribution in the specimen in tensile and bending test. In a simple tensile test the stress distribution in a specimen is fairly homogeneous (only tensile stress is present) whereas in the case of bending, both tensile and compressive stresses are present and, as discussed in Section 13.3, in some cases compressive properties can be higher than tensile ones.

It should be noted that the distribution of stress over specimen width in bending also leads to the early onset of non-linear deformation at the outer surfaces of the specimen experiencing the largest stresses. Thus, linear elastic response in the bulk of the specimen may coexist with yielding of the more heavily strained material. With the increase of load, non-linear deformation prevails, but a gradient in stress results in different intensity of yielding over specimen width in contrast to the tensile test where the specimen is uniformly strained.

Although the discussion presented in the previous paragraphs is based on experimental results from a number of independent sources, there are experimental data that contradict the results presented in Table 13.3 and Figs 13.19–13.22. The tensile and flexural strengths and moduli of PP reinforced with different types of natural fibres (40 wt%) are presented in Fig. 13.23.[29] These results show that the behaviour of NFCs in tensile and flexural tests is not as similar (for example, coir and sisal fibre composites) as was seen in the previous results. Moreover, the tensile modulus and, in some cases, also strength are higher than the respective flexural properties.

Wambua *et al.*[29] use similar arguments to explain these discrepancies as presented in previous paragraph: 'These two loading conditions exhibit different kinds of stresses in the specimen under test. Whereas the stresses in a tensile test are uniform throughout the specimen cross-section, the stresses in flexure vary from zero in the middle to maximum in the top and bottom surfaces.' It is also pointed out[29] that such differences are more likely to occur if material is inhomogeneous and anisotropic. Furthermore, it should be noted that there is a shear stress component present in the flexural test, which is usually neglected when the flexural modulus is calculated. This should normally lead to higher tensile than flexural properties.

As has, however, been demonstrated (Table 13.3, Figs 13.19–13.22) this is not the case for short fibre randomly oriented composites. One of the explanations for the contradiction between results by Wambua *et al.*[29] and the rest of the data presented here is the fact that if shear properties of the material are very low compared with the tensile properties (which is the case for well-aligned long fibre composites) then neglecting the shear stress component when determining the flexural modulus leads to higher tensile than flexural stiffness. If shear properties are fairly close to the tensile properties, which is the case for randomly oriented NFCs, the results may be different.



13.23 Tensile and flexural strength (a) and modulus (b) of PP reinforced with different types of natural fibres (40 wt%).[29]

13.5 Effect of fibre–matrix adhesion on mechanical properties

It has already been shown in previous sections (see, e.g., Figs 13.4, 13.8, 13.19–13.22) that fibre–matrix adhesion directly influences the performance of NFCs, especially strength, which is significantly increased if fibre–matrix adhesion is improved. The adhesion also might influence composite behaviour indirectly; for example, when the addition of an adhesion promoter results in better fibre dispersion (see Fig. 13.9).

To sum up the results presented above, better adhesion between fibre and matrix usually yields better mechanical properties of composite.

13.5.1 Adhesion characteristics and basic evaluation methods

IFSS can be used as the measure of fibre–matrix adhesion. Numerous methods are used to characterise fibre–matrix adhesion, which can be subdivided in three main groups:[30] (1) direct methods (single fibre pull-out, single fibre fragmentation, single fibre microindentation, single fibre compression); (2) indirect methods (variable curvature method, slice compression, ball compression test, fibre bundle pull-out, dynamic mechanical thermal analysis, voltage contrast X-ray photoelectron spectroscopy); and (3) composite lamina tests (transverse flex and tensile strengths, four- and three-point shear, ±45° and edge delamination, short-beam shear, Mode I and Mode II):

> While the indirect methods provide a qualitative method of ranking fibre–matrix adhesion and the composite laminate methods actually measure fibre–matrix interface sensitive composite properties, the direct methods not only measure fibre–matrix adhesion, but can provide information about the fibre–matrix failure mode and the ability to measure the energy involved in fracture of the fibre–matrix interface which is helpful for relating fibre–matrix adhesion to composite properties, especially toughness.[30]

Most popular of the direct experimental techniques for interface characterisation are single fibre pull-out test and single fibre fragmentation (SFF) test. However, these techniques are not always applicable to the characterisation of NFC systems. The main reason is the limited length of the fibres needed to prepare test samples. These limitations can be overcome by some modifications of the original methods used for synthetic fibres. For example, multiple short fibres (e.g., wood pulp[31]) with different orientations can be embedded in the matrix and fragmented. Then strains at failure should be recalculated according to the fibre orientation and data can be treated as in a traditional SFF test. Another technique used to perform successful SFF testing on flax fibres is to extend natural fibres by attaching another filament to the ends of the tested natural fibre.[32] A further obstacle to the use of SFF tests for thermoplastic composites is transparency of the matrix which is required to carry out SFF

Table 13.4 ISS for thermoplastics reinforced with treated and untreated flax fibres[35]

Flax fibre type	Matrix	Fibre treatment	IFSS (MPa)	Test method
Green	PP	–	6.33	SFF
		Acetylation	11.61	
		Stearic acid	9.49	
		–	7.21	Micro-debond
		MAPP treated	7.20	
Dew retted	PP	–	12.75	SFF
		Acetylation	13.05	
		Stearic acid	13.36	
		Transcrystalline layer	23.05	
		–	17.3	Pull-out
	HDPE	–	18.0	
	LDPE	–	5.6	
	PP/MAPP	–	17.8	
Duralin™	PP	–	7.45	Micro-debond
		Hot-cleaned	6.63	
		MAPP treated	7.17	
	HDPE	–	16.2	Pull-out
	LDPE	–	7.1	

experiments. As thermoplastics are often semicrystalline polymers, they are usually opaque. One of the ways to solve this problem is by use of very thin specimens (polymer films in which fibre is embedded).[33,34] However, stress distribution in such specimens might be rather inhomogeneous if the matrix layer surrounding the fibre is thin.

Although these direct methods (particularly SFF) give a lot of useful information, they are time consuming and relatively complicated. Therefore, composite lamina tests are more often the preferred choice for characterisation of fibre–matrix adhesion, even though the result is often qualitative comparison between different composite systems rather than quantitative characteristic, such as IFSS. Results of such investigations are presented further in this chapter.

Some of the values of IFSS for different thermoplastics reinforced with treated and untreated flax fibres[35] are presented in Table 13.4 (results are collected from different sources).

13.5.2 Modification of fibre and matrix to improve interfacial strength

If a ductile polymer is used as a matrix, and many thermoplastics exhibit ductile behaviour, it is practical to assume the yield strength of the resin as the upper limit of interfacial strength. Therefore, if a rigid (compared with the matrix) and elastic fibre is added to the polymer, the alteration of fibre–matrix adhesion significantly changes the overall properties of composite. There are several methods that are used to improve the adhesion between fibre and matrix. These methods can be separated in two main groups:[36] (1) physical methods (stretching, calendering, thermotreatment, corona, cold plasma treatment); and (2) chemical methods (alkaline and silane treatment, impregnation of fibres, graft copolymerisation, treatment with compounds that contain methanol groups, treatment with isocyanates, etc). Modification of the fibre surface as well as the selection of polymer additives is governed by chemical composition of polymer and type of fibre. The classification of adhesion enhancement can also be performed by the following principle: (1) treatment of the fibres as an additional step in fibre manufacturing; and (2) addition of adhesion promoter into the matrix. The latter method is cheaper and easier to implement. Adhesion promoter can be added in the material during the manufacturing (for example, extrusion); it does not require an additional processing step as in the case of fibre treatment. Moreover, fibre treatment might affect the mechanical properties of the fibre itself due to mechanical handling during the treatment step and to chemical and/or thermal degradation. In many instances, addition of adhesion promoter into the polymer appeared very effective.

The large amount of hydroxyl group in cellulose endows natural fibres with hydrophilic properties. When natural fibres are used to reinforce hydrophobic matrices, the result is a very poor interface and poor resistance to moisture absorption.[26] Chemical treatment of fibres may activate hydroxyl groups or introduce new functional groups that can effectively react with polymer: ‘Generally, chemical coupling agents are molecules possessing two functions: the first function is to react with hydroxyl groups of cellulose and the second is to react with functional groups of the matrix’.[37]

For example, a very popular additive that works well with PP and natural fibres is MAPP (maleic anhydride grafted PP). However, not all adhesion modification techniques are equally efficient because they may be incompatible with the particular composite system, thus some of them can actually degrade the properties of composite material. An example of property variation with different fibre treatments of longitudinally oriented LDPE–sisal composite (fibre length 5.8 mm, fibre content 30%) is shown in Table 13.5.[38] These results reveal that fibre treatment by alkali is much less effective than other procedures; moreover, the strain at failure of the composite is actually reduced. Another example of ineffective fibre treatment is presented in Fig. 13.24 (typical stress–strain curves and average mechanical properties) for PLA/flax fibre composites with 30 wt% fibre content (the values of mechanical properties presented in Fig. 13.24 are normalised with respect to the data for untreated material). Neither acetylation nor plasma treatment provides any improvement to the mechanical properties of these materials. Obviously, either the treatment techniques are not suitable for these material systems or the treatment procedure (conditions) is not optimal.

Table 13.5 Properties of longitudinally oriented LDPE–sisal composite with different fibre treatment (fibre length 5.8 mm, fibre content 30%)[38]

Treatment/properties	Tensile strength (MPa)	Tensile modulus (GPa)	Strain at failure (%)
Untreated	31.1	3.09	2
Alkali	34.3	3.33	1
Isocyanate	41.5	4.07	4
$KMnO_4$	38.8	3.82	3

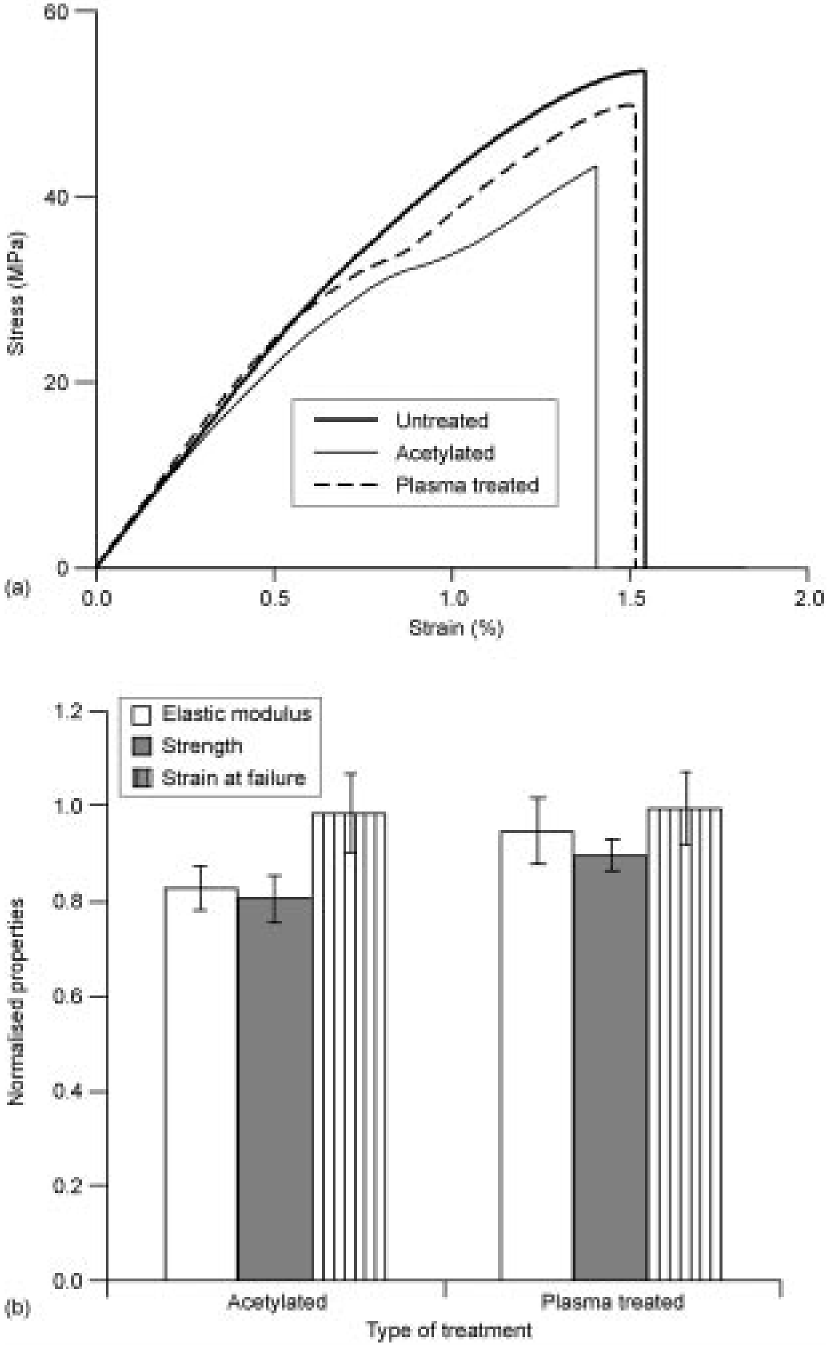
The application conditions (time, temperature) and the amount of adhesion promoter used are also essential for optimisation of composite performance. An example of the effect of concentration of coupling agent and the time of treatment is shown in Fig. 13.25.[39,40] Figure 13.25(a) demonstrates changes of flexural modulus of PP/jute with 30 wt% of fibres with concentration of MAPP and time of application of treatment.[39]

Figure 13.25(b) demonstrates changes of tensile, flexural and impact strengths of a similar PP/jute composite[40] with 30 wt% of 6 mm long fibres. The results presented are normalised with respect to the properties of the untreated material. These graphs suggest that there are optimum conditions and amount of coupling agent at which mechanical properties are best. Another interesting example supporting this conclusion is shown in Fig. 13.26 where a so-called 'factor of compatibilisation' calculated based on the strength of composite (PP/hemp strand) and its constituents[27] is plotted as a function of the amount of adhesion promoter (MAPP). These data show that, regardless of the amount of reinforcement, the maximum for the factor of compatibilisation is achieved at approximately the same amount of MAPP.

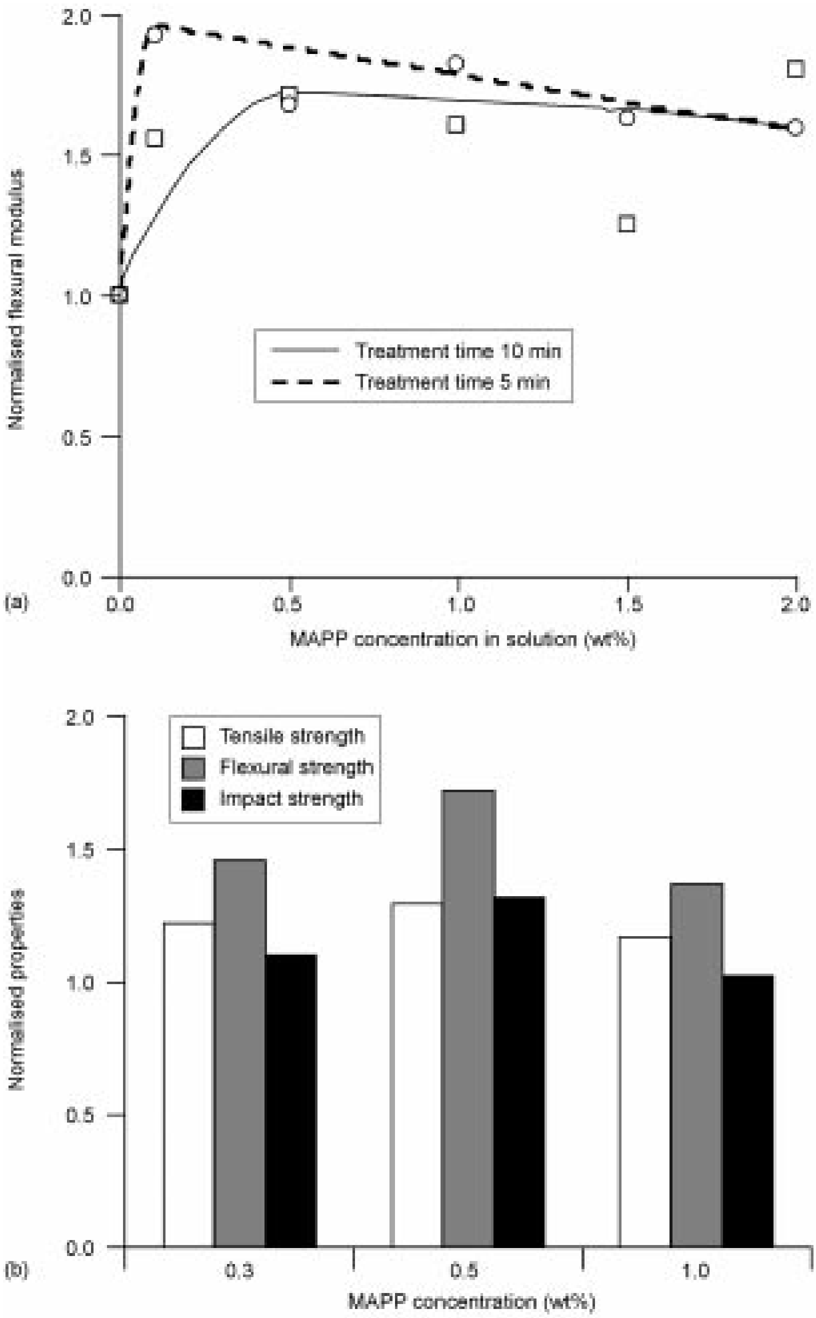
The examples discussed above provide only a general insight into the methods of modification of the fibre–matrix adhesion; the chemical compatibilisation and surface treatment constitute a major research area by themselves.

13.5.3 The leading role of interfacial strength to ensure acceptable mechanical performance of natural-fibre composites

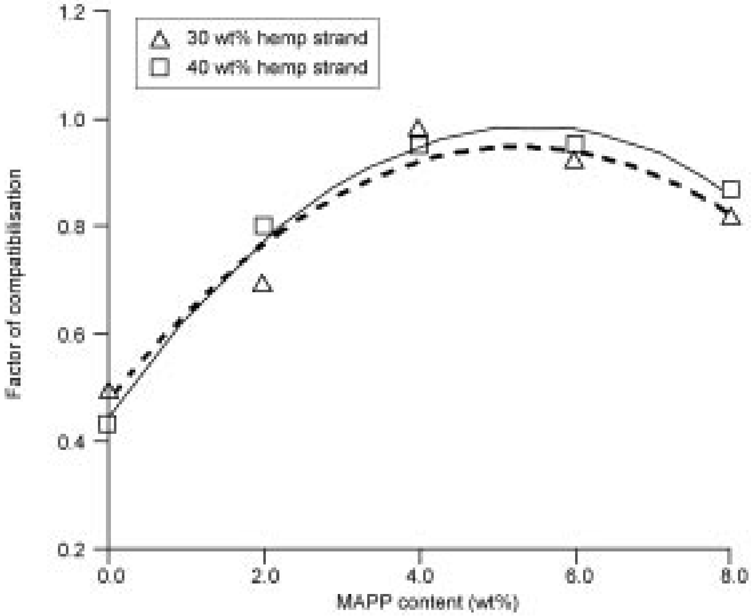
The predicted tensile strength of PP/wood powder composite with 30, 40 and 50 wt% of filler is plotted in Fig. 13.27 as a function of IFSS.[8] Calculations are done according to Eqs. 13.2–13.4. These results show that at low IFSS the composite strength is higher for materials with a lower content of filler. This is in agreement with the experimental results presented in Fig. 13.8(a) (composite without coupling agent). However, if interfacial adhesion is significantly improved, the strength of the composite increases with the increase of filler



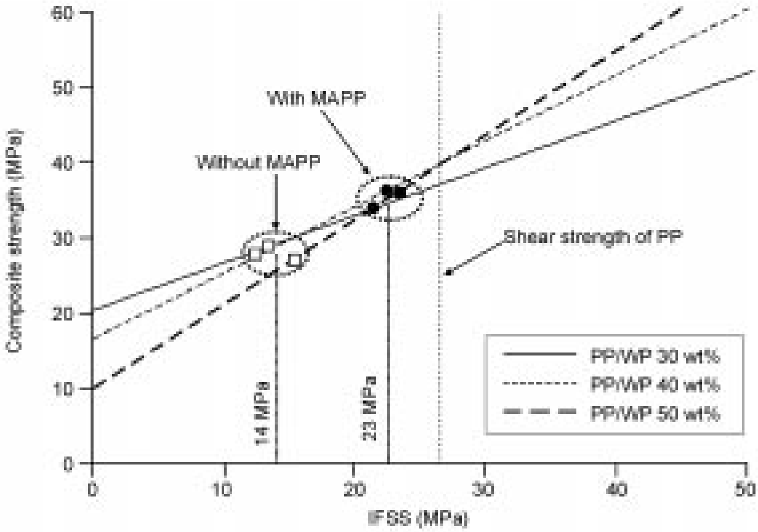
13.24 Typical stress–strain curves for (a) PLA/flax fibre (30 wt%) composites and (b) normalised mechanical properties.



13.25 Dependence of mechanical properties of PP/jute with 30 wt% of fibres: (a) effect of concentration of the coupling agent and the time of treatment;[39] (b) effect of concentration of the coupling agent on tensile, flexural and impact strengths.[40]



13.26 Dependence of the factor of compatibilisation on the amount of MAPP (amount of adhesion promoter is given with respect to the amount of reinforcement).[27]

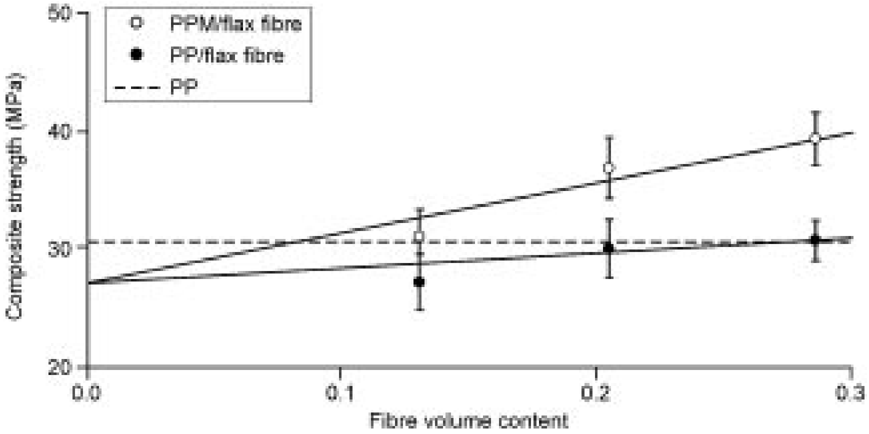


13.27 Tensile strength of PP/wood powder composite as a function of IFSS; modelling results presented as lines and experimental data as symbols.

content. This is also in agreement with the experimental results shown in Fig. 13.8(a) (composite with coupling agent), although the increase of strength is lower than predicted.

The experimental values of strength are also plotted in the same figure as modelling results (Fig. 13.27, filled and opened symbols) for comparison. Since the actual IFSS for these material systems is not known, in order to put experimental points on the graph, measured values of strength were used as the ordinate, and the abscissa was obtained by crossing calculated curve for the composite with the corresponding fibre content. The result of this exercise is very interesting: the values of IFSS which are read from the calculated curves are almost the same for all materials independent of fibre content. The results for the composite without adhesion promoter indicated IFSS of approximately 14 MPa and composites with coupling agent provided value of 23 MPa, which means that the addition of coupling agent improved adhesion between fibre and matrix by almost 65%. Note that in this case the addition of coupling agent was quite effective because the measured IFSS of the composite is very close to the shear strength of the matrix (27 MPa).

Another example of the successful application of adhesion promoter is shown in Fig. 13.28, where results for PP reinforced with flax fibres are presented. Addition of MAPP significantly increases composite strength. The composite without adhesion promoter has a strength lower than the strength of PP and only an improved fibre–matrix interface allows utilisation of the reinforcing effect of flax fibres.

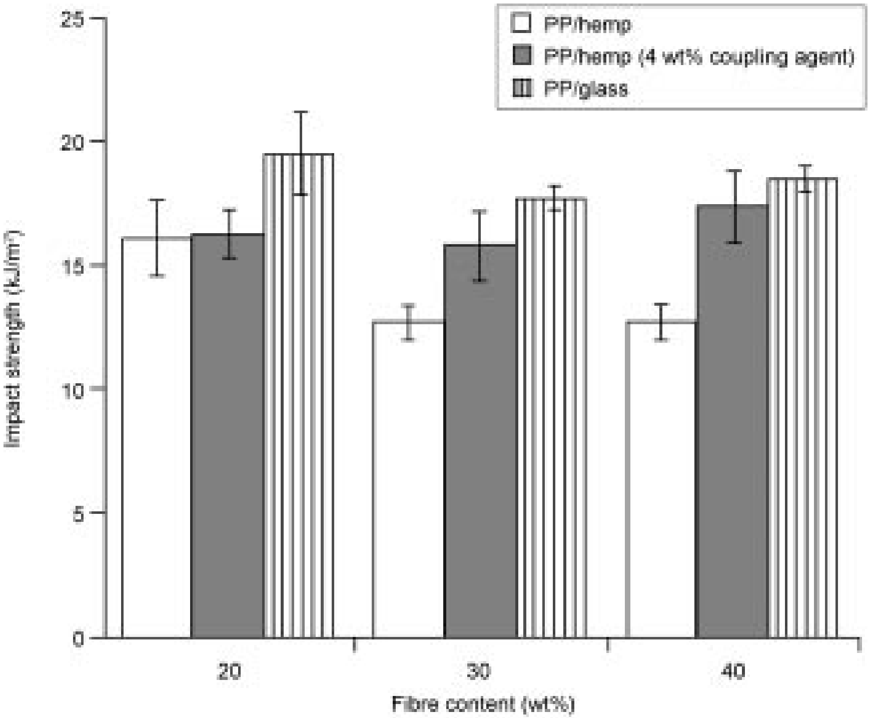


13.28 Tensile strength of PP/flax fibre composite as a function of fibre volume fraction with (PP/flax fibre) and without (PPM/flax fibre) adhesion promoter MAPP.

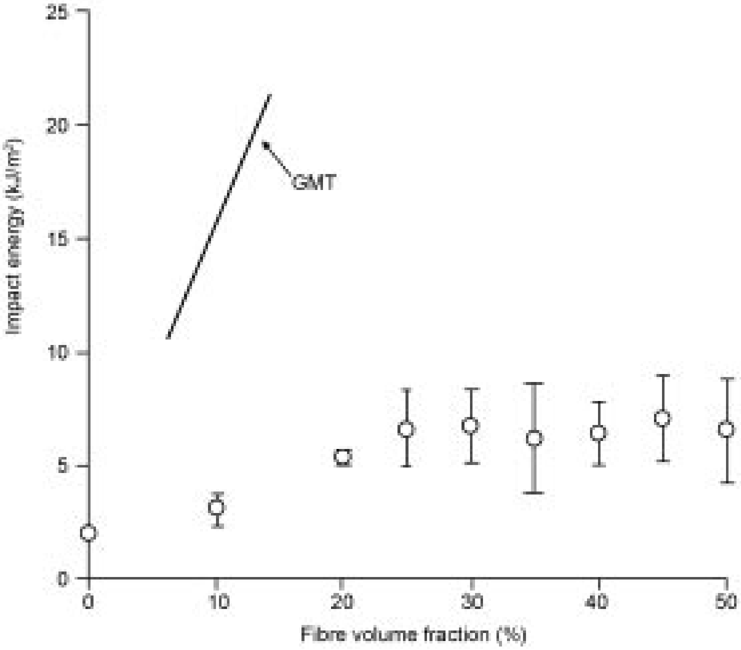
13.6 Impact strength

It has been shown in previous sections (e.g., see Tables 13.1 and 13.3) that NFCs have properties that are competitive in comparison with glass fibre thermoplastic composites (the primary target for substitution by NFCs), especially when specific properties are considered. However, one property of short fibre thermoplastic NFCs which is very important for various applications, namely impact strength, is often listed among the major disadvantages of NFCs in comparison with glass fibre composites (usually glass mat thermoplastics (GMT) are used as a reference). However, it seems that in recent years with development of new fibre manufacturing techniques and improved composite processing methods along with enhancement of fibre–matrix adhesion the situation is somewhat improved. The impact strengths of PP/hemp with and without coupling agent along with results for PP/glass fibre composite are presented in Fig. 13.29.[27]

These results show that if a coupling agent is used then the impact strength of PP/hemp fibre NFC is quite similar to that of a glass fibre composite with the same fibre content by weight. However, it should be noted that, owing to the much higher density of glass fibre compared with natural fibres, the volume



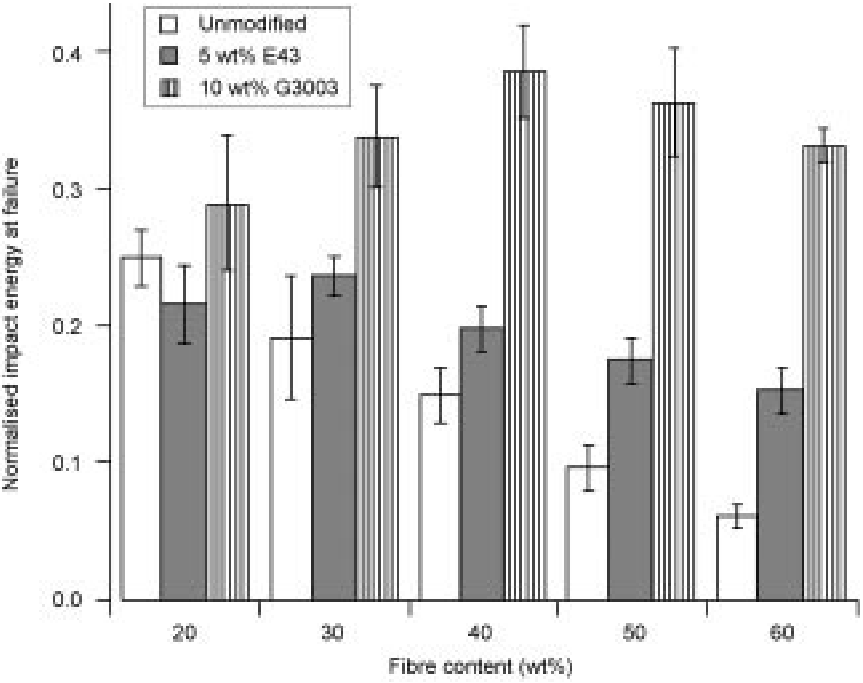
13.29 Impact strength of PP/hemp with and without coupling agent and results for PP/glass fibre composite.[27]



13.30 Impact strength for PP/flax composite and commercial GMT.[41]

fraction of glass fibres in these composites is much lower than that in NFCs. Results presented in Fig. 13.30 show the impact strengths (notched Charpy) for PP/flax composites and data for commercial GMT.[41] It is clear from these results that GMT performs significantly better than the NFCs. It is interesting to note that at low fibre content (<25%) the impact strength increases with addition of reinforcement but then levels out at certain fibre volume content. It is argued[41] that in the case of thermoplastic short fibre randomly oriented NFCs, energy dissipation by fibre pull-out during the impact is very limited owing to low fibre strength. It is pointed out[41] that adhesion in a PP/flax system is almost as good as in PP/glass, but owing to the lesser strength of natural fibres, a brittle failure mode of NFC is observed, with fibre fracture (at much lower strains than for glass fibre) being the main energy dissipation mechanism.

Nevertheless, in many cases energy dissipation by fibre–matrix interface failure (fibre pull-out) is also very significant. Different studies show considerable changes of impact strength of thermoplastic NFC with alteration of fibre–matrix adhesion. For example, results presented in Fig. 13.31 for PP/flax fibre (data are normalised with respect to the impact strength of PP) show that use of different types and amounts of coupling agents does increase impact strength of NFC.[21] These results show that impact strength of NFC is only 40% of the value of neat matrix; decrease of impact strength of thermoplastics with addition of reinforcement is usually observed in short fibre NFCs. Actually,

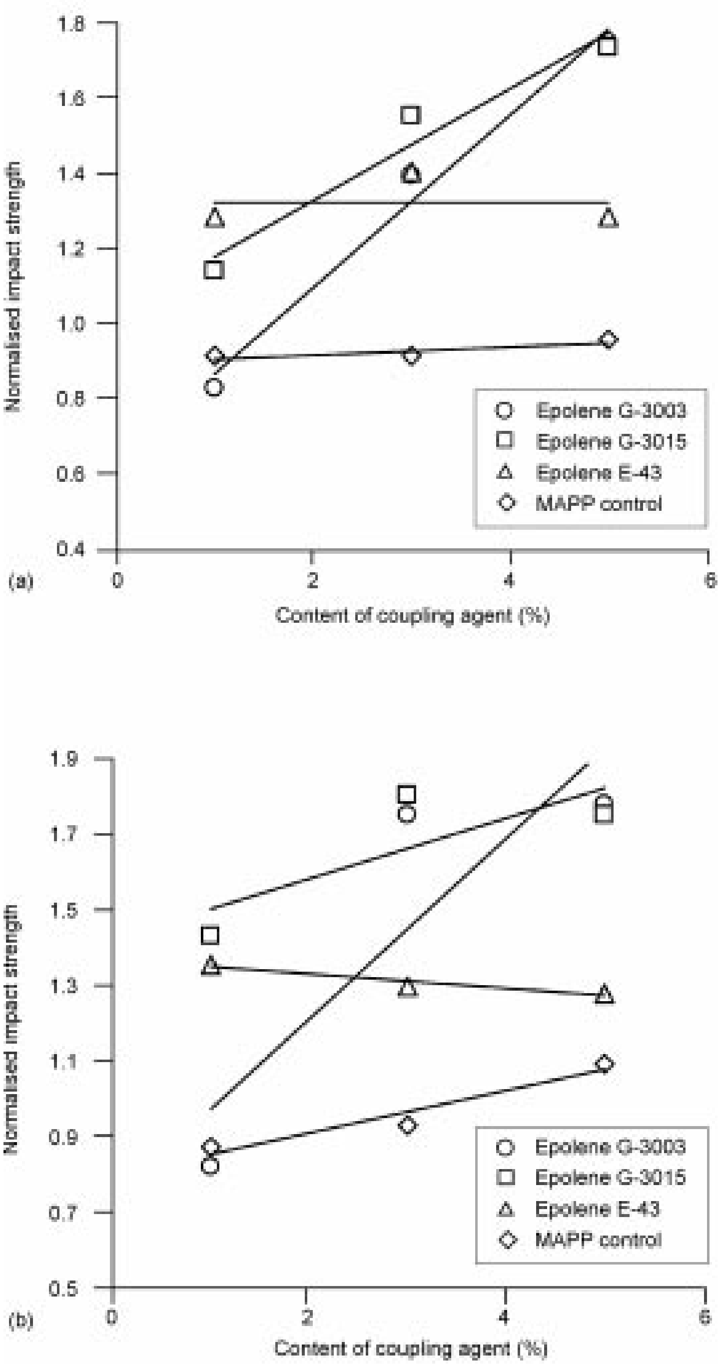


13.31 Normalised impact strength of PP/flax composite with different fibre content.[21]

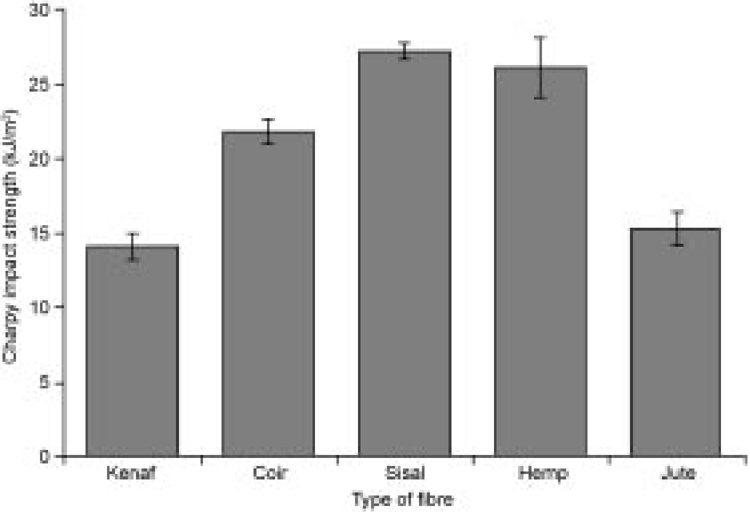
trends observed for impact strength are reasonably similar to those seen for tensile and flexural strength (see Fig. 13.19). This is probably not that surprising, since similar failure mechanisms are observed in all those loading conditions (matrix yielding, fibre fracture, fibre debonding and pull-out). It is interesting to see that there is a peak in impact strength values at 40 wt% fibre content (see Fig. 13.31) which was not observed in Fig. 13.30. It probably indicates that at higher contents of fibres, reinforcement is not as well dispersed and sites of agglomeration may act as crack initiators.

Another example of the effectiveness of coupling agents in improving impact strength (values are normalised with respect to the results for composites without coupling agent) of NFCs is shown in Fig. 13.32 for PP/flax and PP/jute (30 wt%) composites.[22] Once again, similarities between the trends observed for impact, tensile and flexural strength (see Fig. 13.21) can be noted from these results.

Impact strengths (un-notched Charpy) for PP (PP films were made from pellets and composite prepared by hot pressing of stacked film and fiber layers) with different fibre types (40 wt%) are shown in Fig. 13.33.[29] In this case, ranking of materials by impact strength is not exactly the same as for tensile and flexural strengths (see Fig. 13.23) but, nevertheless, there are similarities.

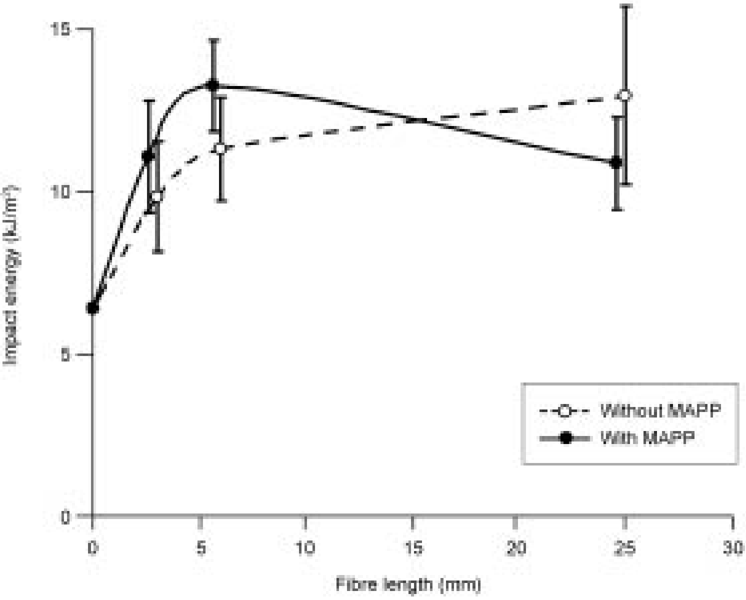


13.32 Normalised impact strength of (a) PP/flax and (b) PP/jute (30 wt%) composites.



13.33 Impact strength for PP with different fibre types (40 wt%).

Fibre length also has a strong effect on impact strength of NFC; for example, results presented in Fig. 13.34 for PP/flax[41] with different fibre lengths show that initially there is increase of impact strength with increasing fibre length. However, at certain fibre lengths the impact strength reaches a plateau for a



13.34 Impact energy as a function of fibre length for PP/flax composite.

composite without a coupling agent and decreases for a composite with MAPP. This phenomenon is clarified by Garkhail *et al.*[41]:

> This behaviour can be explained by the decrease in critical fibre length with the addition of MAPP, thus leading to additional energy contributions by fibre fracture for the shorter fibre system. Whereas at higher fibre lengths the improved adhesion leads to a decrease in energy dissipation because of limited fibre debonding and pull-out mechanisms.

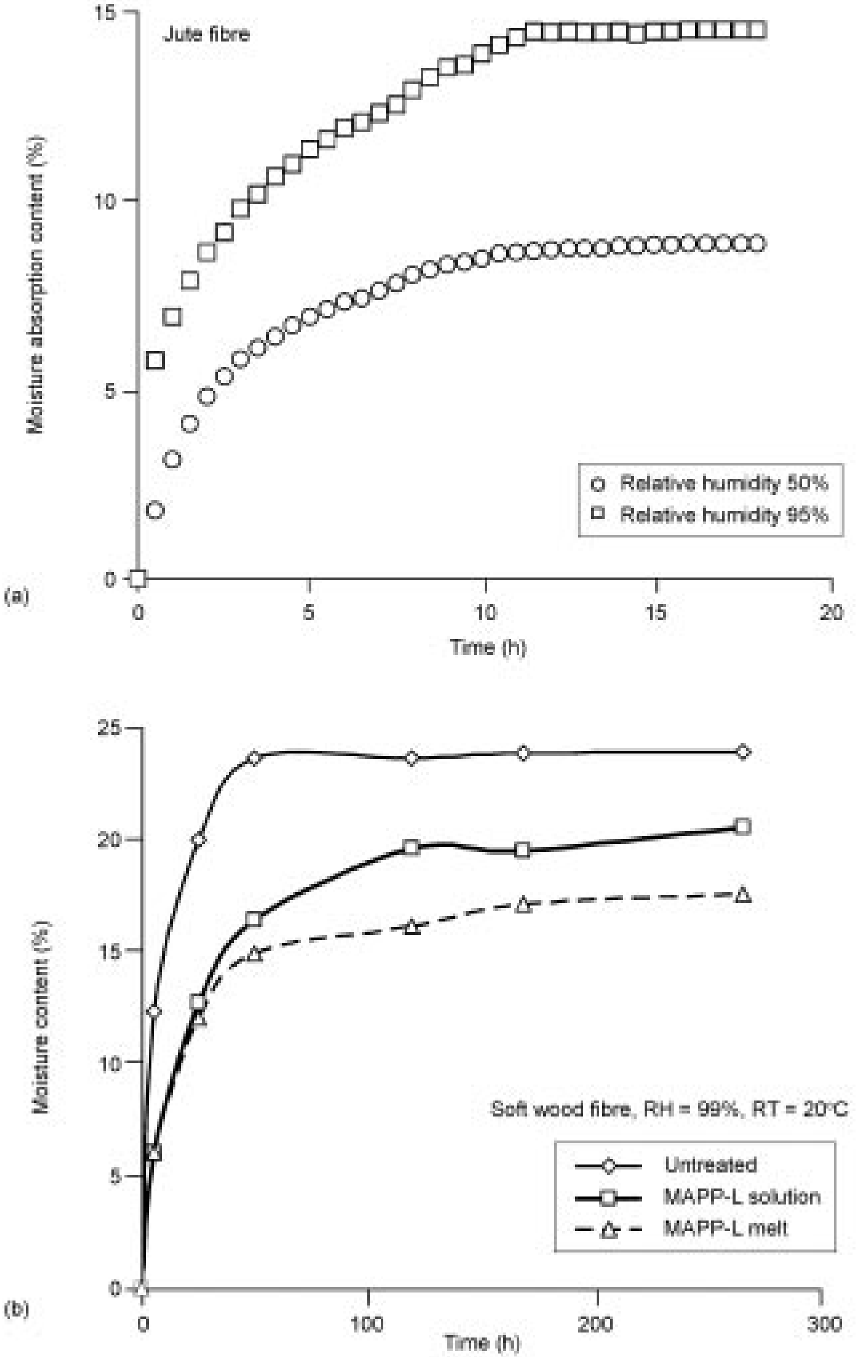
13.7 Effect of conditioning and environment on mechanical performance of thermoplastic matrix natural-fibre composites

One of the drawbacks, probably the most important, of natural fibres is their high moisture absorption and poor dimensional stability. Swelling of fibres within a composite can lead to the build-up of internal stresses and subsequent development of damage (for example, micro-cracking) that, in its turn, leads to degradation of mechanical properties. This is undoubtedly a major limitation of the use of NFCs in durable composite applications. Therefore, the humidity effect on mechanical performance of NFCs will be mostly addressed in this section, although there are other very important parameters of environment that can influence performance of NFCs (for example, temperature, UV radiation).

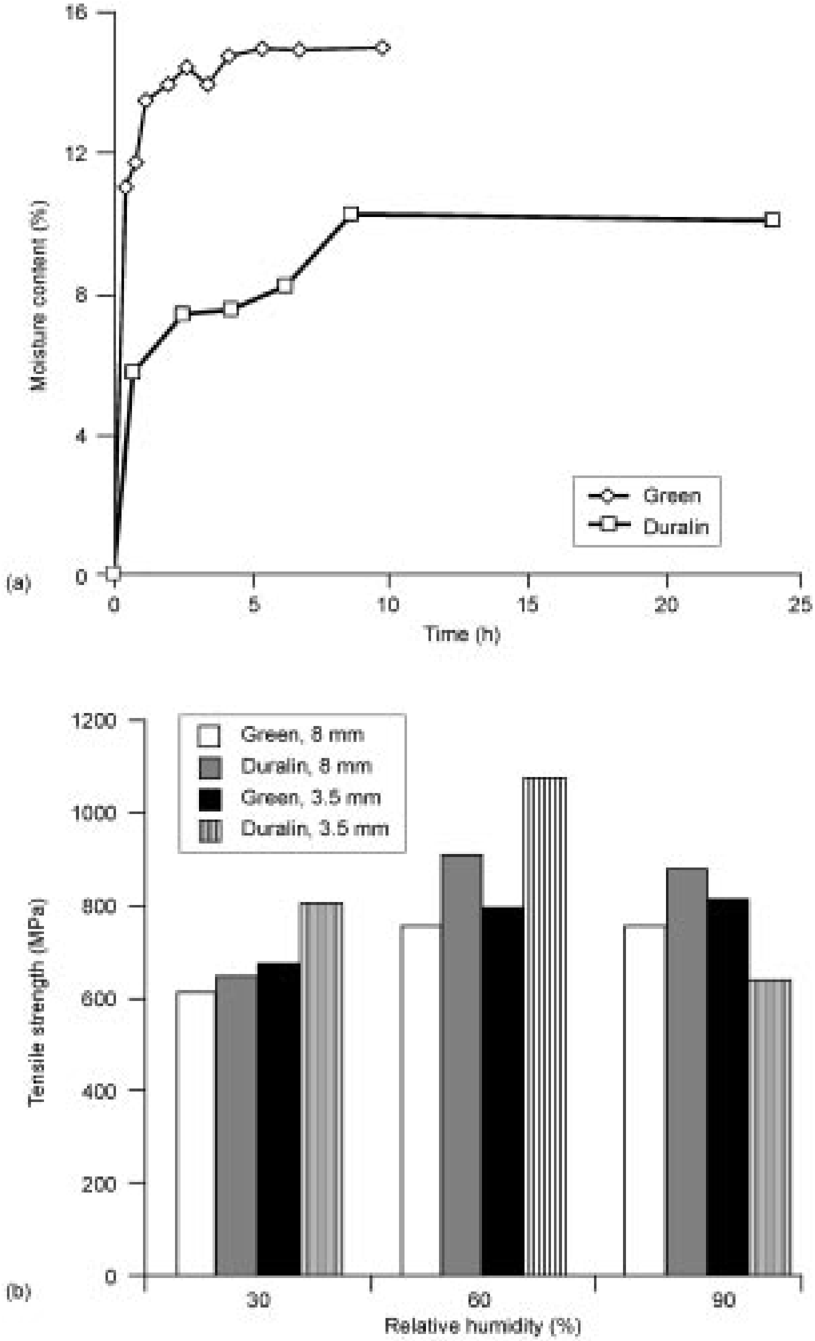
The largest part of moisture uptake in NFCs is attributed to the reinforcement. In order to overcome this problem, different types of fibre treatments are used; some of the techniques were discussed in Section 13.5 on fibre–matrix adhesion. Examples of moisture accumulation in natural fibres with time under different conditions (relative humidity) and for different fibre treatments are shown in Figs 13.35 and 13.36(a).[42–44]

Analysis of these results shows that moisture content as well as the rate at which it accumulates is directly related to the ambient relative humidity. However, the treatment of fibres can reduce, very significantly, both moisture saturation level and the rate of absorption. Results in Fig. 13.36(b) show that at intermediate relative humidity (rather low moisture saturation level), fibre strength is actually increasing, but at higher levels of relative humidity (90%), strength is again decreasing. This is a very interesting result which indicates that modest amount of water molecules in the fibres can be advantageous. Most likely this is due to the plasticising effect of free water molecules in the material.

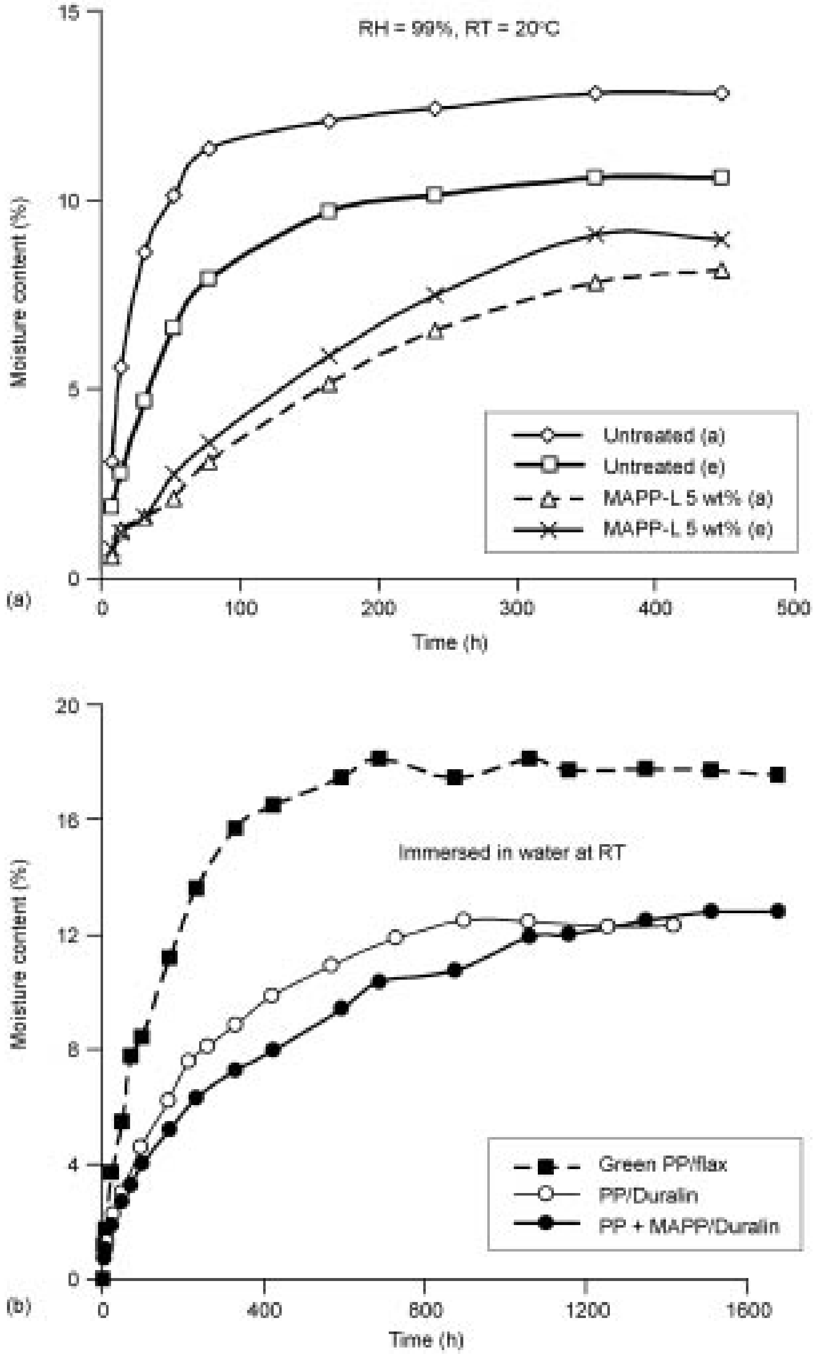
Since NFCs contain very significant amounts of fibres, their behaviour in terms of moisture uptake is very similar to that of the fibres. The main difference is the time needed to reach saturation level, approximately by a factor of 10, since composites are much thicker than fibres and it takes much longer for water to penetrate through the material. Examples of water absorption in NFCs are presented in Fig. 13.37.[43-44] Results in Fig. 13.37(a) for PP/hard wood fibres (50 wt%) demonstrate the influence of fibre distribution on moisture uptake (‘a’ –



13.35 Moisture content as a function of time: (a) at different relative humidity;[42] (b) for different fibre treatments.[43]



13.36 Moisture uptake (a) of flax fibres with (empty squares) and without treatment and effect of moisture (b) on strength of flax fibres with and without treatment.[44]



13.37 Water absorption in NFC: (a) PP/hardwood fibres (50 wt%)[43] and (b) PP/flax fibre (38 wt%).[44]

agglomerated, composites prepared by using high-speed Hencel mixer; 'e' – extruded, materials prepared in twin-screw Haake extruder) and the effect of coupling agent. Data in Fig. 13.37(b) for PP/flax fibre (38 wt%) show a positive effect of fibre treatment and coupling agent on the resistance to moisture absorption.

Clearly, natural fibres usually dominate in the water uptake behaviour of NFC. For example, it is shown by Khalil *et al.*[45] that the saturation moisture content in the matrix of PP/wood sawdust composite is very low (<2% after 100 days of immersion in water) while during the same time interval NFCs with 50 wt% of filler take up 12–22% of water, depending on the length of the fibre. It is interesting to note that the length of reinforcement significantly influences the saturation level of moisture content: for 100 μm long fibres the saturation level is 12%, for 212 μm – 16% and for 300 μm – 22%.

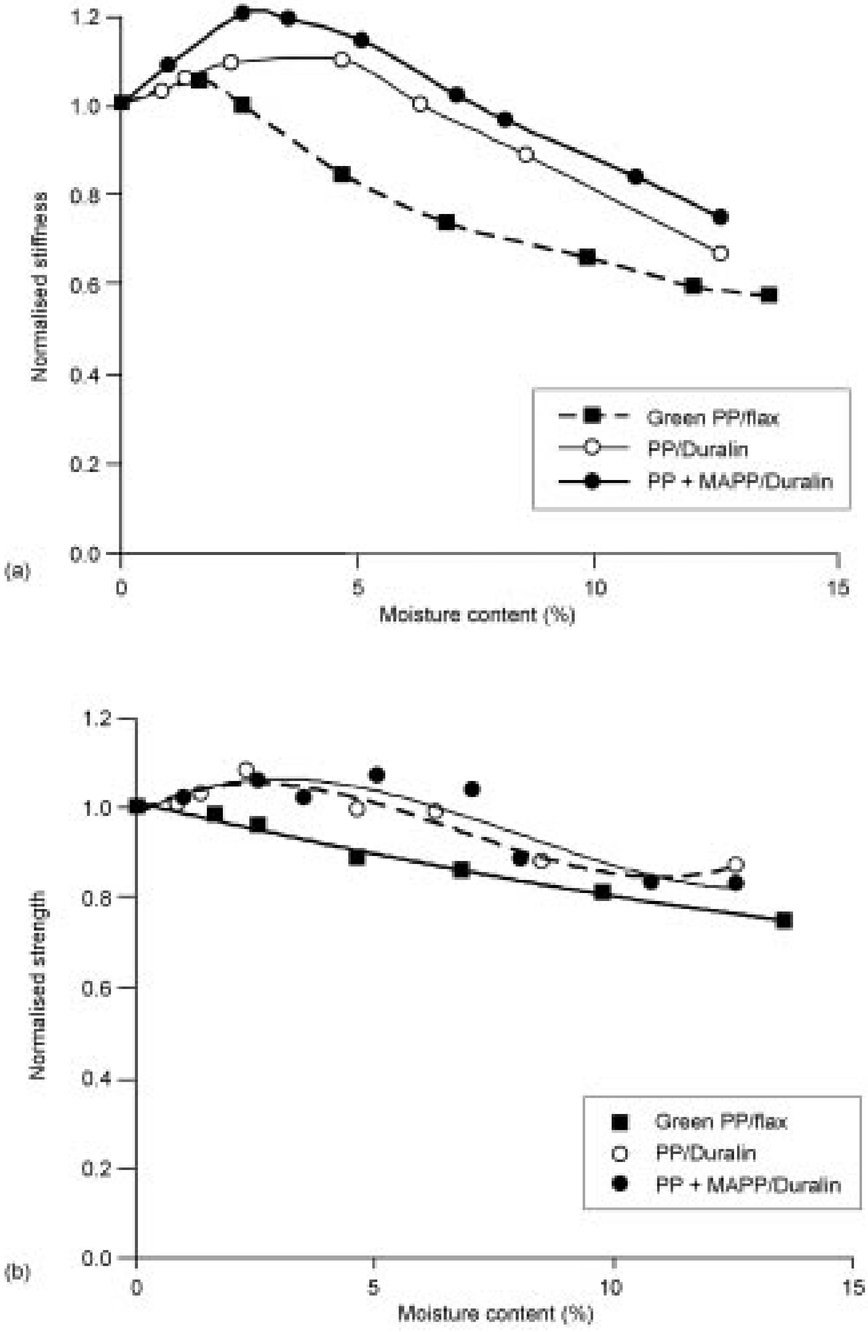
Similar results for moisture uptake by PP matrix are presented by Panthapulakkal and Sain.[46] After 150 days in distilled water, moisture content in the neat polymer is only 0.4%, whereas in PP/hemp fibre composite (40 wt%) the moisture content is approximately 9% after the same exposure to water. It should be noted, however, that there are also some polymers, especially bio-based resins, that can be as sensitive to moisture as natural cellulose-based fibres.

Some of the experiments that have shown very high moisture content and rapid accumulation of moisture in material have been aquired by immersion of specimens into water. One should be careful with these kinds of experiments and ensure that specimens do not contain large voids which can be filled with water because this will lead to false results about actual moisture content in the material.

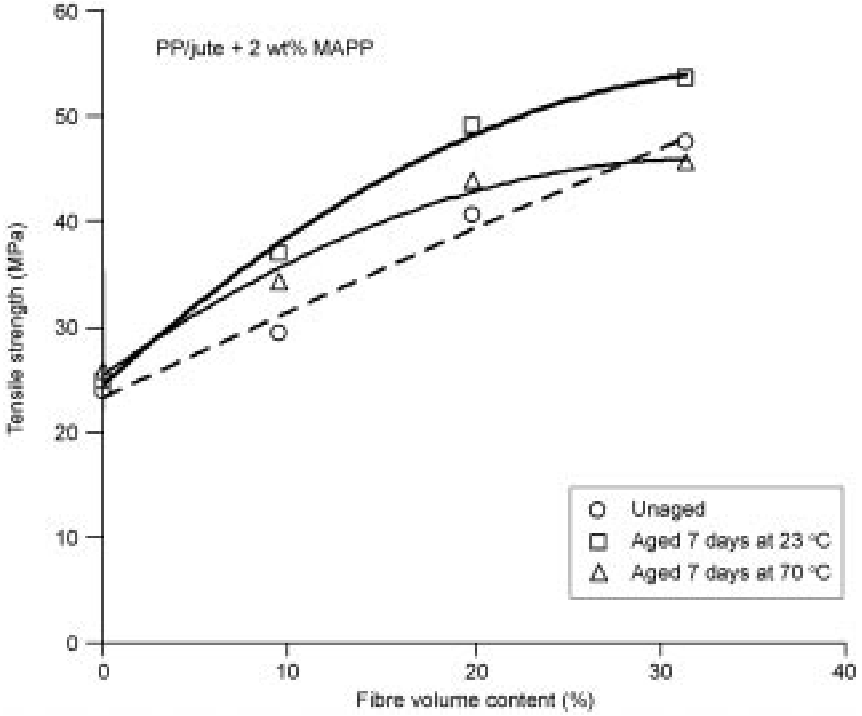
Mechanical properties (normalised with respect to dry composite properties) as a function of moisture content for PP/flax fibre (38 wt%) composite are presented in Fig. 13.38.[44] It is interesting to note that, similar to fibres (see Fig. 13.36(b)), the properties of composites do not vary monotonically with moisture content. A similar phenomenon is shown in Fig. 13.39 for PP/jute composite[42] with different fibre fractions after humidity ageing.

The improvement of composite properties at low moisture content is attributed to the swelling of fibres and resulting increase of the effective interfacial adhesion.[42,44] IFSS,[42] back-calculated from composite strength, changes from 19.8 MPa for unaged material to 27.1 and 22.7 for a composite aged at room temperature and 70 °C respectively.

Generally speaking, however, moisture is definitely detrimental for performance and long-term use of NFCs. A small amount of moisture in material might probably be advantageous in some instances owing to the mentioned factors (fibre swelling and plasticising effect of water). An example of degradation of starch/flax fibre (20 and 40 wt%) composite properties is shown in Fig. 13.40. The materials were conditioned for 3 weeks at 34% and 61% relative



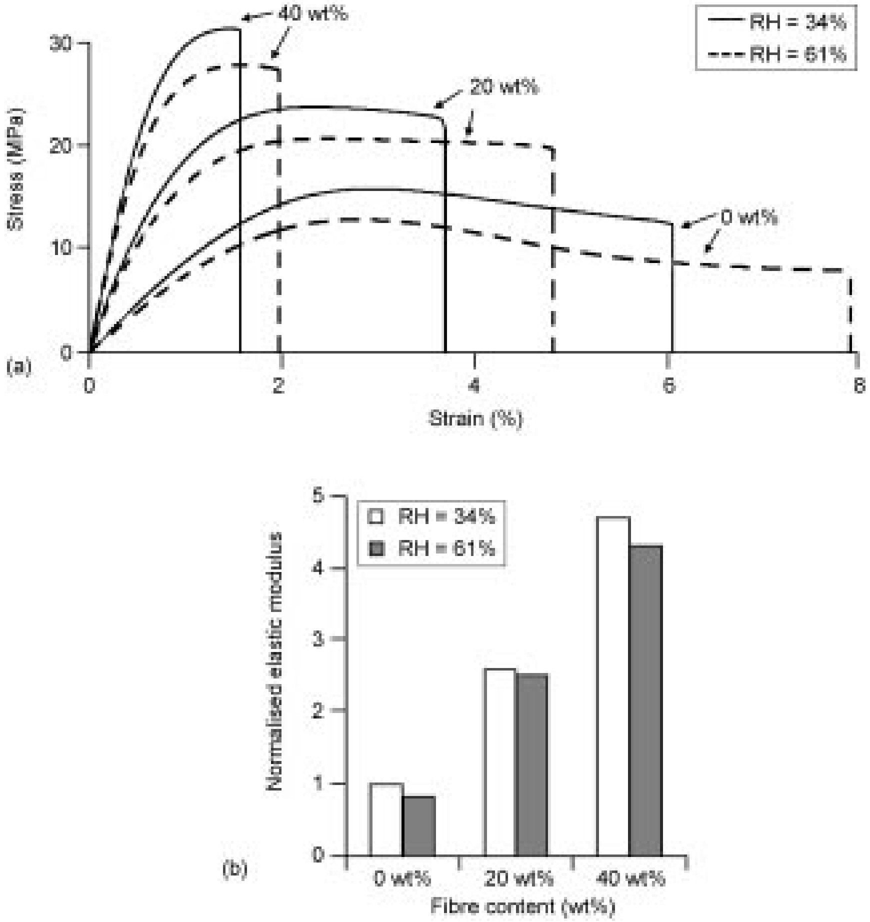
13.38 Mechanical properties of PP/flax fibre composite (38 wt%) as a function of moisture content.[43]



13.39 Mechanical properties of PP/jute fibre composite with different fibre contents and different extent and conditions of ageing.[42]

humidity at room temperature (20 °C). Unfortunately, absolute numbers for moisture content are not known for these composites because they were not completely dried before exposure to humidity, but it is known that the additional moisture content gained during 3 weeks was higher for materials conditioned at 61% relative humidity. Results in Fig. 13.40(a) show that there is a consistent reduction of material stiffness and strength with increasing relative humidity at which materials were conditioned. It should also be noted that strain at failure increases with increasing relative humidity, which can be attributed to the plasticising effect of water (in this case for both matrix and fibres). Although the additional moisture gain was larger for composites with higher fibre content (as expected), neat polymer shows a larger drop in modulus (≈19%) compared with 20 wt% (modulus decrease ≈3.3%) and 40 wt% (modulus decrease ≈8.8%) composites (see Fig. 13.40(b)). On the other hand, in composites with a higher content of fibres the content of matrix is lower (elastic modulus of matrix is also lower than that of reinforcement), and therefore decrease of modulus in composites cannot be attributed to the changes of properties of the polymer only.

Similar indications of degradation of mechanical properties of NFC can be found in other sources, for example a decrease of compressive strength of



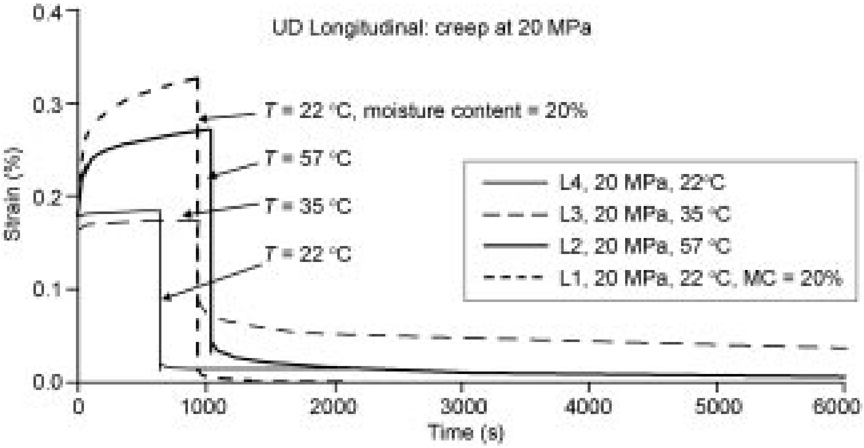
13.40 Stress–strain curves (a) of starch/flax fibre composite with different fibre contents and different RH; (b) elastic modulus (normalised with respect to modulus of matrix conditioned at 34% RH) as a function of fibre content and relative humidity.

HDPE/wood fibre composite at moisture content as low as 3.5% is reported by Huang *et al.*[18] The same paper reports reduction of flexural modulus and strength at water uptake of 2% and decrease of fracture toughness at moisture content of only 1%.

Results presented by Panthapulakkal and Sain[46] show that wet (moisture content 8.73%) injection moulded PP/hemp (40 wt% fibres and 5 wt% compatibiliser) composite loses 35% and 56% of tensile strength and modulus respectively. In this case, the major impact of moisture on mechanical properties of NFCs can be attributed to fibres because the moisture content in the matrix (PP) at equilibrium was only 0.4% and the decrease of tensile strength and modulus was only 1% and 19% respectively. The reduction of matrix stiffness probably occurred because water molecules acted as a plasticiser.

As mentioned before, there are other important factors of the environment apart from moisture that can severely influence the performance of NFCs. For thermoplastic composites, temperature is a factor. It should be noted that the combined action of humidity and elevated temperature is extremely damaging for mechanical response of thermoplastic NFCs. First of all, elevated temperature promotes the rate of moisture uptake by matrix and reinforcement. Secondly, the properties of matrix material are significantly affected, especially if the temperature approaches the levels of thermal transition (for example glass transition temperature) of polymer. However, effects of temperature on thermoplastic polymers are well studied and levels of temperature that affect polymer properties are very individual for each material, therefore this subject will not be further discussed here.

One example of the temperature and moisture effect on the mechanical performance of PLA/wood fibre composite is shown in Fig. 13.41 (creep test is performed at 20 MPa, static strength of the composite ≈170 MPa). These results show that creep resistance of the composite is not affected if temperature is raised to 35 °C but at a temperature of 57 °C (close to the glass transition of PLA), significantly higher strains are registered. However, creep strains at the moisture content of 20% and room temperature are even higher than those registered at higher temperatures. As this is a composite with rather high fibre content (≈40 wt%) and the fibres are well aligned, the effect can be explained by the fact that temperature affects only the matrix, whereas moisture mostly (as was discussed before) has an effect on natural fibres.



13.41 PLA/wood-fibre unidirectional composite creep at different ambient conditions.

13.8 Conclusion

There is little doubt that natural-fibre composites will gain even more popularity in the near future due to their decent mechanical properties. However, there is still a lot of work to be done to improve their performance to the desired level. One of the major disadvantages of these materials is the large variability of properties, which makes it difficult to design structural components. Often contradictory results are obtained for similar material systems because the performance of NFC is very sensitive to a large number of parameters that can be affected by processing of these materials. Some of these parameters are: fibre properties, fibre length distribution, fibre–matrix adhesion and fibre dispersion. Another problem that has to be solved is the sensitivity of NFCs to environmental conditions, mainly humidity and temperature.

Work on the development of thermoplastic NFCs is an ongoing process, and new improved methods of fibre processing and treatment as well as optimised composite manufacturing will lead to the development of materials that will be up to the task of substituting glass fibre-based composites. Another very promising and appealing direction of expansion of NFC use is whole bio-based composites in which both fibres and matrix are obtained from plants.

13.9 Acknowledgements

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14

Long-term performance of natural-fiber composites

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14.1 Introduction

Natural-fiber polymer composites (NFPC) are receiving the attention of academia, industry and government bodies from all over the world. Recent environmental regulations and shortage of petroleum derivatives has forced us to look for viable and sustainable sources for manufacturing consumer products. Substituting petroleum-based products with products from NFPC has never been an easy task from either the engineering or performance/acceptance point of view. NFPC products are facing a lot of challenges especially for outdoor applications. Long-term performance of these products under changing environmental conditions is the major issue that needs to be addressed. Moisture, temperature, and ultraviolet radiation alter the product properties in the long term, making it unsuitable for the specific use. In addition to that, under constant stress, NFPC products are more vulnerable to creep. These are the factors hindering acceptance of NFPC products industrially. Researchers are making efforts to understand the effect of these environmental factors on the properties of NFPC products and are trying to improve performance by altering the composition of the composites through addition of different additives. However, as most of these experiments are carried out in the laboratory for a comparatively short period with small samples, it is often difficult to predict the long-term performance of the product in the real world. Therefore, more research needs to be carried out in accelerated weathering conditions with commercial scale samples.

14.2 Natural fiber plastic composite products

Natural fibers have been associated with various aspects of human life for a long time. For the last two decades, NFPC products have been gaining importance in various industrial applications including furniture, automobile, packaging and especially in building and construction materials. NFPC products have great potential to replace timber, concrete, steel, and glass fibers which are in use in conventional building and construction industries. Natural fibers are the fastest-growing types of fillers used as reinforcements in commodity plastics throughout the world. In North America, natural fibers, especially wood fibers, are widely used in construction, whereas in Europe, flax, and hemp fibers are in use in automotive applications. Wood/thermoplastic composite lumbers with up to 50 wt% plastic have been used by the construction industry and homeowners, primarily for decking applications in North America (Lundin *et al.*, 2004). According to a report (Eckert, 2000), these composites are estimated to constitute 3–10% of the decking market. Low maintenance, property and performance uniformity, light weight, high strength and stiffness, corrosion resistance, and lower impact on the environment are the primary advantages of these composite products over the traditional structural lumbers.

There are also new growth opportunities that exist for other natural fibers such as rice hulls, straw, coconut husk, cotton stalk, flax, and hemp fibers in both structural and non-structural applications. The use of renewable natural fibers for the design and development of new automobile parts is growing owing to the increasing environmental concerns and the assumption of the future exhaustion of the crude reserves. It has been foreseen that the production of parts with low-cost composites based on natural fibers will offer both environmental and cost advantages in this extremely competitive market. The importance of use of NFPC in various industrial applications lies in:

- reduction of CO_2 emissions;
- reduction of vehicle emissions;
- conservation of other natural resources such as natural gas, mineral oil and coal;
- recycling through biodegradation;
- providing alternatives for agriculture;
- low cost in comparison with mineral or glass fiber filler;
- good specific mechanical properties;
- less abrasive than glass fibers;
- good acoustic and thermal insulation properties;
- very good flexibility to complex shapes.

When considering natural fibers for incorporation in the plastic matrix for manufacturing engineering materials, it is essential to consider some basic concepts regarding the natural fibers. According to Rowell (1998) natural fibers are made from carbon dioxide and water and recycled back to the starting chemicals by nature through different degrading reactions as summarized in Table 14.1. Hence, in order to manufacture durable natural-fiber-based composite materials, interference with the natural degradation processes is essential. The polymer matrices are also susceptible to environmental stresses, including temperature, moisture, light, and chemical agents such as organic solvents, ozone, acids, and bases. The mechanical properties of NFPC are dependent upon

Table 14.1 Degradation reactions in natural fibers upon outdoor exposure

Types of degradation	Agents	Reactions
Biological	Fungi, bacteria, insects, termites	Enzymatic and chemical – oxidation, hydrolysis, reduction Mechanical – chewing
Chemical	Acids, bases, salts	Chemical – oxidation, hydrolysis, reduction, dehydration
Water	Rain, ice, sea, acid rain, dew	Water interactions – swelling, shrinking, freezing, cracking
Weather	UV radiation, water, heat, wind	Chemical – oxidation, hydrolysis Mechanical – erosion

Source: Rowell (1998).

the interfacial adhesion between the polymer matrix and the reinforcing fiber and hence the degradation of fiber, matrix, or interface caused by weathering can reduce these properties. Therefore it is necessary to understand the different degradation mechanisms for natural fibers and their interaction with the polymer matrix degradation mechanism as the durability of NFPCs depends both on fiber and matrix.

Long-term performance or durability is one of the major aspects to be considered for the acceptance of NFPCs in outdoor applications. It is generally measured through physical appearance and mechanical performance. The service life of the product shortens when physical, mechanical, and aesthetic properties deteriorate such as color change and fading, surface erosion, loss of mechanical properties, and weight loss (Lopez *et al.*, 2006). The durability of NFPCs is largely influenced by thermal stability, moisture uptake, fungal resistance, and UV stability of NFPCs. To overcome the detrimental effects of these weathering agents, the properties of NFPCs are usually enhanced by using coupling agents, fungicides, UV absorbers, etc., during the manufacturing process.

14.3 Hygrothermal expansion

NFPC products are susceptible to dimensional changes with changes in both relative humidity and temperature. As natural fibers are hygroscopic, under exposure to higher relative humidity, they readily absorb moisture and undergo expansion. On the other hand, under low humidity conditions, they lose moisture and shrink. Similarly, with exposure to higher temperature, natural fibers expand and shrink when the temperature decreases. As the thermoplastics used in NFPCs are hydrophobic, they show no changes with the change in relative humidity, but undergo expansion on heating and shrink on cooling. Owing to the differences in thermal and hygroscopic properties of natural fibers and thermoplastics, hygro-thermal stresses develop during the manufacturing process. These stresses lead to the deformation and ultimate failure of NFPC products in the long term. In outdoor applications, NFPC products are also subject to continuous temperature and relative humidity fluctuations which result in compression, shear and tensile stresses in both components of NFPC and their interface. These stresses play important roles in product deformation such as bowing, cupping and twisting of products and eventual product failure.

14.3.1 Effect of moisture and temperature

Riccieri *et al.* (1999) studied the moisture absorption behavior of vegetable fiber/polyester composites. Table 14.2 shows the equilibrium moisture content, M_∞ at 50% and 90% relative humidity (RH) for sisal and jute/polyester composites with or without resin modification by isocyanate or polyurethane. The sisal fiber reinforced composites showed higher values of equilibrium moisture content at both RH conditions compared with jute fiber reinforced composites. Isocyanate modification of polyester has been proved to be effective in lowering the equilibrium moisture content in both types of composites, especially for jute/polyester composites. By increasing the RH content from 50 to 90%, the equilibrium moisture content in jute/polyester–isocyanate composite increased by a factor of 4.

Effect of moisture absorption on the mechanical properties of polypropylene (PP) composites with natural cellulosic fibers from wood and other crops (sisal, coir and luffa sponge) was studied by Espert *et al.* (2004). They used PP homopolymer and a post-industrial PP containing 3 wt% of ethylene vinyl acetate copolymer (EVA) for this study. It has been observed that the mechanical properties of these composites decrease after moisture absorption because it changes the structure and properties of the fibers, matrix, and the fiber–matrix interface. When the water molecule penetrates the composite

Table 14.2 Moisture absorption in NFPC

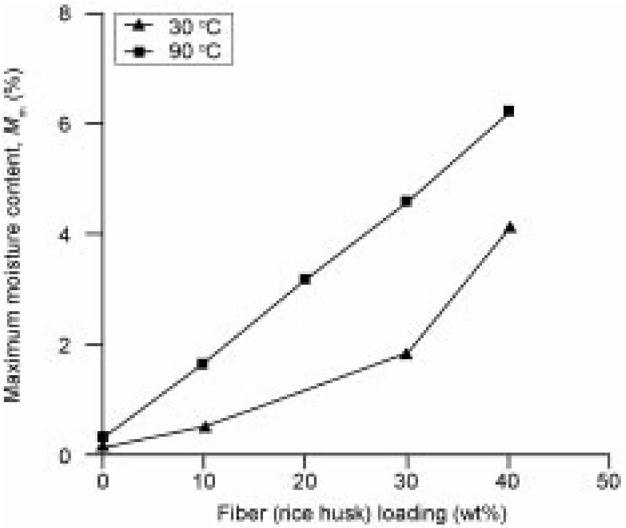
NFPC	Equilibrium moisture content, M_∞	
	50% RH	90% RH
Sisal/polyester	1.25	2.50
Sisal/polyester–isocyanate	0.78	2.25
Jute/polyester	0.52	1.45
Jute/polyester–polyurethane	0.38	0.70
Jute/polyester–isocyanate	0.14	0.56

Source: Adapted from Riccieri *et al.* (1999)

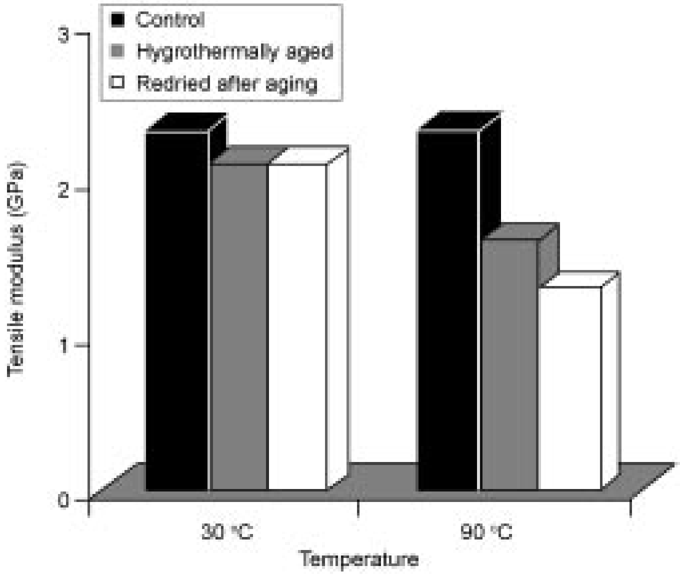
materials, the fibers undergo swelling, and also chain reorientation and shrinkage occur in the matrix structure. This has led to poor mechanical properties such as lower values of Young's modulus and stress at maximum load. The use of a post-industrial PP with a low percentage of EVA has led to improved resistance of the composite due to improved compatibility of the fiber–matrix interface. EVA contains hydrophilic vinyl acetate groups which bind to the cellulosic fibers and also aid the adhesion to the PP matrix, so EVA acts as a coupling agent between fibers and matrix. Hygrothermal aging also leads to the degradation of natural fibers by a hydrolysis mechanism.

Hygrothermal aging of rice husk/PP composites has been investigated by Ishak *et al.* (2001) by immersing the specimens in distilled water at 30 and 90 °C. The extent of moisture absorption was dependent on both the fiber loading and the immersion temperature as shown in Fig. 14.1. The maximum moisture content, M_m, increased with increasing fiber content due to the increase in the hygroscopic hydroxyl groups (–OH) in rice husk. By increasing the temperature from 30 to 90 °C, the moisture content of the composite also increased. The tensile properties such as tensile modulus of the composite deteriorated as a result of the combined effect of thermal aging and moisture attack (Fig. 14.2) and the properties were not fully recovered after drying the samples. The extent of deterioration was dependent on the water-immersion temperature. This has been attributed to the interfacial degradation and structural breakdown of the cell wall in the rice husk, which resulted in permanent damage to the fiber.

The resistance of bamboo fiber/PP composite and bamboo–glass fiber/PP hybrid composite to hygrothermal aging was studied by Thwe and Liao (2003).



14.1 Effect of fiber loading and temperature on moisture absorption of rice husk/PP composites (source: Ishak *et al.*, 2001).



14.2 Effect of hygrothermal aging on tensile modulus of rice husk/PP composites (source: Ishak *et al.*, 2001).

Accelerated aging was chosen to predict the long-term performance of the composite. The samples were exposed in water at 25 and 75 ºC for up to 6 and 3 months respectively. Table 14.3 summarizes the moisture absorption percentage and decrease in tensile properties of the composites after the two aging conditions. It has been observed that the degradation of mechanical properties of the composites depends on the amount of water uptake, soaking time, and temperature of the aging. It has been suggested that the bamboo fiber degraded

Table 14.3 Moisture absorption and decrease in tensile properties in bamboo/PP composites with or without glass fiber

Composites	Moisture absorption (%) 25 °C for 6 months	Moisture absorption (%) 75 °C for 3 months	Tensile strength decrease (%) 75 °C for 3 months	Tensile modulus decrease (%) 75 °C for 3 months
Bamboo (20 wt%)/PP	1.2	3.6	16	61
Bamboo–glass (15–5 wt%)/PP	0.9	3.2	11	55
Bamboo–glass (10–10 wt%)/PP	0.7	2.8	9	29

Source: Adapted from Thwe *et al.* (2003).

by decomposition into thin fibrils and detached layers while the PP matrix degraded by dissolution. The incorporation of glass fiber into the composite decreased the moisture absorption and improved the mechanical properties of the composite under the combined effect of moisture and temperature. This study indicated that to improve the durability of NFPC under environmental aging, the hybrid approach of incorporating more durable glass fiber into the natural fiber–matrix composition may be proved to be effective.

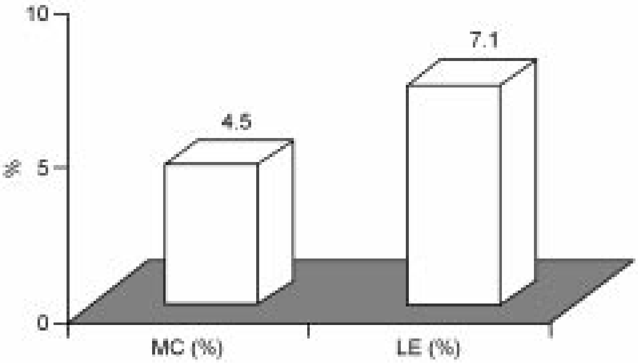
Retegi *et al.* (2006) studied the water uptake and change in mechanical properties of flax fiber/PP composites containing maleic anhydride-grafted polypropylene (MAPP) coupling agent at temperatures between 30 and 100 °C. They observed that an increase in immersion temperature resulted in a drastic decrease in the mechanical properties of the composite. It has been suggested that the presence of water induces a plasticization effect by developing interfacial shear stress (IFSS), which leads to adhesive debonding. Furthermore, hygrothermal aging at higher temperatures disrupts the bonding quality between fiber and matrix, resulting in poor mechanical properties of the composite. MAPP-modified composites exhibited a reduction in water uptake and hence improved the mechanical properties due to involvement of MAPP chains in inter-chain entanglements.

Hygrothermal weathering of commercial decking boards extruded from rice hull/ HDPE composites containing 50 wt% of fiber was investigated by Wang *et al.* (2005) under simulated extreme climatic exposure conditions. Table 14.4 summarizes the consecutive weathering steps, climatic conditions, exposure time, and property measurements in each step of the weathering procedure. It has been observed (Fig. 14.3) that the samples absorbed 4.5% moisture after 2000 h exposure to 93% RH and 40 °C in step 1 and the walls of the samples swelled significantly (7.1%) in thickness. In step 4 as shown in Fig. 14.4, the sample wall thickness did not change and there was a slight increase in the moisture content. The samples also exhibited different degrees of bowing after

Table 14.4 Summary of weathering steps, climatic conditions, exposure time, and property measurements in commercial decking boards (rice hull/HDPE)

Steps	*T* (°C)	RH (%)	Time (h)	Moisture content (%)	Linear expansion (%)	Bowing (%)
1	40	93	2000	4.5	7.1	0.82 (2 of 5 samples)
2	20	60	500	3.7	4.7	–
3	40	20	2000	1.6	2.7	0.33 (40% recovery)
4	20	30	500	1.8	2.7	No change
5	4	77	2000	3.25	3.6	No change

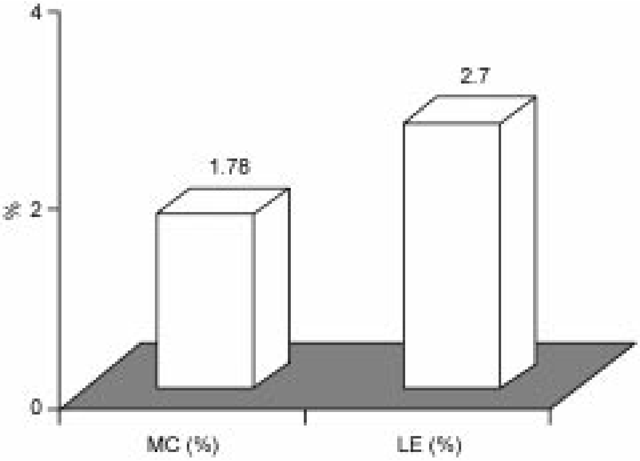
Source: Wang *et al.* (2005).



14.3 Moisture content (MC) and linear expansion (LE) in commercial decking board (rice hull/HDPE) after 2000 h exposure to 93% RH and 40 °C (source: Wang *et al.*, 2005).

exposure to step-wise weathering conditions. Out of five samples, two samples showed recovery in bowing (40%) after 2000 h exposure to 20% RH and 40 ºC and there was no further deformation observed during the later stages of exposure. It has been suggested that this dimensional change in the composite samples may be due to three factors:

1. the recoverable swelling and shrinking of the rice hull component of the NFPC under the humidity changes;
2. thermal expansion/contraction effects; and
3. irrecoverable swelling due to relaxation of the compressive stresses induced during the extrusion process.



14.4 Moisture content (MC) and linear expansion (LE) in commercial decking board (rice hull/HDPE) after 500 h exposure to 30% RH and 20 °C (source: Wang *et al.*, 2005).

For NFPC decking boards, it has been observed (Wang, 2005) that a hot and humid environment is the most damaging factor. The stresses developed from adsorbed moisture at elevated temperatures resulted in both reversible and irreversible dimensional changes in decking boards in the form of bowing. However, when ambient conditions were changed, dimensional equilibrium occurred more quickly than the moisture equilibrium.

The influence of water absorption on the mechanical properties of sisal/PP composites has been studied by Joseph *et al.* (2002). The water absorption characteristic of the composite was largely dependent on fiber loading, chemical treatment, and temperature. With increase in fiber content, the water uptake of the composite was found to be increased owing to the increase in cellulose content and leveled off at longer periods. Temperature increase also influenced the water uptake of the composite as the diffusion process became activated by the temperature. The sisal fibers were modified by three different chemical treatments: PPG (urethane derivative of polypropylene glycol), PMPPIC (poly[methylene poly(phenyl isocyanate)], and MAPP to improve the water absorption properties of the composite. It has been observed that all the chemically modified fiber composites showed a reduction in water uptake owing to better interfacial bonding. Substantial reduction in the tensile properties of the composites was observed after water immersion and described as being due to the plasticization effect of water, the fiber/matrix bonding became weak with increasing moisture content resulting in interfacial failure.

The moisture absorption and mechanical properties of wood flour/PP composites have been studied (Lin *et al.*, 2002) by immersing the composites in water at 23, 60, and 100 °C. It was observed that the rate of moisture absorption was dependent on the matrix modification, the temperature, the filler content, and surface treatment of wood flours. The moisture absorption rate increased with the increase in immersion temperature and wood flour content. The tensile strength, flexural strength and modulus of all composites decreased when immersed in 60 and 100 °C water baths.

Tajvidi and Ebrahimi (2003) studied the water uptake characteristics and mechanical properties of PP composites containing three types of natural fillers, purified α-cellulose, wastepaper fibers and wood flour. The composites also contained 2% MAPP as the compatibilizing agent. It has been observed that the wastepaper filled composites showed the highest water absorption (1.03%) followed by wood flour composites (0.83%), whereas the α-cellulose filled composite showed the lowest (0.49%) water absorption and this might be due to better fiber–matrix interfacial adhesion. By increasing the filler content from 15 to 35%, a sharp increase in water absorption was observed because of fiber agglomerations. When compared with pure PP, tensile strength and elongation at break in all types of composites declined after water uptake.

The moisture resistance of natural-fiber-mat-reinforced thermoplastics (NMTs) based on flax fibers and a PP matrix has been improved (Stamboulis *et al.*, 2000) by the use of upgraded Duralin flax fibers. The Duralin treatment was consist of a water-heating step of the rippled straw-flax at temperatures above 160 ºC for approximately 30 minutes in an autoclave followed by a drying step and a curing step above 150 ºC for approximately 2 h. It has been found that the Duralin flax/PP composites showed lower moisture absorption (30%) and improved dimensional stability than those of green flax composites.

14.3.2 Mechanism of moisture absorption

Mechanism of moisture absorption in NFPCs is a complex process owing to the involvement of two different systems, hydrophilic natural fibers, and hydrophobic matrix. Various researchers have explained this process by making some assumptions and suggested two distinct mechanisms: (1) diffusion theory and (2) percolation theory.

Diffusion theory

Diffusion is the process by which matter (in this case water) is transported from one part of a system to another as a result of random molecular motions (Sahimi, 1994). Composite materials absorb moisture through three different diffusion mechanisms (Mohanty *et al.*, 2002):

1. diffusion of water molecules inside the microgaps between polymer chains;
2. capillary transports into the gaps and flaws at the fiber–matrix interface; and
3. transportation through matrix microcracks formed during the compounding process.

These diffusion mechanisms are mathematically represented as:

$$\frac{M_t}{M_\infty} = kt^n \qquad 14.1$$

where M_t is the moisture content at time t; M_∞ is the moisture content at the equilibrium; and k and n are diffusion kinetic parameters. Depending upon the value of coefficient n, three diffusion mechanisms are distinguished. For Fickian diffusion, $n = 1/2$, for non-Fickian diffusion, $n = 1$, and for anomalous diffusion, $n = 0.5 - 1$. For NFPC, Fickian diffusion has been proved to be the dominant mechanism for moisture absorption.

According to Fick's first law (Wang *et al.*, 2006), the diffusion process is represented quantitatively as:

$$F = -D\,\frac{\partial C}{\partial x} \qquad 14.2$$

where F is the rate of transfer per unit area of section, C is the concentration of diffusion substance, x is the space coordinate measured normal to the section, and D is the diffusion coefficient. For one-dimensional diffusion in an isotropic medium, the differential equation of diffusion, known as Fick's second law is derived as:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{14.3}$$

Fick's laws of diffusion are based on two assumptions: (1) the composite structure is homogeneous; and (2) the matter transfers from higher to lower concentration only because of random molecular motion of the diffusion agent.

Moisture absorption for a plane sheet with uniform initial distribution and equal initial surface concentrations under non-steady state can be derived from eqn 14.3 and expressed as:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left[\frac{-D(2n+1)^2\pi^{2t}}{4l^2}\right] \tag{14.4}$$

where l denotes the half thickness of sheet.

By simplifying eqn 14.4 for the moisture absorption by the sheet at initial absorption stage, M_t, can be represented as:

$$M_t = \frac{2M_\infty\sqrt{D}}{\sqrt{\pi}}\frac{\sqrt{t}}{l} \tag{14.5}$$

From eqn 14.5, the average diffusion coefficient, D can be calculated as:

$$D = \frac{\pi}{4}M_\infty^{-2}l^2\theta^2 \tag{14.6}$$

where θ is the slope of M_t vs. $\sqrt{t}$ plot.

Although diffusion theory is a major mechanism of moisture absorption in composites and is able to quantify the matter transfer, it has some drawbacks and hence fails to explain the complex moisture absorption mechanism in NFPCs. It has been proved through experiments that the fiber distribution and fiber concentration in polymer matrix influence the moisture absorption in NFPCs. Therefore, a more sophisticated model is required to fully explain the mechanism of moisture absorption in NFPCs.

Percolation theory

According to percolation theory, the properties of a macroscopic system such as an NFPC are determined by the connectivity between system elements. The percolation theory is developed (Berkowitz and Ewing, 1998) from the network modeling which considers the randomness of both diffusion agent and medium. So, the apparent diffusion coefficient, D, is integrated into percolation theory.

In a composite system, at low fiber content, fibers either exist individually or form finite clusters and as they are completely encapsulated by matrix, they do not contribute to the moisture absorption. On the other hand, at high fiber content, fibers connect together to form infinite clusters and are not totally encapsulated by the matrix, so moisture can penetrate through the composite. The fiber content at the point of formation of infinite clusters is called 'percolation threshold' or 'critical fiber content', p_c (%). The probability that a fiber belongs to the infinite cluster is known as P_∞. There will be no infinite cluster formed at the fiber content lower than critical fiber content, and hence P_∞ is zero. If the fiber content exceeds the p_c value, then P_∞ is given as:

$$P_\infty \sim (p - p_c)^\beta \tag{14.7}$$

where p is the fiber content (%) and β is a critical static exponent. The value of β depends on the dimension of the lattice and for a three-dimensional lattice, $\beta \approx 0.42$.

According to percolation theory, the apparent diffusion coefficient D is defined as:

$$D = \chi D_0 (p - p_c)^\mu \tag{14.8}$$

where χD_0 represents a scaling factor, and μ the conductivity exponent, which is 2.0 for a three-dimensional lattice.

Wang *et al.* (2006) applied the percolation theory in understanding the moisture absorption mechanism in NFPC, where the infinite fiber cluster is a 3D network, by making certain assumptions:

- Natural fibers are only responsible for moisture absorption as the matrix is considered hydrophobic.
- The moisture absorption can be quantified by fiber saturation point (FSP) of the accessible fibers as the composite is void free.
- The moisture can penetrate through the whole infinite 3D network above the percolation threshold during a specific time period, and all the natural fibers belonging to the infinite 3D network can reach FSP after water submersion.
- There are two types of free fibers. Type I fibers have no access to moisture as they are completely encapsulated in the matrix and Type II fibers absorb moisture as they are on the proximate surface.

Wang *et al.* derived the accessible fiber ratio r from the percolation concept P_∞, and considered both the fibers belonging to the infinite 3D network and the fibers on the proximate surface of composite as accessible fibers. Ratio r is computed as:

$$r = \frac{M_\infty}{C * \mathrm{FSP}} \tag{14.9}$$

where C is the fiber loading in composites. The critical accessible fiber ratio, r_c, is the percolation threshold of r and this is the ratio at which the infinite 3D network formed for the first time.

As the moisture absorption behavior of NFPC depends on both the diffusion coefficient and the percolation network, the authors defined a new property of composite called the diffusion–permeability coefficient, DP, and presented as:

$$\mathrm{DP} = \frac{\theta}{\surd(2 * C - r)} \tag{14.10}$$

where θ is the slope of Fickian M_t vs. $\sqrt{t}$ plot.

By combining eqns 14.8 and 14.10, *DP* can be expressed as:

$$\mathrm{DP} = \frac{\theta}{\surd(2 * C - r)} = k(r - r_c) \tag{14.11}$$

where k is a constant.

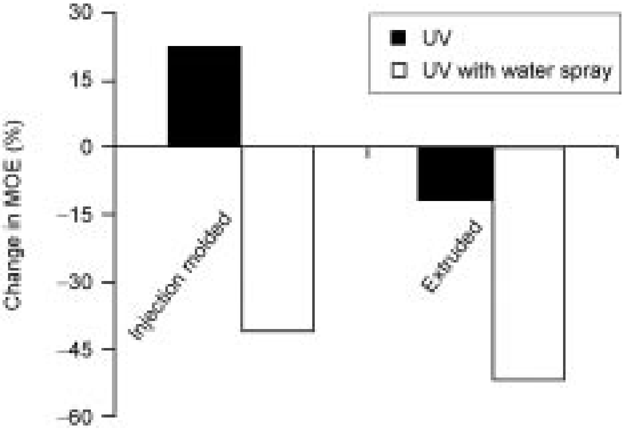
DP values can be obtained from the moisture absorption curve of composites with different fiber loadings near the percolation threshold, and then the critical accessible fiber ratio r_c can be obtained through the linear regression by plotting DP vs. r. The authors suggested that the diffusion theory is the dominant mechanism at high fiber loading when fibers are highly connected, and percolation is the dominant mechanism at low fiber loading near the percolation threshold where a continuous 3D network is formed.

14.4 Ultraviolet radiation

NFPC products are susceptible to the UV portion of sunlight. Solar irradiance on these materials causes various deteriorations including color change, fading, surface erosion and loss of gloss, which reduce product lifetime. Under UV exposure, surface chemistry of the composite changes due to photodegradation, which leads to discoloration (Falk *et al.*, 2000; Matuana and Kamden, 2002; Stark and Mantuana, 2002, 2003) of the product, making it aesthetically unappealing. Stark and Mantuana (2003) also suggested that prolonged UV exposure may also lead to the development of fracture in the product and make the product more vulnerable to other weathering elements in the surroundings such as water and wind, which ultimately result in mechanical failure of the product. So, UV radiation is one of the major practical problems that NFPC products encounter in outdoor applications.

14.4.1 Property degradation

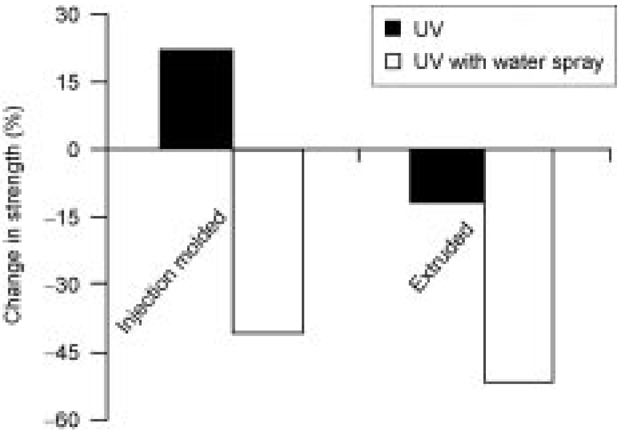
Stark (2005) studied the changes in wood flour/high-density polyethylene (HDPE) composites after accelerated weathering with and without water spray. Injection molded and extruded HDPE composites filled with 50 wt% wood flour were used and the samples were exposed to UV light of wavelength between 300 and 400 nm, where maximum photodegradation occurs. It was found that exposure to UV light resulted in an increase in flexural modulus of elasticity (MOE) for the injection molded composite because of less wood at the surface,



14.5 Change in flexural MOE of injection molded and extruded wood flour/HDPE after UV weathering with or without water spray (source: Stark, 2005).

whereas a decrease in flexural MOE (12%) for extruded composite with more wood at the surface (Fig. 14.5). From this study, it has been suggested that the processing method of wood–polymer composites (WPCs) affects the degradation by UV exposure. Both injection molded and extruded composites showed decrease in flexural MOE (41 and 52% respectively) when exposed to UV light with water spray (Fig. 14.5). The decrease in flexural strength was also apparent in WPC composites after exposure to UV light and water spray as shown in Fig. 14.6. This observation supports the fact that moisture absorption plays a critical role in degrading the mechanical properties of UV weathered WPCs.

In another study by Rowell (2006), it has been found that there was a decrease in flexural strength of wood flour/PE composites by 5.7% after 1000 h

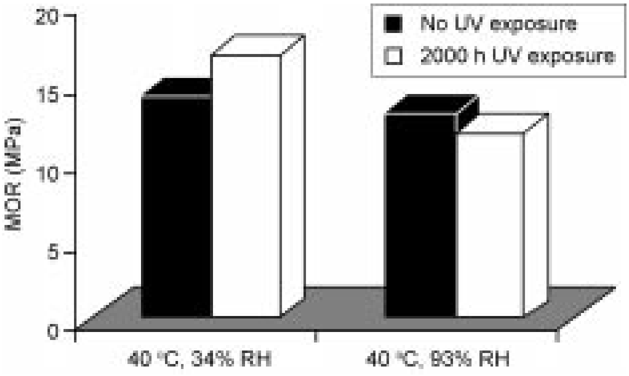


14.6 Change in flexural strength of injection molded and extruded wood flour/HDPE after UV weathering with or without water spray (source: Stark, 2005).

of UV exposure which was increased to 22.4% by increasing the UV exposure time to 2000 h. The percentage of fiber content in the matrix also affects the property degradation by UV weathering. Selden *et al.* (2004) studied the effect of accelerated UV aging on properties of wood fiber/PP composites with different fiber content. The composite samples containing 3% UV stabilizer were subjected to accelerated UV aging in a QUV weatherometer for up to 8 weeks. The exposure procedure followed in this experiment was 4 h of exposure of dry UV at a temperature of +60 °C, followed by 4 h of condensation exposure, at a temperature of +50 °C without radiation. With regard to mechanical properties, their results showed that the wood fiber/PP composites displayed good UV resistance; however, physical and chemical analyses (differential scanning calorimetry, DSC; Fourier transform infrared, FTIR; and scanning electron microscopy, SEM) of the surface layers of the composite showed the occurrence of PP matrix degradation. By increasing the fiber content from 25 to 50 wt% the rate of degradation of the composite increased by approximately a factor of two as the number of chromophores (light-absorbing groups) increased with increased fiber content. The melting temperature of the composite also decreased by 33% in the case of 50% wood fiber content and was explained as being due to molecular chain scission and the formation of carbonyls and hydroperoxides.

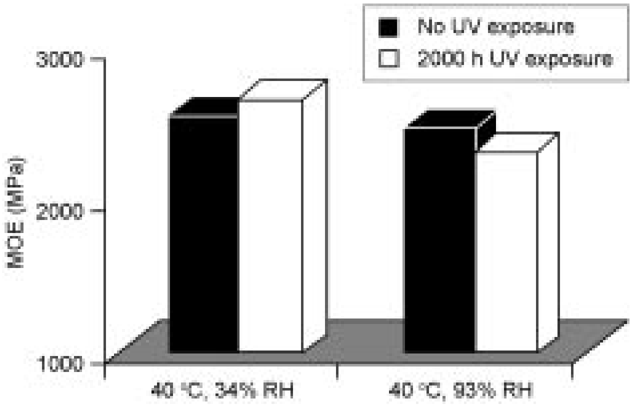
Lopez *et al.* (2006) studied the effects of moisture, temperature and UV light on performance of NFPC. They conducted short-term accelerated weathering tests on commercial extruded profiles of NFPC protected by UV absorbers used in outdoor deck railings by exposing the samples to UV light of wavelength 365 nm at different combinations of relative humidity and temperature for a period of 2000 h. The experiment was carried out inside the environmental chamber in the Forestry Laboratory at the University of Toronto. This experiment showed the combined effect of moisture, temperature and UV aging on the properties of the composite. Figure 14.7 illustrates the flexural strength (modulus of rupture, MOR) of NFPC samples under no UV and 2000 h UV exposure at two relative humidity conditions (34% and 93% RH) at 40 °C temperature. For both unexposed and UV exposed samples, MOR decreases at higher relative humidity, but the decrease is more apparent (29.8%) for UV exposed samples. A similar trend is observed for flexural stiffness (MOE) as shown in Fig. 14.8. At 93% RH, the MOE of NFPC samples decreased by 13% under UV exposure. The combined effect of moisture and UV light has been proved to be detrimental to the mechanical properties of NFPC products for outdoor applications.

Long-term testing on the samples from the same composite has also been carried out (Lopez, 2004) by exposing the samples to outdoor environment on the roof of the Forestry Building at the University of Toronto for 30 months in order to measure the effect of variable weather factors on the composite properties and to establish the relationship between short-term laboratory testing

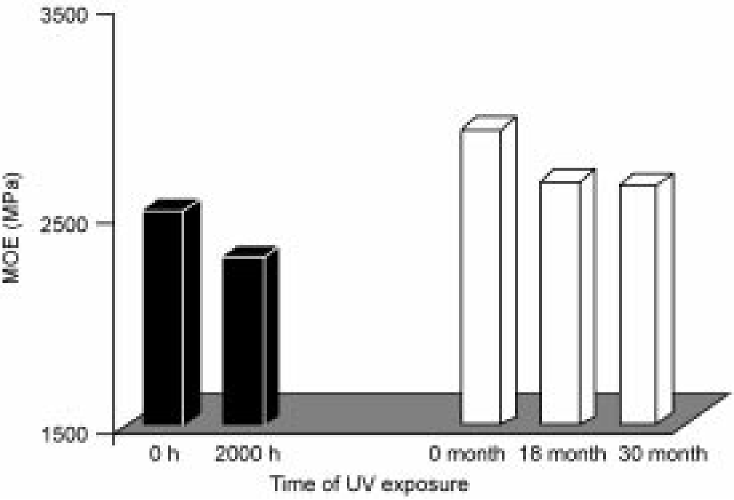


14.7 Flexural strengths of commercial extruded NFPC samples under no UV and 2000 h UV exposure at different environmental conditions (source: Lopez *et al.*, 2006).

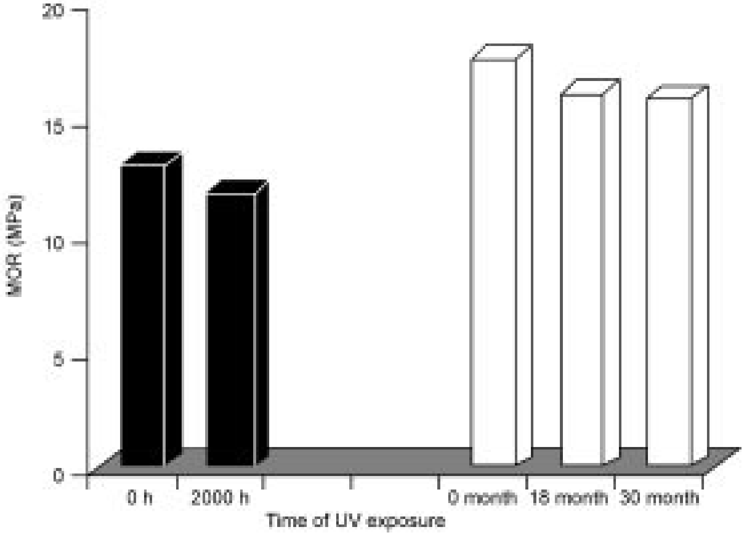
and long-term outdoor testing of NFPC samples. Figure 14.9 shows the MOE of composites with no UV exposure (40 ºC, 34% RH) and 2000 h UV exposure (40 ºC, 93% RH) under short-term testing and 0, 18 and 30 months outdoor exposure of long-term testing. The decrease in MOE after 2000 h of UV exposure is 8.9% whereas the decrease is 9.2% after 30 months' outdoor exposure. Flexural strength of the composites also changes in a similar fashion for both short-term and long-term tests as shown in Fig.14.10. After 2000 h of UV exposure at 40 ºC and 93% RH, MOR decreases by 9.2% whereas it decreases by 10.1% after 30 month's outdoor exposure. These results show that the short-term accelerated test could well predict the mechanical performance of NFPC in the long term.



14.8 Flexural MOE of commercial extruded NFPC samples under no UV and 2000 h UV exposure at different environmental conditions (source: Lopez *et al.*, 2006).



14.9 Flexural MOE of commercial extruded NFPC samples after short-term and long-term tests (source: Lopez *et al.*, 2006).



14.10 Flexural MOR of commercial extruded NFPC samples after short-term and long-term tests (source: Lopez *et al.*, 2006).

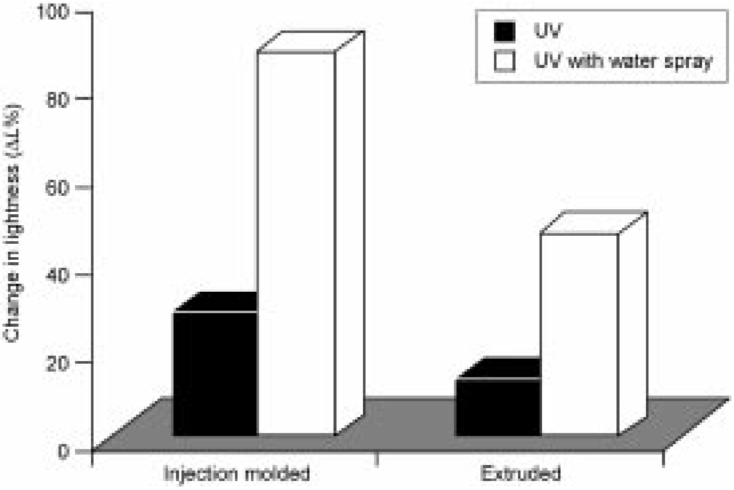
14.4.2 Discoloration

Discoloration and surface roughness are the characteristic degradation features of UV exposure of NFPC. In one of the studies by Sharma *et al.* (2006), surfaces of coir/PP laminates showed a slight change in surface roughness after 10 h of

UV exposure; however, with increased exposure time of 20 h, the surfaces started to turn white and after 200 h of exposure, the surfaces became very rough and chalky with clearly visible fibers. Stark (2005) studied the color change in injection molded and extruded wood flour/HDPE composites under UV exposure and UV exposure with water spray. A Minolta CR-200 Chroma Meter was used to measure color using the CIELAB color system. In the CIELAB color system, the L^* value is considered as lightness factor where L^* represents reflectance of a sample. If $L^* = 0$, the sample does not reflect light and if $L^* = 100$, the sample reflects 100% light. An increase in L^* $(+\Delta L^*)$ represents fading or lightening of the sample and decrease in L^* $(-\Delta L^*)$ represents darkening of the sample. In this color system, a^* and b^* are chromacity coordinates and represent red–green and yellow–blue coordinates. A positive Δa^* value represents a color shift towards red while a negative Δa^* value represents a shift towards green. Similarly, a positive Δb^* values represents a color shift towards yellow while a negative Δb^* value represents a shift towards blue. The resultant color change ΔE was calculated according to ASTM D 2244 (Muller *et al.*, 2003) as seen in Equation 14.12:

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \qquad 14.12$$

In this study it has been found that both injection molded and extruded composites lightened after UV exposure. Severe fading occurred (87% and 46% in injection molded and extruded composite samples respectively) after exposure to UV with water spray as shown in Fig. 14.11. This suggests that fading of composite is largely affected by the presence of moisture. The water spray cycle



14.11 Change in lightness (fading) of injection molded and extruded wood flour/HDPE after UV weathering with or without water spray (source: Stark, 2005).

accelerated the rate of discoloration of wood and hence of WPC by washing the degraded surface and exposing the new wood surfaces for further degradation resulting in a cyclic erosion of the composite surface. Wood extractives, major components for imparting color, were also washed away, causing further fading of the composite. In wood-fiber/PP composites, Selden *et al.* (2004) observed that the color of the composite changed from brown to chalky white at the exposed area for 50 wt% wood-fiber content after 8 weeks of accelerated UV aging. This was explained as being due to PP matrix degradation resulting in chemi-crystallization and extensive surface cracking. Lopez (2004) observed the changes in color and fading of commercial deck samples from natural fiber reinforced HDPE composites under short-term laboratory test and long-term outdoor weathering conditions. After 2000 h of UV exposure at wavelength of 365 nm, the *L* value of the composite samples increased by 5.3 and after 1 year outdoor exposure, the *L* value increased by 7.9. It had been also observed that the outdoor weathered samples turned bluish, whereas there was a slight change in color in the short-term exposed samples.

14.4.3 Mechanism of degradation

The components of NFPC, natural fiber and plastic, absorb UV radiation of different wavelengths leading to free radical photo-oxidation and undergo thermo-oxidation as a result of increased temperature. Polymer degradation through photo-oxidation has been studied in different materials by various researchers around the world. Discoloration, i.e. photo-yellowing and photo-bleaching of NFPC products, has been proved to be caused by light at different wavelengths. According to Hon (1991), lignocellulosic materials such as wood and paper readily undergo light-induced photo-yellowing. Lignin, which is a major constituent of natural fiber, contains chromophores which readily absorb UV radiation (Heitner, 1993). According to Rowell (1998), lignin, which is responsible for holding the cellulose fibers together, degrades owing to exposure to UV radiation, making the surface richer in cellulose content. After lignin degradation, the poorly bonded fibers erode easily from the surface, exposing new lignin to further degradation. With time, this degradation process makes the composite surface rough and accounts for a significant loss in surface fibers, and hence composite properties. In another study made by Winandy *et al.* (2004) for recycling consideration of wood–plastic composites (WPC), it has been stated that the surface of the WPC oxidizes upon UV exposure. Owing to the presence of oxygenated functional groups, polyolefins are responsible for further photo-oxidation that results in a decrease in tensile strength and elongation (La Mantia, 2004). It has been also shown (Stark and Matuana, 2003) that the properties of WPC degrade by the addition of wood to plastic due to the formation of further oxidation sites.

Sharma *et al.* (2006) studied the effect of UV and moisture on the surface of coir/PP laminates and suggested that the discoloration and surface roughness in the laminates was due to complex processes of photochemical degradation of polymers, hydrolysis, and oxidation. Free radical formation occurs at the surface of the laminates as the UV light absorption provides the energy to the polymer for breaking molecular bonds, such as C=C, C–H, C=O. In the case of coir/PP laminates, the PP forms free radicals owing to the presence of a large number of tertiary carbon sites. These free radicals form peroxy radicals by reacting with oxygen, which attack the polymer molecules in the laminates and change the color of the laminate from white to yellow. Coir fibers also undergo UV degradation through free radical reactions with the decomposition of polymer in the cell wall. The surface area increases as the composite swells, which allows more material to be UV exposed and more moisture to be absorbed, therefore changing the color from brown through bleaching to white. The same authors also studied the effect of UV and moisture on glass/PP laminates and found that as glass fiber is inert to UV radiation, the color change of laminate is from opaque white to yellow because of PP reactions only.

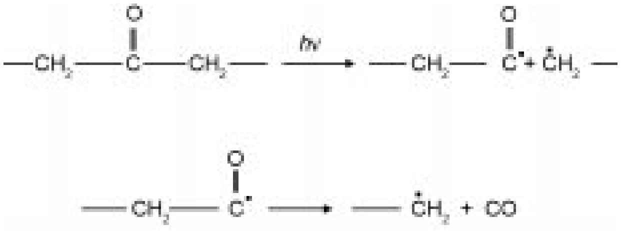
Photodegradation mechanism of polyolefins

Polyolefins are susceptible to photo-oxidation under the exposure of UV radiation due to the presence of chromophores. The reaction mechanism of the oxidation process in polyolefins follows scheme 1 (Muasher, 2005). The free radicals formed in the initiation stage attack the polymer in the propagation stage and form new free radicals. In the termination stage, two free radicals combine together and seize the reaction.

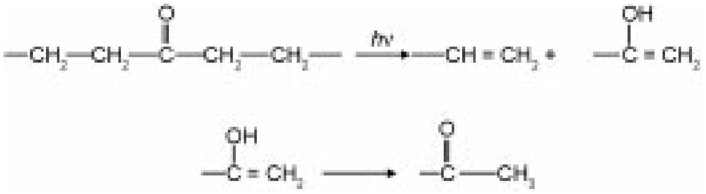
Initiation: Chromophores $\longrightarrow$ Free radicals $(P\bullet, PO\bullet, HO\bullet, HO_2\bullet)$ 14.13
Propagation: $P\bullet + O_2 \longrightarrow PO_2\bullet$ 14.14
$PO_2\bullet + PH \longrightarrow POOH + P\bullet$ 14.15
Termination: $PO_2\bullet + PO_2\bullet \longrightarrow POOP + PO_2$ 14.16
$P\bullet + PO_2\bullet \longrightarrow POOP$ 14.17
$P\bullet + P\bullet \longrightarrow PP$ 14.18

Scheme 14.1 Sequence of oxidation reactions in polymers, 'P' = polymer chain.

During the initial stage of UV exposure, vinylidene and hydroperoxide concentrations act as initiators of photo-oxidative degradation, where as at the later stage, carbonyl groups act as auto-accelerating photoactivators (Jabarin and Lofgre, 1994). It has been reported (Jabarin and Lofgre, 1994; Kaci *et al.*, 2000; Wypych, 1995), that the degradation of carbonyl groups occurs according to Norrish type I (Fig. 14.12) or II (Fig. 14.13) reactions. In the Norrish type I reaction, the free radicals formed can attack the polymer according to Scheme 1 and lead to termination via chain scission or crosslinking (Wypych, 1995). In the Norrish type II reaction, carbonyl and terminal vinyl groups are produced and lead to chain scission. Furthermore, the carbonyl groups formed may undergo



14.12 Norrish Type I reaction (source: Muasher and Sain, 2006).



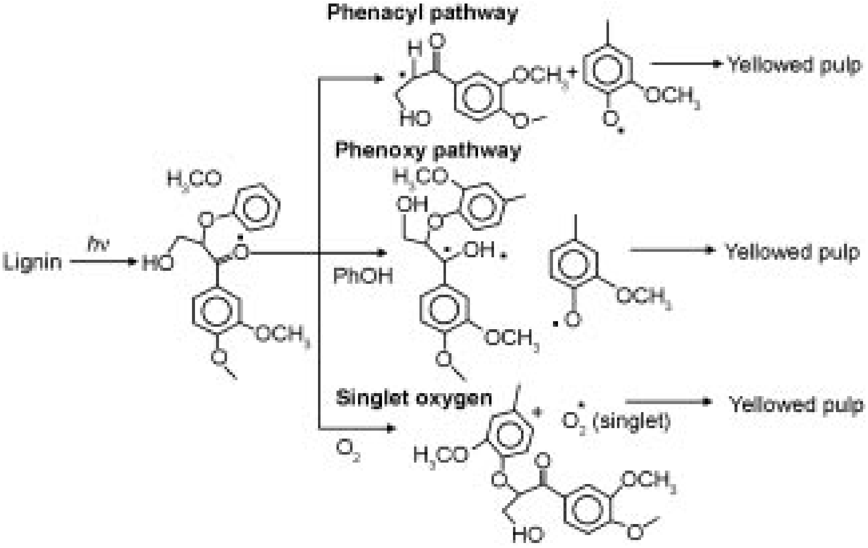
14.13 Norrish Type II reaction (source: Muasher and Sain, 2006).

further degradation. Chain scission and crosslinking are found to be competing reaction mechanisms during UV degradation of polyethylene (Jabarin and Lofgre, 1994; Kaci *et al.*, 2000; Sebaa *et al.*, 1993; Wypych, 1995). However, chain scission is proved to be more dominant in natural weathering (Jabarin and Lofgre, 1994; Zhao *et al.*, 2003). The researchers (David *et al.*, 1992; Tidjani, 2000; Tidjani *et al.*, 1993) argued that the formation of carbonyl groups and vinyl groups is the indicator of chain scission. Another indicator of chain scission is the increase in polyethylene crystallinity after weathering (Jabarin and Lofgre, 1994; Wypych, 1995). The chain scission produces shorter chains with high mobility that crystallize more readily, resulting in increased crystallization and associated embrittlement of the polymer. According to Hamid and Amin (1995), the chain scission occurs in the amorphous phase of the polymer, but imperfect crystalline regions degrade because of crosslinking.

Photodegradation mechanism of wood/natural fiber

Photo-oxidation of wood basically occurs on the surface of the wood as UV radiation can penetrate only up to 75 μm (Hon, 2000). However, studies have shown that degradation occurs at deeper layers of wood through an energy transfer process which dissipates excess energy to create new free radicals. Lignin, one of the major constituents of wood, breaks down into water-soluble products due to UV exposure and generates light absorbing species, chromophoric functional groups such as carbonyls, carboxylic acids, quinines, and hydroperoxide radicals (Hon, 2001).

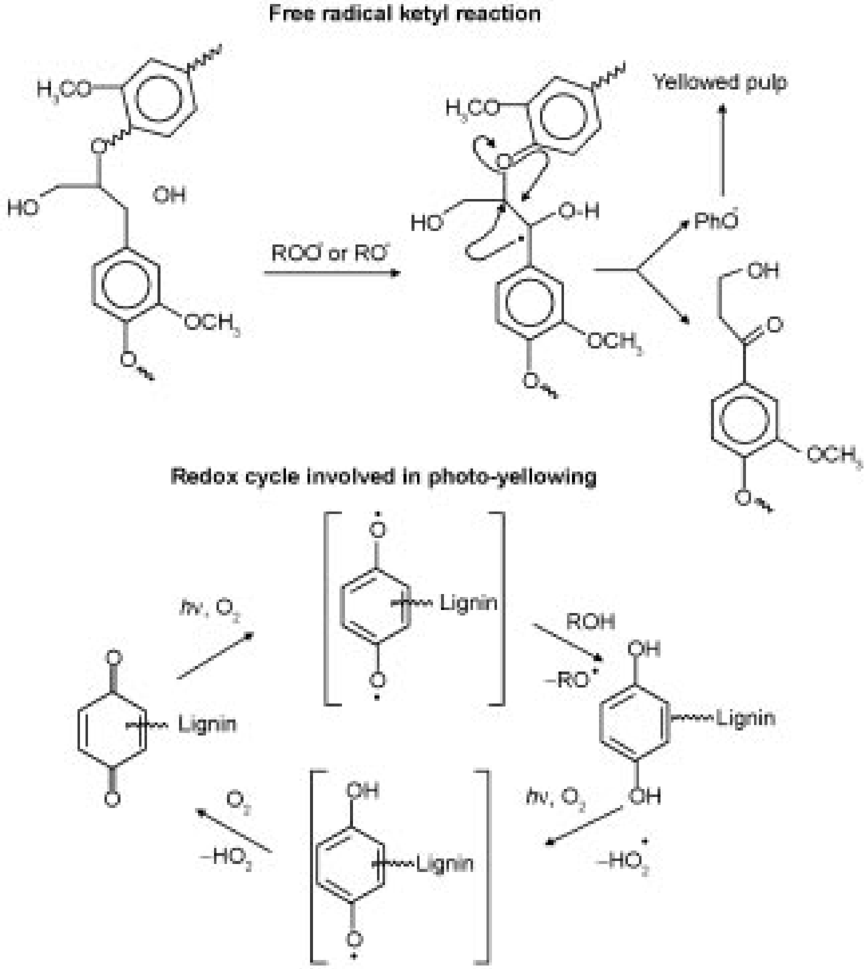
Various reaction pathways have been suggested (Li and Ragaukas, 2000;



14.14 Pathways involved in photo-yellowing of lignin from excitation of carbonyl group (source: Muasher, 2005).

Muller *et al.*, 2003) for chromophoric structure formation from lignin decay, which cause photo-yellowing of lignin, out of which the phenacyl, phenoxy and the singlet oxygen pathways initiated by the excitation of the carbonyl group. As shown in Fig. 14.14, the phenoxy pathway involves the abstraction of a hydrogen from the phenolic hydroxyl group by excited carbonyl group and production of a ketyl-phenoxyl free radical system. The phenoxyl free radical undergoes further oxidation and demethylation to produce *ortho* or *para* quinonoid chromophores. In the phenacyl pathway (Fig. 14.14), the excited carbonyl group leads to the cleavage of the ether bond, which is followed by the same phenoxy pathway to form quinonoid structures. The singlet oxygen pathway (Fig. 14.14) involves the formation of a singlet oxygen from the photoexcited carbonyl group by the energy transfer which leads to the cleavage of the ether bond. The singlet oxygen abstracts hydrogen from the phenolic hydroxyl group to produce the phenoxyl free radical.

In addition to these pathways, free radical ketyl reaction and redox cycle (Li and Ragaukas, 2000; Muller *et al.*, 2003) are also responsible for chromophore formation. The ketyl pathway (Fig. 14.15) is initiated by photoinduced radical reactions in which photolysis of lignin generates the radical which combines with O_2 to produce peroxyl (ROO•) and alkoxyl (RO•) radicals. These reactive intermediates form ketyl radicals via abstraction of a benzylic hydrogen atom in the β-O-aryl ether structure. In phenoxyl quinone redox cycle (Fig. 14.15), hydroquinone structures undergo oxidation to form paraquinones, which are chromophoric structures, resulting photo-yellowing of lignin. In the reverse



14.15 Pathways involved in photo-yellowing of lignin (source: Muasher, 2005).

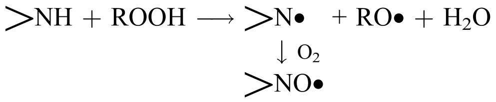
cycle paraquinones reduced to hydroquinones, causing photo-bleaching of lignin.

14.4.4 UV stabilization

As UV aging through photodegradation of both polymer and fiber is one of the major hindrances in the outdoor applications of NFPCs, it is essential to slow down or stop these reactions for UV stabilization. Photostabilizers are a class of compound developed to protect polyolefin and hinder UV degradation. These photostabilizers are categorized according to the degradation mechanism they hinder. The first category of photostabilizers prevents the absorption of harmful UV radiation and is called an ultraviolet absorber (UVA). UVA has high absorption coefficients in the UV part of the solar spectrum. Upon the absorbance of UV light, a rapid internal hydrogen transfer occurs that leads to the transformation of absorbed radiation energy into less harmful thermal energy via a photophysical process (Gugumus, 1993) sending the UVA to the original state. The second category is quenchers, which reduce the photo-initiation rate through deactivating the excited states of the chromophoric groups. The third category consists of hydroperoxide decomposers, which transform the chromophoric hydroperoxides into more stable compounds without generating free radicals, thus preventing further photolytic cleavage. However, the concentration of hydroperoxide in polyethylene decreases quickly on UV exposure (Gächter and Müller, 1990), thus restricting its use as photostabilizer. The fourth category of photostabilizers are free radical scavengers which inhibit the photo-oxidative degradation by scavenging the free radicals either as alkyl radicals or peroxy radicals (Gugumus, 1990; Wypych, 1995). In addition to these photostabilizers, the pigments are also used as photoblockers to inhibit the photodegradation of polymers (Schellenberg and Fienhold, 1998).

Hindered amine light stabilizers (HALS), a class of free radical scavengers developed three decades ago, have been proven to protect polyolefin from outdoor weathering (Gijsman, 2002; Gijsman *et al.*, 1993; Gugumus, 1995). Several researchers (Gugumus, 1993, 2002b; Stark and Matuana, 2002) reported HALS as the photostabilizing agent for unfilled HDPE and PP. HALS is the derivative of 2,2,6,6-tetramethylpiperidine molecule, as shown in Fig. 14.16. The 'X' and 'Y' position are usually occupied either by a diester or a triazine functional group. There are two distinct mechanisms through which HALS has been found to protect polymers from UV degradation:

1. Formation of stable nitroxyl radicals through the reaction of HALS with polymeric hydroperoxides which are formed during polymer processing as shown in Scheme 14.1 (Sedlar, 1990; Wypych, 1995). This decreases the amount of oxygen available to degrade the polymer chain.



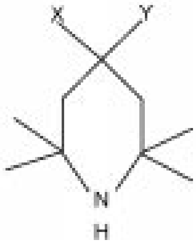
$$\begin{array}{lll} >\mathrm{NH} + \mathrm{ROOH} \longrightarrow & >\mathrm{N}\bullet & + \mathrm{RO}\bullet + \mathrm{H_2O} \\ & \quad\downarrow \mathrm{O_2} & \\ & >\mathrm{NO}\bullet & \end{array}$$

Scheme 14.2 Transformation of parent amine HALS to nitroxyl radical

2. Termination of the chain reaction of free radical formation by the reaction of nitroxyl radical with another polymer radical as seen in Scheme 14.3 (Sedlar, 1990; Wypych, 1995).

$$>\mathrm{NO}\bullet + \bullet\mathrm{R} \longrightarrow >\mathrm{NO{-}R}$$

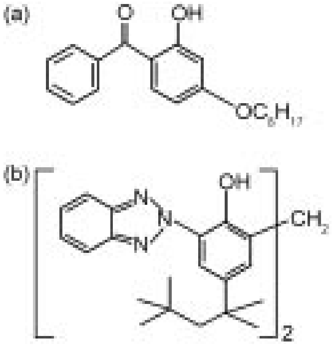
Scheme 14.3 Stabilization of HALS with polymer by scavenging free radicals



14.16 Basic structure of HALS-2,2,6,6 tetramethylpiperidine.

The effectiveness of HALS for hindering photodegradation in polyolefins depends upon the chemical structure and molecular weight of HALS. In one study, Gugumus (2002b) found that low molecular weight diester HALS was superior to polymeric triazine-based HALS for stabilizing PE plaques exposed to natural weathering. In addition to HALS, some researchers (Gugumus, 2002a; Stark and Matuana, 2002, 2004) also used UVA for photostabilizers. The most studied commercially available UVA are hydroperoxybenzophenones (Fig. 14.17(a)) and hydroperoxybenzotriazoles (Fig. 14.17(b)). Owing to the complexities involved in the photodegradation process of polymers, a proper combination of stabilizers is required to protect the polymer from photodegradation. As HALS are proven to be effective in increasing light fastness of UVA, a synergistic effect can be obtained using combination of UVA and HALS for polymer UV stabilization by different activity mechanisms (Bauer *et al.*, 1990; Gerlock *et al.*, 1995). The combined effect by using various combinations of HALS and UVA has been tried (Stark and Matuana, 2002; Gugumus, 2002a) in the UV protection of low-density polyethelene (LDPE) films and unfilled HDPE.

Although not many studies have been found on the photostabilization of natural fiber, the methods to reduce the photodegradation effect on wood have been well reported. The general methods are surface coating of wood with an

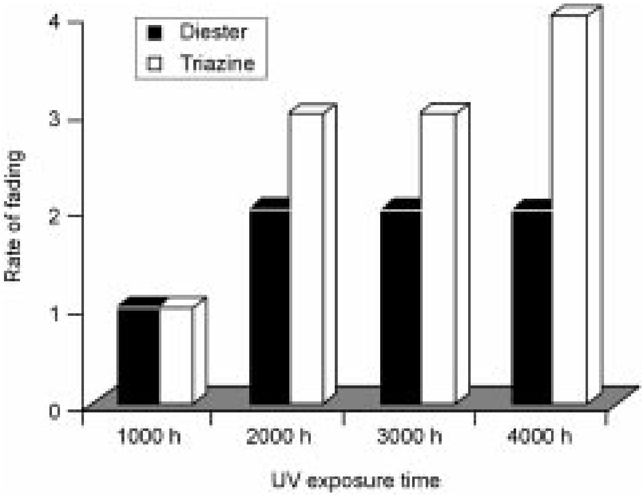


14.17 (a) Hydroxyl benzophenone UVA; (b) hydroxyl benzotriazole UVA.

organic solvent containing UVA or adding pigments such as titanium oxide and chemical modification of the light absorbing species such as the carbonyl groups and phenolic hydroxyl groups by acetylation, methylation, and benzoylation (Hon, 2000). On the basis of the degradation mechanisms of both polymer and fiber and the photostabilization chemistry of polyolefins and wood, researchers around the world are now investigating the effect of different photostabilizers on the UV stabilization of composites derived from wood/natural fibers. Though most of the work has been reported for WPCs, Stark and Matuana (2003) studied the effect of adding a colorant, UVA and HALS stabilizers on the change in color and mechanical properties of 50% wood flour-filled HDPE composites exposed to UV weathering. They found that the lightening effect was less pronounced when UVA and colorant were added to the composite and suggested that the combination of a colorant and UV absorber work synergistically to block the penetration of UV radiation and mask the bleaching of wood flour. This combination also significantly decreased the strength loss of the composite. No significant effect was found of HALS on the color fading and strength loss. This was explained as due to acid-base interactions resulting from the acid-sensitive hindered amines of HALS and the acid characteristics of the wood particles.

A combination of UVA and HALS has been employed by de la Caba *et al.* (2007) to improve long-term performance of wood-faced construction panels under expected weathering conditions. They have used a polymethyl methacrylate (PMMA) film as a light and water barrier for exterior wooden wall construction. It has been found that protection failed after 3000 h of exposure of panels in a Ci3000 Weather-ometer in the absence of PMMA film. The use of the film reduced the deterioration of the surface without any stabilizer additions. However, the combined use of photostabilizers and PMMA films resulted in increased outdoor durability of wood. After 3000 h exposure no significant change in mechanical properties or surface structure was observed.

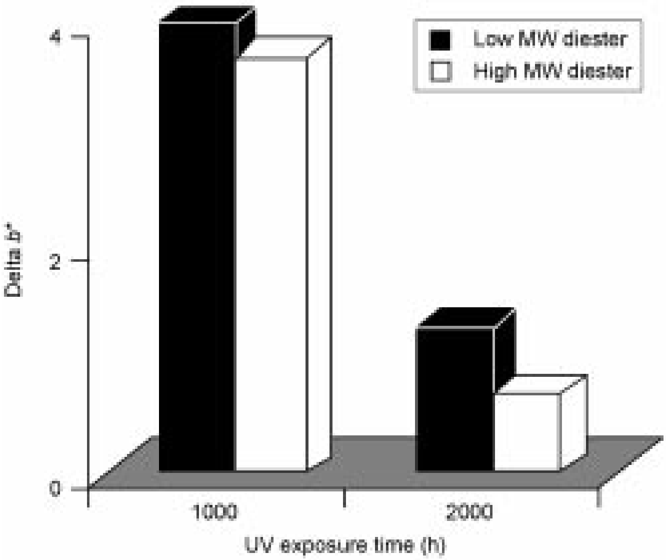
Muasher and Sain (2006) studied the effect of photostabilizing additives, UVA, and HALS on the color stability of WPC subjected to natural weathering for 2000 h. They compared the performances of HALS based on diester and triazine functional groups with different molecular weights and benzotriazole and benzophenone UVA. The results indicated that diester-based HALS were ineffective in initially preventing the formation of paraquinone chromophoric structures compared with triazine-based HALS in the first 250 h of exposure. However, the efficacy of diester-based HALS in scavenging free radicals increased with time, as shown in Fig. 14.18, and they were capable of preventing the reduction of paraquinones to hydroquinones and decreased the rate of fading or lightening of the WPC over prolonged period of exposure. It has also been found that high molecular weight diesters exhibit greater long-term stabilizing ability over the low and medium molecular weight diesters (Fig. 14.19). Benzotriazole UVA showed superiority over benzophenone UVA as shown in Fig.



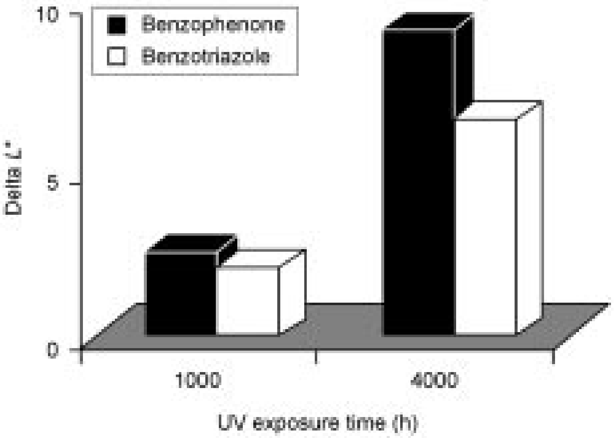
14.18 Effect of diester and triazine-based HALS on WPC fading under UV weathering for 2000 h (adapted from Muasher, 2005).

14.20 for protecting the color, and the combination of benzotriazole UVA and diester HALS showed a synergistic effect on decreasing color fading in WPC.

In a further study by Muashar (2005), it has been suggested that the most effective photostabilizer formulation against color change for long-term UV

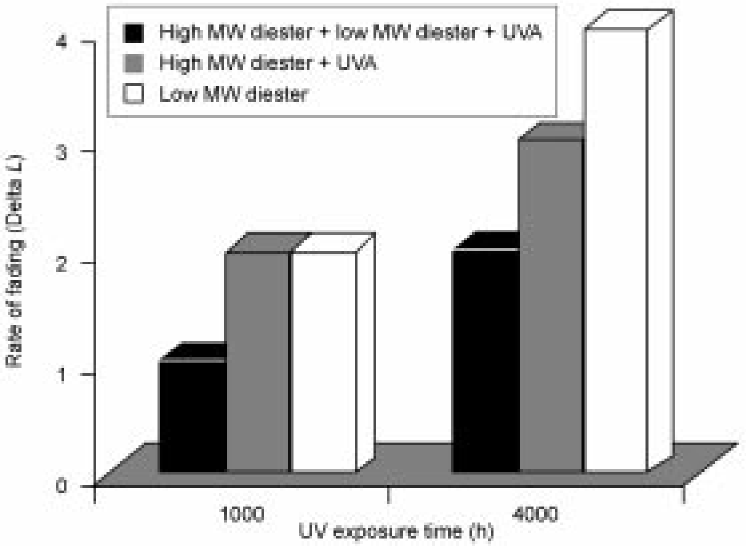


14.19 Effect of low and high molecular weight diester-based HALS on WPC yellowing under UV weathering for 2000 h (adapted from Muasher, 2005).



14.20 Effect of benzophenone and benzotriazole-based UVA on WPC fading under UV weathering (adapted from Muasher, 2005).

exposure of WPC is a combination of high molecular weight diester HALS (0.2 wt%), low molecular weight diester HALS (0.1 wt%), and benzotriazole UVA (0.1 wt%). Figure 14.21 shows the synergistic effect of the combination of HALS and UVA on rate of fading in WPC under 1000 and 4000 h of UV exposure.



14.21 Synergistic effect of HALS and UVA on rate of fading in WPC under UV weathering (adapted from Muasher, 2005).

14.5 Creep resistance

Creep is an inherent property of a material and may be defined as the maximum stress the material can withstand under a constant load at elevated temperature. In a creep test, a constant load is applied to a tensile or flexural specimen maintained at a constant temperature. When solids are subjected to an applied stress, the time-dependent strain occurs in three stages. In Stage I, there is a period of decreasing creep rate known as primary transient creep. During this period of deformation the resistance to creep increases to Stage II. In Stage II, the creep rate remains roughly constant and is known as secondary steady-state creep. This is the most important stage of creep since the time to failure is determined primarily by the secondary creep rate. The slope of the curve in Stage II is the strain rate or the creep rate of the material. In Stage III, tertiary creep occurs, which is characterized by internal fracturing of the material, creep acceleration, and subsequent failure.

Natural-fiber plastic composites creep under constant stress and the overall creep behavior of such viscoelastic materials is a complex phenomenon, which depends on both polymer properties such as molecular orientation, and crystallinity (Pomeroy, 1978) and fiber properties such as fiber-volume fraction, fiber-aspect ratio, orientation, and mechanical properties. The creep behavior of the composites is also sensitive to the external parameters such as applied stress, temperature, and humidity.

14.5.1 The theory of creep

When polymeric materials are subjected to external stress, molecular chain rearrangement on a local scale occurs rapidly, followed by a large-scale deformation, which occurs more slowly (Farid *et al.*, 2002). Polymer creeps due to both elastic deformation and viscous flow, which is known as viscoelastic deformation and the resulting creep strain increases non-linearly with time (Park and Balatinecz, 1998). Therefore, in NFPC the creep is controlled mainly by the polymer matrix and to some extent by fiber–matrix interfacial adhesion. It also depends on stress level and temperature.

The creep behavior of polymers has been described by various researchers by using numerous mathematical expressions and models and these models are now being applied for analyzing creep behavior of NFPCs. Generally, these models are based on two fundamental theories of viscoelastic nature of the material. For the material to be tested in the linear viscoelastic range, its creep behavior can be represented by simple rheological models by using the mechanical analogies that include viscous elements (dashpots) and elastic elements (springs). In order to simulate creep behavior, Nuñez *et al.* (2004) and Marcovich and Villar (2003) used a viscoelastic liquid model (Bürgers model) with multiple retardation or relaxation times as described in the Bürgers model. For the non-linear viscoelastic creep test of the material, the creep power law model known as Schapery's model and other models derived from it such as Findlay's model are in use. These models were developed using the constitutive relation to explain the creep behavior of materials.

Bürgers model

Bürgers model is a four-element model, which is a combination of the Maxwell element and Kelvin–Voigt element in series. The advantage of using this model is that it is the simplest model described by a differential equation, whose response to an applied stress can be easily solved analytically, and thereby describes the polymer behavior explicitly. According to this model, the total strain, $\epsilon_{(t)}$, is expressed as:

$$\epsilon_{(t)} = \frac{\sigma}{E_0} + \sum_{i=1}^{n-1} \frac{\sigma}{E_i} \left[1 - \exp\left(-t \frac{E_i}{\eta_i} \right) \right] + \frac{\sigma}{\eta_n} t \qquad 14.19$$

where σ is the applied stress, t is the creep time, E_0 is the modulus of initial deformation occurs by instantaneous elastic response of the single spring, E_i is the elastic modulus of the spring from the later deformation and η_i is the viscosity of the dashpot of the ith Kelvin–Voigt element. The ratio η_i/E_o is the relaxation time (τ_i) of the ith element, which is a measure of the time required for the extension of the spring to its equilibrium length while retarded by the dashpot. Thus, the summation represents the retarded response, i.e. decreasing creep rate of the material. The last viscous element of the Maxwell element, η_n, contributes to the region of steady-state creep, where the viscous flow is the predominant behavior.

Creep compliance, $J(t)$, is the viscoelastic material property used to describe material behavior during creep loading and for the linear viscoelastic region where the material properties are functions of time only. It is represented by:

$$J(t) = \frac{1}{E_0} + \sum_{i=1}^{n-1} \frac{1}{E_i} \left[1 - \exp\left(-\frac{t}{\tau_i} \right) \right] + \frac{1}{\eta_n} t \qquad 14.20$$

By the sudden removal of stress during the creep test, the strain decreases with time and this process is known as creep recovery. The rate of recovery depends on the material viscoelastic properties. In the linear viscoelastic region, the creep recovery behavior is usually predicted by the Boltzmann superposition principle (Nuñez *et al.*, 2004) and the creep recovery-compliance predicted by Bürgers model, $J_{r(t)}$, is given by:

$$J_{r(t)} = J(t_r) - \frac{1}{E_0} - \sum_{i=1}^{n-1} \frac{1}{E_i} \left[1 - \exp\left(-\frac{t - t_r}{\tau_i} \right) \right] \qquad 14.21$$

where $J(t_r)$ is the compliance value at the moment when the specimen is unloaded (t_r).

Findlay model or creep power law

The Findlay model (Sain *et al.*, 2000), derived from the constitutive equation for a non-linear viscoelastic material, is represented by:

$$\epsilon(t) = \epsilon_0 + At^{\tau} \qquad 14.22$$

where ϵ_0 is the initial instantaneous strain, A is the amplitude of the transient creep strain, and t is the time constant. ϵ_0, A and t are creep parameters. As the creep power law model used for composites is not a total reflection of the material property, the model was modified by expressing the creep strain as a percent of the instantaneous strain and redefine this strain as relative creep strain by rearranging eqn (14.22):

$$\epsilon(t)/\epsilon_0 = 1 + (a/\epsilon_0)t^{\tau} \qquad 14.23$$

$$\epsilon_r = (A/\epsilon_0)t^{\tau} \qquad 14.24$$

where ϵ_r is the relative creep strain. For a given natural fiber and plastic composite, the creep parameters A and τ can be evaluated by experimentally determining the strain as a function of time and then fitting it to a non-linear expression in the form given by eqn (14.24).

Park and Balatinecz (1998) modified the creep power law or Findlay model (eqn 14.24) by taking common logarithms to represent the relative creep as:

$$\log \epsilon_r = \log A + n \log t \qquad 14.25$$

where A represents A/ϵ_0 and n represents τ of eqn (14.24). By plotting log ϵ_r as a function of log t, a linear least square procedure was fitted to eqn (14.25).

According to this model, the creep compliance, which is the measure of the strain per unit of applied stress (Jiang *et al.*, 2007) is mathematically represented as:

$$J(t) = \frac{\epsilon(t)}{\sigma_0} \qquad 14.26$$

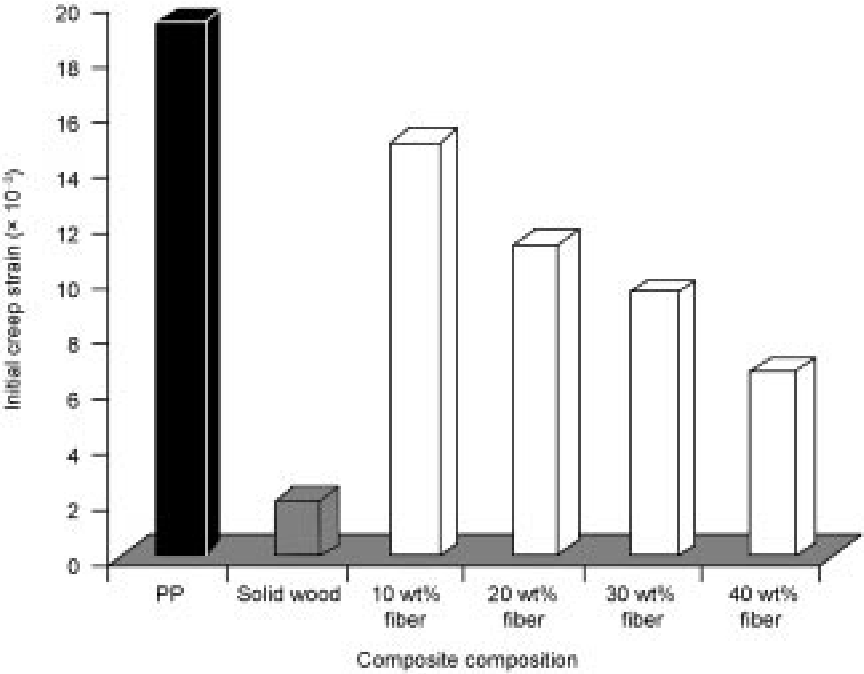
where σ_0 is the applied stress.

14.5.2 Effect of filler content, stress, temperature, and additives

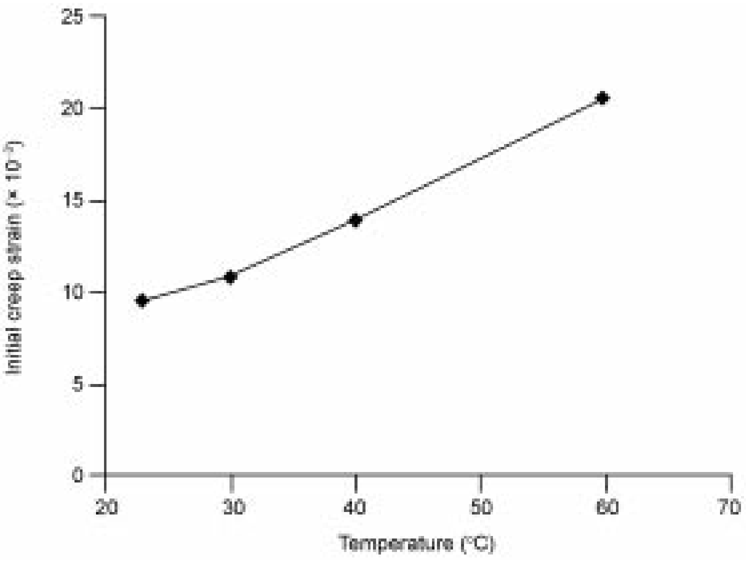
The mechanical properties such as creep of a composite are largely dependent upon the composition, i.e. the filler and polymer content of the composite. Nuñez *et al.* (2004) studied the effect of the wood flour content to the PP matrix on the creep behavior at 20 ºC. They observed that as the filler concentration increased, the creep deformation decreased owing to increased rigidity of the composites. However, at higher fiber content (60 wt%) the creep resistance decreased because of insufficient wetting of the wood flour by the matrix. It was suggested that physical or mechanical bonds, which were generated by the presence of direct particle–particle interactions, are easily broken during deformation. Thus, if filler wetting and dispersion can be efficiently achieved, the addition of wood flour will help in stiffening the composite and hence improve creep resistance. The temperature also plays an important part in the creep resistance of NFPC as the temperature alters the material structure, which in turn affects the creep response of the material. With increase in temperature, the chain mobility increases, and hence results in increased creep deformation.

Nuñez *et al.* have observed the strong temperature dependence of the creep behavior of the PP composite with 26 wt% of wood flour. It was found that with an increase in temperature from 20 to 50 °C, the creep strain increased 2.15 times and at 80 °C, the increase factor was 3.93. At 80 °C, the creep curve reached Stage III where the strain rate increased with time, leading to the final material failure. Owing to material softening, E_0 and η_n parameters of Bürgers model showed a reduction with increase in temperature. They have also analyzed the change in creep behavior of the wood flour/PP composite by addition of a compatibilizing agent, PPMAN, a copolymer of maleic anhydride and polypropylene. The composites with PPMAN showed better creep resistance and the deformation decreased with increasing percentages of added PPMAN (5–10%) as a result of the better dispersion of the particles during the mixing step and the improved final adhesion between the wood flour and PP matrix.

The creep behavior of wood-fiber/PP composites has been studied by Park and Balatinecz (1998). The effect of wood-fiber concentrations on creep was investigated and it was found that incorporation of wood-fibers into the neat polymer greatly improve the creep resistance of the polymer matrix. As shown in Fig. 14.22, the initial creep strain (measured 30 s after load application) of the composite decreased with increase in fiber concentration. The relative creep of the composite also showed a similar trend. After 200 min, the neat PP showed the ~141% relative creep, whereas the composite containing 40 wt% wood-fiber exhibited ~52% relative creep. Figure 14.23 shows the effect of temperature on initial creep strain of wood-fiber/PP composite. With increase in temperature, the extent of initial creep strain increased. Also the relative creep strain increased with an increase in time and temperature. The relative creep at 60 °C was found to be ~120% after 200 min, which was almost twice that of room temperature creep after the same duration. The temperature effect on creep was explained as higher temperatures typically soften thermoplastic materials and therefore reduce the creep resistance of matrix-dominant composites. To investigate the effect of the addition of wetting agent, creep tests were performed on both untreated and treated composites with a 5 wt% wetting agent, a maleated PP wax. At a lower stress level (35% of the flexural strength of the treated composites), the treated composite showed slightly less creep than an untreated one; however, at higher stress level (50% of the flexural strength of the treated composites), the untreated specimen ruptured within 90 min after load application with 166% relative creep, whereas the treated specimen sustained up to



14.22 Effect of fiber concentration on initial creep strain of wood fiber/PP composite (source: Park and Balatinerz, 1998).

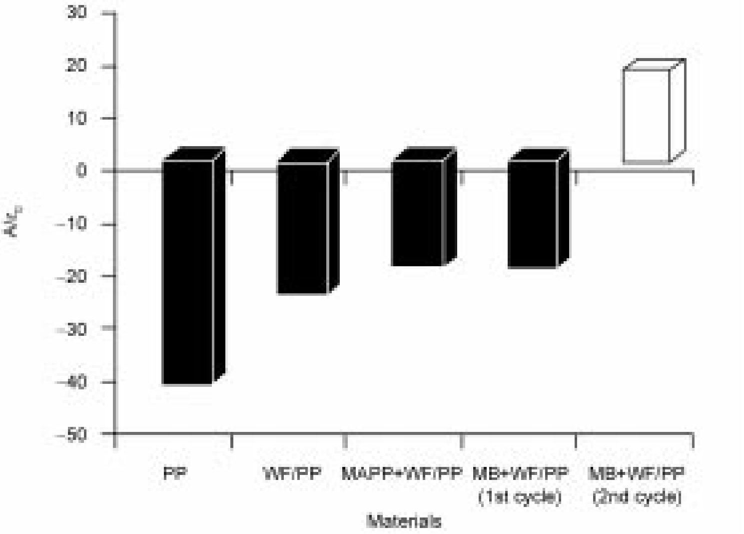


14.23 Effect of temperature on initial creep strain of wood fiber/PP composite (source: Park and Balatinerz, 1998).

200 min with 93% relative creep. Creep resistance at the higher stress level indicated a drastic improvement if a wetting agent was used due to an improvement in the compatibility between the fiber and the matrix.

Short-term creep tests of wood-flour/LDPE composites were carried out by Marcovich and Villar (2003). In this study, the LLDPE matrix was modified with organic peroxide and with maleic anhydride (MAn) and was simultaneously compounded with untreated wood flour. The creep resistance of the composites was improved by the addition of wood flour because the creep deformation decreases steadily with an increasing filler concentration. The effect of the LDPE matrix modification on the creep strain of 40 wt% composites was also studied. The creep resistance of the peroxide-treated LDPE/wood-fiber composite was lower than that of the untreated and MAn-treated LDPE/wood-fiber composites. This was explained as filler particle agglomeration might occur because of the reduced compatibility between the polar reinforcement and the non-polar matrix. Also, the lower crystallinity of the peroxide-treated matrix might be responsible for the relatively large creep deformation of their composites. On the other hand, MAn-treated LDPE/wood-fiber composites showed improved creep resistance due to improved interfacial adhesion.

Sain *et al.* (2000) studied the creep behavior of unmodified and functionally modified thermoplastic/wood-fiber composites. They observed that for poly(vinyl chloride) (PVC), PE and PP-based composites creep was strongly dependent on the amount of load, time, and temperature. Under the applied load of 30% of the flexural breaking load, the instantaneous creep strain was more dominant than the transient creep strain, whereas under 65% of the flexural breaking load, the transient creep became more significant. This observation also confirmed that wood-fiber/PVC composites are not suitable for use under unusually high-load fatigue conditions. Under an increase in load from 40 to 65% of the flexural breaking load, the time constant of the composites almost doubled. The elevated temperature had also a detrimental effect on creep resistance of wood fiber/PVC composites. A small rise in the temperature above ambient temperature resulted in significantly increased creep deformation of the composites. An increase in the temperature from 30 to 40 °C increased the time constant by more than five times, and the creep of wood-fiber-filled PVC at 40 °C was almost equal to the creep of unfilled PVC at 30 °C. Maleic and maleimide modification of wood-fiber resulted in a marginal improvement of the transient creep behavior of wood-fiber/PP composites, but such modifications had a negligible effect on instantaneous creep. For the maleimide-modified wood-fiber/PP composite, the instantaneous creep remained almost constant and the transient creep strain decreased significantly during the second load application, which was also evident from a significant change in the A/ϵ_0 value (relative creep parameter – see eqn 14.24) after repeated loading as demonstrated in Fig. 14.24. The creep resistance of wood-fiber/PE was found to be very low for unmodified and modified compositions.



14.24 Effect of interface modification on relative creep parameter of wood fiber/PP composite (source: Sain *et al.*, 2000).

The flexural creep properties of wood-fiber reinforced LDPE composites were measured at various temperatures and stress levels (expressed as the percentage of ultimate flexural strength, UFS) by Farid *et al.* (2002). It was observed that creep rupture occurred at 60 °C at all three load levels and at 40 °C with 40% UFS. As shown in Table 14.5, at 60 °C the rupture strain increased with the increase in load level and rupture occurred in less time. It was also observed that at a given load, the creep rupture strain increased with temperature.

Jiang *et al.* (2007) tried to improve the creep properties of WPC decking boards by reinforcing them with the commingled polymer glass fiber composite (CPGC) sheets. The composition of board was 58.8% pine wood flour, 33.8% PP, 4.0% talc, 2.3% MAPP, and 1.0% lubricant by weight. The CPGC used in

Table 14.5 Effect of load and temperature on creep rupture strain of wood flour/PE composites

Load (% of UFS)*	Temperature (°C)	Time (h)	Creep rupture strain (%)
25	60	42	2.0
30	60	36	2.8
40	60	2	3.0
40	40	42	2.9

* UFS = ultimate flexural strength.
Source: Farid *et al.* (2002).

this study consisted of unidirectional glass/PP filaments (60/40 wt/wt). The stresses employed for the creep testing were 11.0, 19.9, and 33.1 MPa respectively. It was observed that greater stress leads to bigger creep strain. The creep strain under 11.0 MPa stress was about half the values of that of 19.9 MPa stress. By CPGC reinforcement of WPC decking board, the creep strain was greatly reduced. At 7000 s of load time, the creep strain ratios are smaller at higher stresses, indicating a larger degree of creep property improvement. It has been explained as the addition of glass fiber generally reduces creep by establishing a strong fiber/polymer interface. This may be due to the fiber–fiber network structure, restraining polymer chain movement or to stress transfer from the polymer matrix to the fiber under the application of load. In this study, the glass fiber was continuous and oriented along the tension direction, and therefore was able to share a large portion of load and remarkably reduced creep of the composite.

Creep resistance of wood filled polystyrene (PS)/HDPE blends has been studied by Xu *et al.* (2001). They have investigated the effect of blending lower-creep PS with HDPE on the creep properties of composites. The PS–HDPE blends of different ratios (100:0, 75:25, 50:50, 25:75, and 0:100) were melt blended with wood flour. It was observed that creep speed decreased with increasing PS content, except for pure PS. Therefore, the most effective creep reduction strategy they found was to stiffen the matrix by incorporating PS rather than adding filler. The wood flour/PS–HDPE composites with plastic matrices of 50/50 wt/wt% PS/HDPE and 75/25 wt/wt% PS/HDPE showed lower creep speeds than the pure PS matrix and this was attributed to the changes in polymer elongation induced by processing. The least creep was obtained for the wood flour composite containing 75/25 wt/wt% of PS–HDPE blend.

Short-term flexural creep tests were conducted by Bledzki and Faruk (2004) to investigate the effects of hard wood and long wood-fiber content, temperature, and compatibilizer on creep behavior of wood-fiber/PP composites. Both hard wood and long wood fiber/PP composites containing 40 wt% wood-fiber showed lowest creep modulus, i.e. highest creep. When wood-fiber content increased to 60 wt%, the creep modulus increased significantly (165%) for both wood-fiber/PP composites. It was also observed that with an increase in time and temperature, the creep resistance (creep modulus and creep strength) of the composite decreased. After 180 min of loading, the creep modulus was around 1800 MPa at 60 °C, which was nearly 65% lower that of room temperature modulus after the same duration. The creep modulus of the composites made of untreated and MAPP-treated wood-fibers at 60 °C were evaluated and it was observed that the MAPP-treated composite showed increased creep modulus and hence increased creep resistance. Most of the work on creep behavior of NFPC has been carried out on wood-fibers/flour. Only few researchers reported the creep behavior of other natural-fiber composites. Pramanick and Sain (2006a) attempted to develop a generic creep prediction model for HDPE–rice husk composites that describes the creep behavior of composites with the constituents' creep behavior. This model was validated by using power-law–Boltzmann's superposition principles. The non-linearity in creep was also well described by this model. This was the first model to describe creep for a two-phase bio-based composite. In another study by same authors (Pramanick and Sain, 2006b), the temperature–stress equivalence of the HDPE–rice husk composite was reported. The temperature shift factor was incorporated while determining the material constants by using a modified Schapery's model. In this characterization, the temperature effect was found to be linear but was thermo-rheologically complex, exhibiting vertical shifts.

Feng *et al.* (2007) studied the effect of compatibilizer on dynamic creep properties of kenaf fiber–polymer composites. A polypropylene homopolymer, PP, and two impact ethylene–propylene copolymers of low and high molecular weight were blended with kenaf fibers. The fiber content in the composite was 50 wt% and the coupling agent used in this study was 3% MAPP. It was observed that both coupling agent and molecular weights of the copolymers strongly influenced the creep behavior of the composites. For the low molecular weight impact copolymer, the creep behavior improved significantly with the presence of the coupling agent, whereas the coupling agent influences lowered for the high molecular weight impact copolymer.

Alvarez *et al.* (2004) studied the influence of the fiber content on the flexural creep deformation of injected molded composites based on sisal fiber reinforced cellulose derivatives/starch commercial blends. The addition of sisal fibers (15 wt%) to the polymeric matrix resulted in significant improvement of the composite creep resistance. It was also observed that the creep modulus decreased with the increasing of time and temperature.

Vázquez *et al.* (1999) have performed flexural-creep tests on bagasse fiber/PP composites. They treated the fiber with an alkaline solution and the treated fiber improved the creep behavior of the composites due to the higher adhesion between the fiber and the matrix. Saha *et al.* (1999) chemically modified the jute fiber by cyanoethylation to improve of the creep properties of jute/unsaturated polyester composites. The cyanoethylated jute fiber composites showed much more creep resistance than untreated jute composites up to 80 °C due to an improved bonding at the interface between the fiber and the matrix.

14.5.3 Long-term creep prediction

It has been suggested (Turi, 1997) that the effects of time and temperature on mechanical behaviors of materials are equivalent. The short-time data are equivalent to data obtained at cooler temperatures and long-time data are equivalent to data obtained at warmer temperatures. These observations lead to the development of time and temperature correlation equations by numerous investigators to predict long-term creep performance from short-term data. The time–temperature superposition (TTS) is one of the most useful extrapolation techniques with a wide range of applications and it has been applied to various mechanical properties of different kinds of plastics. Generally, TTS is formulated based on two empirical equations (Tajvidi *et al.*, 2005):

1. The Arrhenius equation based on the activation energy (E) and represented as:

$$\ln a_T = \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad 14.27$$

where a_T is the horizontal or time shift factor, R is the universal gas constant, T_0 is the reference temperature, and T is the temperature at which a_T is desired.

2. The Williams–Landel–Ferry (WLF) equation, which relates temperature shift with time shift and is given as:

$$\log a_T = \frac{17.4(T - T_g)}{51.6 + T - T_g} \qquad 14.28$$

where T_g is the glass transition temperature and T is the test temperature.

With this principle of TTS, the creep deformation curves obtained under different stresses and temperatures can be shifted and assembled into a master curve, covering a much longer timescale. In one of the studies on the application of TTS to wood-fiber/plastic composites, Pooler (2001) suggested that only a horizontal shifting is adequate to correctly superimpose the creep data in wood flour/HDPE composites. They have conducted dynamic mechanical analysis (DMA) tests to determine shift factors. Tajvidi *et al.* (2005) have evaluated the use of horizontal and vertical shifting and two-dimensional minimization methods to obtain master curves covering a higher range of frequencies than that evaluated empirically for kenaf fiber/HDPE composites and have compared TTS master curves with actual creep test data. They have extrapolated short-term creep data to predict longer-term creep data, and validated this by comparing it with actual long-term test data. They observed that at longer times (higher temperatures), the TTS curves deviated from the experimental curve, which indicates that the effect of temperature on the viscoelastic response of such materials is much more significant than the effect of time, and so the TTS method would overestimate longer-term creep.

Nuñez *et al.* (2004) found that master curves constructed from short-term creep data for wood flour/PP composites could not predict the long-term creep behavior very accurately at low temperatures. However, at 70–80 °C temperatures, where molecular relaxation takes place, there was a good superposition of the short-term and the long-term data. A master curve with the Arrhenius model was used (Alvarez *et al.*, 2004) to determine the creep resistance of sisal fiber reinforced cellulose derivatives/starch blends at longer times and different temperatures and it was found that this model was useful to estimate the long-term behavior of this material. Pramanick and Sain (2005) derived a relationship between deformation, time, temperature, relative humidity, and stress for predicting long-term creep behavior of rice husk/HDPE composites. According to them, non-linearity can exist in the stress, temperature and moisture-related deformation. They studied the stress-related non-linear creep behavior of the composites by subjecting the composite to creep and recovery in flexural mode. With modified models, they determined both linear and non-linear region constants and developed a predictive model to predict long-term creep deformation in natural-fiber composites.

14.6 Conclusion

As government and people become more aware and concerned about the environmental hazards of petroleum-based products, natural-fiber polymer composites are gaining more importance and acceptance as viable alternatives. However, NFPC products have to overcome some hurdles, especially the issue of durability, in order to successfully substitute conventional materials. Durability or long-term performance of NFPC products is largely dependent on the environmental conditions in which the product is in use. For outdoor applications, the changing weathering conditions such as temperature, humidity, and UV radiation retard the useful service life of the product. Property detoriation and discoloration are among the major detrimental effects of hygrothermal and UV exposure. In addition to this, NFPC products creep or deform under constant stress for a longer duration. The combined effect of these environmental conditions often proves to be more detrimental on the performance of these products. Significant research has been in process to address and limit these environmental effects on NFPC products around the world. There is also an ongoing effort to develop NFPC materials with improved performance for real world applications.

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15

Modelling natural-fibre composites

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15.1 Introduction

Natural-fibre reinforced polymer composites have a very complex hierarchical structure covering the whole range of length scales from nano to micro to meso to macro. The macrocomposite consists of resin and fibers with a certain fibre orientation distribution. Fibres have an anisotropic wall material surrounding the lumen, which may be empty or filled with resin. In the fibre wall one can distinguish anisotropic layers, each characterised by a specific thickness and orientation of the material's symmetry axes with respect to the fibre axis. At the smallest scale each fibre wall layer consists of microfibrils of oriented cellulosic chains, hemicellulose and lignin.

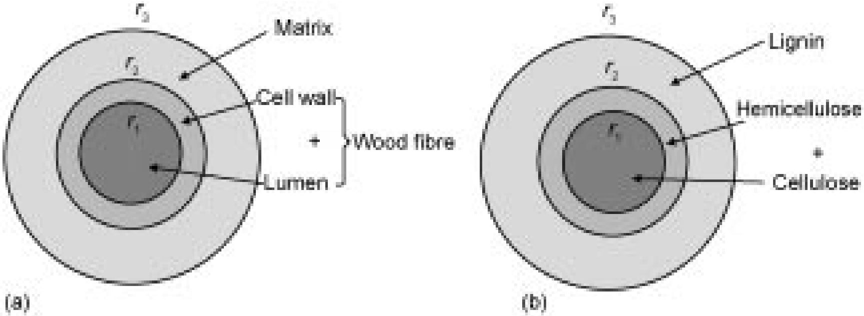
An advantage for modelling is that the length scales are sufficiently different that multi-scale analysis is possible instead of developing a model that would account for the whole complexity of the described system. In the multi-scale modelling approach the different length scales are linked by micromechanical models. Thus a model with a detailed description of mechanisms, material and geometrical parameters on one scale gives as an output homogenised (averaged) properties which serve as an input in the next (higher) scale modelling.

Applying this methodology, the averaged properties of a *fibre wall layer* may be modelled by considering cellulose, hemicellulose and lignin as an assembly of constituents and applying elasticity theory (including moisture expansion terms) or simple engineering models. Classical laminate theory (CLT) may be used to calculate average *fibre wall* properties based on the fibre wall layer properties obtained earlier. On the next scale the average *natural-fibre composite* properties corresponding to a given fibre volume fraction may be calculated using the resin and cell wall properties. This modelling includes two steps: (a) properties of *aligned fibre composite* with the same fibre volume fraction are determined; and (b) properties of *composites with given fibre orientation distribution* are modelled using so-called 'laminate analogy' and the properties of the aligned composite.

Geometrical characteristics of the internal structure on each scale are used in these models. Two types of models are distinguished: models with axial symmetry and models of layered structures. Layered structures with thin layers may be analysed using CLT. This group of models does not require further introduction and relevant details will be explained in this chapter.

Models with axial symmetry can be applied on two scales as illustrated in Fig. 15.1. In the concentric cylinder assembly model on the composite scale (macro-scale), the fibre wall in Fig. 15.1(a) is a cylinder represented by its effective properties. The lumen can be empty or filled with resin. A more detailed and complex analysis may be performed by including the ultrastructure of the wood fibre. In this case, each layer of the fibre wall is represented by a cylinder with corresponding properties. This approach is not consistent with the multi-scale analysis philosophy used in this chapter and therefore will be not applied.

In analysing the average properties of the fibre wall layer, one way of representing the heterogeneous internal structure by assembly of concentric lignin, hemicellulose and cellulose cylinders is shown in Fig. 15.1(b). Both models shown in Fig. 15.1 require methods that can calculate average hygro-elastic properties of concentric cylinder assemblies consisting of cylinders with orthotropic or monoclinic symmetry. Similar models for two- and three-phase composite materials with isotropic or transversely isotropic properties have been used previously, for example in Hashin[1] and Wagner and Nairn.[2] In the transverse isotropic case, the lumen was not included in analysis. Fibres with helical microfibril orientations were analysed by Jolicoeur and Cardon[3] and Neagu *et al.*[4] In Section 15.2 a generalised version of the *N*-concentric cylinder assembly model (CCA model) is presented for orthotropic constituent cylinders and including the lumen. The following sections of this chapter contain application of the CCA model and the CLT model for multi-scale modelling. All numerical examples and discussion in this chapter are limited to but not restricted to wood-fibre composites. In Section 15.3 the CCA model is applied to calculate the fibre wall layer elastic properties and then the fibre wall properties



15.1 Schematic showing of a three-layered cylindrical unit cell: (a) wood fibre composite and (b) microfibril.

are calculated using CLT. In Section 15.4 the macroproperties of aligned natural fibre composites are first analysed using the CCA model. Then the results obtained are used in the 'laminate analogy' model to deal with 'non-aligned' composites with the same fibre volume fraction. Finally, in Section 15.5 the moisture expansion on all scales is considered and moisture expansion coefficients are calculated. To achieve this goal the N-cylinder CCA model and the CLT are complemented with moisture expansion terms.

15.2 Elastic properties of *N*-phase concentric cylinder assembly

15.2.1 Definition of the model

The unit cell of the fibre wall layer and also the unit cell of the aligned natural-fibre composite (which is a sub-model on the way to analyse more realistic composites) can be visualised as a concentric cylinder assembly (CCA model). In the unit cell, constituents (phases) have lengths much larger than other dimensions and their cross-section is approximately constant. Owing to the large length versus diameter ratio, which may reach 100 in wood-fibres, the average stress state in a phase is almost that in the model with infinitely long phases and the local stress perturbations at the ends have negligible effect on the overall properties of the unit cell. Hence, infinitely long cylinders are considered in the model. A poor-quality interface between phases may result in large debonded regions at fibre ends which would increase the end effect.

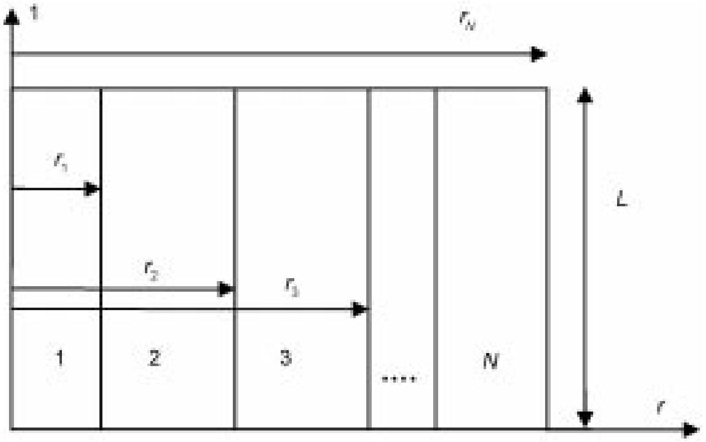
To simplify calculations a circular cross-section of phases (axial symmetry) is assumed. It was shown by Marklund,[5] comparing numerical results for fibres with circular, square and elliptical cross-sections, that the shape of the cross-section has a rather small effect on results.

The unit cell of the multi-material system described is shown in a most general form in Fig. 15.2. It consists of N concentric cylinders made of orthotropic materials. The length L of the model is much larger than the other dimensions and the stress–strain state is assumed to be independent of the axial coordinate 1 (thus neglecting all end effects).

Interfaces of the kth cylinder have the coordinates r_{k-1} and r_k ($r_0 = 0$). Since the calculated effective elastic properties of the assembly depend only on the relative dimensions of constituents, one can use $r_N = 1$ for the outer boundary of the assembly, $r = r_N$. An empty lumen is modelled as a cylinder with elastic properties approaching zero.

The volume fraction of the kth phase in the unit cell can be expressed through its interface coordinates:

$$V_k = \frac{r_k^2 - r_{k-1}^2}{r_N^2} \qquad 15.1$$



15.2 The microstructure of the unit cell represented by *N* concentric cylinder assembly.

The material of a phase, except for phase 1 which has to be transverse isotropic, is assumed to be orthotropic with orthotropic symmetry axes oriented in directions 1, r and θ respectively. This implies that r and θ are directions 2 and 3, respectively. The linear elastic stress–strain relationship in material symmetry axes, using Voigt notation, is:

$$\epsilon_i = S_{ij}\sigma_j, \qquad \sigma_i = C_{ij}\epsilon_j \qquad i,j = 1,2,\ldots,6 \tag{15.2}$$

Expanded forms of these equations and calculation expressions for compliance S_{ij} and stiffness C_{ij} are given in Appendix 15.1.

Several loading cases of the unit cell have to be simulated, with each of them determining a certain averaged elastic property. Perfect bonding is assumed at the interface between phases. This assumption is valid only at low stresses used to define elastic properties and is not satisfied if the interface is damaged by high loads. Independent of the particular loading case, the following conditions on the symmetry axis $r = 0$ and on the interfaces between cylinders have to be satisfied:

1. The solution must be limited at $r = 0$.
2. Continuity of radial, tangential and axial displacements at internal interfaces:

$$u_r^k(r_k) = u_r^{k+1}(r_k) \tag{15.3}$$

$$u_\theta^k(r_k) = u_\theta^{k+1}(r_k) \tag{15.4}$$

$$u_1^k(r_k) = u_1^{k+1}(r_k) \qquad k = 1,2,\ldots,N-1 \tag{15.5}$$

3. Stress continuity at internal interfaces:

$$\sigma_r^k(r_k) = \sigma_r^{k+1}(r_k) \qquad 15.6$$

$$\sigma_{r\theta}^k(r_k) = \sigma_{r\theta}^{k+1}(r_k) \qquad 15.7$$

$$\sigma_{1r}^k(r_k) = \sigma_{1r}^{k+1}(r_k) \qquad 15.8$$

Conditions at outer boundaries of the unit cell can be either in displacements or in stresses. For example, in calculating the transverse plane strain bulk modulus, the axial strain is zero and a constant radial displacement is applied on $r = r_N$. These conditions will be discussed in more detail in the following, determining particular average properties.

15.2.2 Transverse plane strain bulk modulus, axial modulus and Poisson ratio

The homogenised transverse isotropic material is shown in Fig. 15.3. The 'longitudinal' z-axis of the Cartesian (x, y, z) coordinate system coincides with the 1-axis of the circular cylindrical sub-domain representing the N-cylinder assembly. The 1 r, θ axes are the orthotropic symmetry axes of the assembly. The (x, y) plane is called the 'transverse plane'.

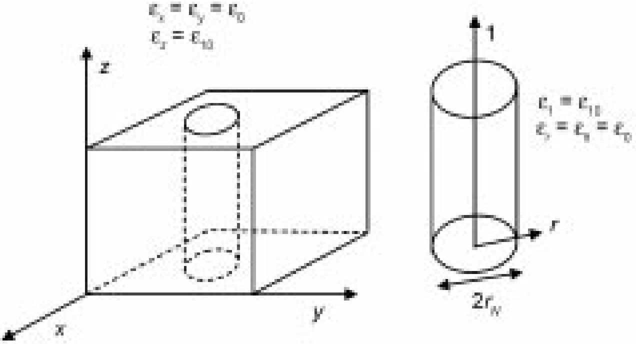
Let us consider a case when uniform normal strains only are applied to the homogenised composite:

$$\epsilon_z = \epsilon_{10}, \qquad \epsilon_x = \epsilon_y = \epsilon_0 \qquad 15.9$$

The shear strain components are equal to zero. Obviously the stresses are also uniformly distributed. The strains on the surface of this cylinder $r = r_N$ in cylindrical coordinates, calculated using strain transformation expressions, are:

$$\epsilon_r = \epsilon_\theta = \epsilon_0 \qquad \epsilon_1 = \epsilon_{10} \qquad 15.10$$

The shear strains are $\epsilon_{1r} = \epsilon_{1\theta} = \epsilon_{r\theta} = 0$. The radial and hoop stress along the



15.3 Homogenised composite subjected to normal strains and the strains applied to cylindrical unit cell: (a) macrocomposite and (b) unit cell consisting of cylinder assembly.

surface is also constant and all shear stresses are zero. Thus, the strains (15.9) applied at the outer composite boundary result in the same stress–strain state at the cylinder assembly boundary which for this reason is considered as the representative volume element (RVE).

Non-zero solutions in the case (15.10) are only for the radial displacement, radial and axial stress components. They were derived by Marklund[5] and may be written for the *k*th phase as follows:

$$u_r^k = A_1^k r^{\alpha_k} + A_2^k r^{-\alpha_k} + \psi_k \epsilon_{10} r \tag{15.11}$$

$$\sigma_r^k = A_1^k \beta_k r^{\alpha_k - 1} + A_2^k \gamma_k r^{-\alpha_k - 1} + \phi_k \epsilon_{10} \tag{15.12}$$

$$\sigma_1^k = g_k \epsilon_{10} + A_1^k f_k r^{\alpha_k - 1} + A_2^k h_k r^{-\alpha_k - 1} \tag{15.13}$$

Expressions for $\alpha_k, \psi_k, \beta_k, \gamma_k, \phi_k, g_k, f_k, h_k$ are given in Appendix 15.2. The axial displacement is constant. The $2N$ unknown constants A_i^k are determined using $2 * (N - 1)$ interface conditions, condition (1) on the symmetry axes and the given radial strain or stress at $r = r_N$.

To determine the average *transverse plane strain bulk modulus* $K_{23} = \frac{1}{2}(C_{22} + C_{23})$ of the assembly we consider a plane strain case, $\epsilon_{10} = 0$ but with a given non-zero ϵ_0, leading to $u_r^N(r_N) = \epsilon_0 r_N$. The stress state is found as described above. The strain energy of the homogenised composite cylinder with volume V can be written as:

$$U = 2K_{23}\epsilon_0^2 V \tag{15.14}$$

On the other hand the stored strain energy is

$$U = \tfrac{1}{2}\sigma_r^N(r_N) u_r^N(r_N) 2\pi r_N L \tag{15.15}$$

Since $V = \pi r_N^2 L$, we obtain from (15.14) and (15.15):

$$K_{23} = \frac{1}{2\epsilon_0}\, \sigma_r^N(r_N) \tag{15.16}$$

Using (15.11) in (15.16) we obtain:

$$K_{23} = \frac{1}{2\epsilon_0}\left(A_1^N \beta_N r_N^{\alpha_N - 1} + A_2^N \gamma_N r_N^{-\alpha_N - 1}\right) \tag{15.17}$$

The *longitudinal modulus* E_1 and *Poisson ratio* $\nu_{1T} = \nu_{1r} = \nu_{1\theta}$ of the CCA model are calculated applying $\epsilon_1 = \epsilon_{10}$ only. The radial stress on the outer boundary $r = r_N$ of the assembly is assumed to be zero, $\sigma_r^N(r_N) = 0$. Hence, the strain in the radial direction of the cylinder assembly, ϵ_0, is the result of calculation and corresponds to free contraction in the *r*-direction, i.e. it may be used to define the average Poisson ratio of the RVE:

$$\nu_{1T} = -\frac{\epsilon_0}{\epsilon_{10}} \tag{15.18}$$

where the average radial strain is

$$\epsilon_0 = \epsilon_r^{av} = \frac{u_r^N(r_N)}{r_N} \qquad 15.19$$

According to definition the average stress in direction 1, σ_1^{av} is used to determine the average longitudinal modulus E_1 of the assembly:

$$E_1 = \frac{\sigma_1^{av}}{\epsilon_{10}} \qquad 15.20$$

where the average stress may be calculated as:

$$\sigma_1^{av} = \frac{2}{r_N^2}\sum_{k=1}^{N}\int_{r_{k-1}}^{r_k} r\sigma_1^k(r)\mathrm{d}r \qquad 15.21$$

15.2.3 Shear modulus G_{12}

In order to determine the shear modulus G_{12} of the cylinder assembly we consider the homogenised material in a pure shear loading with $\gamma_{1x} = \gamma_{12}^0$ being the only non-zero strain component ($\epsilon_x = \epsilon_y = \epsilon_1 = \gamma_{1y} = \gamma_{xy} = 0$); see Fig. 15.4. Obviously the only non-zero stress component of the transversely isotropic composite is $\sigma_{1x}^0 = G_{12}\gamma_{12}^0$. This strain field is obtained applying u_1 as a linear function of x.

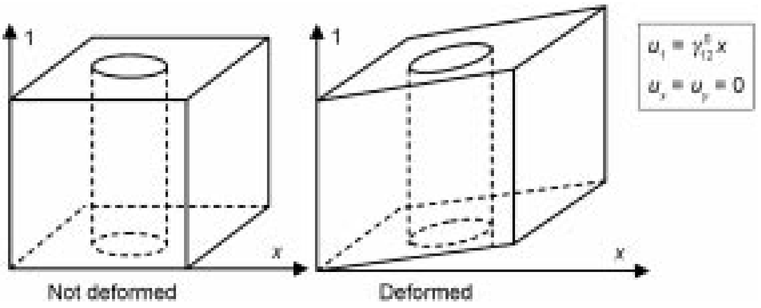
From the above the displacements applied on the surface of the cylindrical assembly in cylindrical coordinates can be calculated as:

$$u_r(r_N) = u_\theta(r_N) = 0, \qquad u_1(r_N) = \gamma_{12}^0 r_N \cos\theta \qquad 15.22$$

Here θ is the angle between x and r directions.

The solution for the field equations in this case is given by Marklund *et al.*[5] For the kth phase we obtain:

$$u_1^k = \left(A_1^k r^{\alpha_k} + A_2^k r^{-\alpha_k}\right)\cos\theta \qquad 15.23$$



15.4 Deformation of the composite in a pure shear mode.

$$\sigma_{1r}^{k} = C_{66}^{k}\left(A_1^k a_k r^{a_k-1} - A_2^k a_k r^{-\alpha_k-1}\right)\cos\theta \qquad 15.24$$

where a_k are defined in Appendix 15.2. The boundary condition for axial displacement at the outer boundary $r = r_N$ is given by the second equation of (15.22).

When all the constants in displacement and stress field for each phase are found, the longitudinal shear modulus of the assembly can then be determined as follows. Transforming the applied strain γ_{12}^0 to cylindrical system leads to the following shear stress distribution along the boundary $r = r_N$:

$$\sigma_{1r}(r_N) = G_{12}\gamma_{12}^0\cos\theta \qquad 15.25$$

This stress component also comes as a part of solution given by (15.24):

$$\sigma_{1r}^{N} = C_{66}^{N}\left(A_1^N a_N r_n^{a_n-1} - A_2^N a_N r_n^{-a_N-1}\right)\cos\theta \qquad 15.26$$

From (15.25) and (15.26) we find:

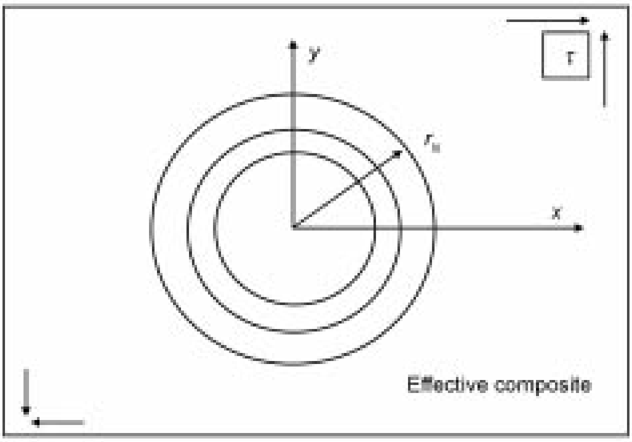
$$G_{12} = \frac{\sigma_{1r}^N(r_N)}{\gamma_{12}^0\cos\theta} \quad \text{or} \quad G_{12} = \frac{C_{66}^N}{\gamma_{12}^0}\left(A_1^N a_N r_N^{a_n-1} - A_2^N a_N r_N^{-a_n-1}\right) \qquad 15.27$$

15.2.4 Transverse shear modulus G_{23}

We consider the (*x*,*y*) plane of the composite to homogenise. Shear stress $\sigma_{xy} = \tau$ is applied at infinity as shown in Fig. 15.5. The stress components in the cylindrical coordinate system related to the concentric cylinder assembly are:

$$\sigma_r = \tau\sin 2\theta, \quad \sigma_\theta = -\tau\sin 2\theta, \quad \sigma_{r\theta} = \tau\cos 2\theta \qquad 15.28$$

The assembly of orthotropic cylinders is embedded in an infinite domain of effective composite material which is transversely isotropic. The shear modulus



15.5 Infinite composite loaded in shear at infinity.

of the effective composite is one of the unknowns. This model and method of solution, called the generalised self-consistent scheme, was first suggested by Christensen and Lo[6] to analyse transverse isotropic cylinder assemblies. It was generalised for orthotropic cylinders by Marklund *et al.*[5]

The solution of the corresponding plane strain problem for one cylindrical phase is given by Marklund *et al.*[5] For an orthotropic *k*th phase the radial and circumferential displacements and stress components relevant for the following analysis are:

$$u_r^k = \sum_{i=1}^{4} A_i^k r^{\lambda_i^k} \sin 2\theta, \quad u_\theta^k = \sum_{i=1}^{4} A_i^k b_i^k r^{\lambda_i^k} \cos 2\theta \qquad 15.29$$

$$\sigma_r^k = \sum_{i=1}^{4} A_i^k \left[C_{22}^k \lambda_i^k + C_{23}^k \left(1 - 2b_i^k\right)\right] r^{\lambda_i^k - 1} \sin 2\theta \qquad 15.30$$

$$\sigma_{r\theta}^k = G_{r\theta}^k \sum_{i=1}^{4} A_i^k \left[\lambda_i^k b_i^k + 2 - b_i^k\right] r^{\lambda_i^k - 1} \cos 2\theta \qquad 15.31$$

The constants λ_i^k and β_i^k are defined in Appendix 15.2. The solution for each cylinder contains four unknown constants A_i^k, $i = 1, \ldots, 4$.

To replace a cylindrical region in the effective composite (denoted with index 'c') with concentric cylinder assembly inclusion, the 'energy condition' (formulated by Eshelby[7]) must be satisfied:

$$\int_0^{2\pi} \left(\sigma_r^0 u_r^c + \sigma_{r\theta}^0 u_\theta^c - \sigma_r^c u_r^0 - \sigma_{r\theta}^c u_\theta^0\right)\Big|_{r=r_N} r_N d\theta = 0 \qquad 15.32$$

where stress and displacement components with upper index 0 denote the solution for a composite without any inclusion.

For shorter notation we assume that $\tau = 1$ (with a unit of stress). The solution for the effective transverse isotropic composite material, see Marklund *et al.*[5] for details, is:

$$u_r^c = \frac{1}{2G_{23}} \left[r + A_4^c \frac{1}{r^3}\right] \sin 2\theta, \quad u_\theta^c = \frac{1}{2G_{23}} \left[r - A_4^c \frac{1}{r^3}\right] \cos 2\theta \qquad 15.33$$

$$\sigma_r^c = \left[1 - A_4^c \frac{3}{r^4}\right] \sin 2\theta, \quad \sigma_{r\theta}^c = \left[1 + A_4^c \frac{3}{r^4}\right] \cos 2\theta \qquad 15.34$$

It has to be emphasised that the shear modulus G_{23} of the effective composite is also an unknown.

Summarising, we see that we have four unknown A_i^k for each phase of the assembly, one unknown A_4^c for the effective composite and the unknown G_{23} for the effective composite. To find these $4N + 2$ constants we use (a) $4N - 4$ conditions at internal interfaces; (b) the condition that the solution on the axis $r = 0$ must be limited, leading to $A_2^1 = A_4^1 = 0$; (c) two displacement continuity conditions at the interface between the assembly and the effective composite:

$$u_r^N(r_N) = u_r^c(r_N), \quad u_\theta^N(r_N) = u_\theta^c(r_N) \qquad 15.35$$

and (d) stress continuity at the assembly/effective composite interface:

$$\sigma_r^N(r_N) = \sigma_r^c(r_N) \qquad 15.36$$

$$\sigma_{r\theta}^N(r_N) - \sigma_{r\theta}^c(r_N) = 0 \qquad 15.37$$

Since the total number of conditions is $4N + 2$, all unknowns including G_{23} may be determined. The system is non-linear with respect to G_{23} and its solution requires numerical procedure. A recommended efficient method of numerical solution is as follows. Assume an 'initial' value for G_{23} (for example, equal to the shear modulus of the weakest cylinder) and find the remaining $4N + 1$ constant using the above conditions except the last one. Substituting the obtained solution in the last condition of (15.37) we obtain a value that is not equal to zero. The left side of (15.37) may be considered as a 'misfit function' which is non-zero if the assumed composite modulus G_{23} is not selected correctly. The calculations must be repeated by stepwise increasing G_{23} until the sign of the misfit function changes. Thereby the correct G_{23} value is localised and may be refined with required accuracy.

For assemblies with the lumen as the central sub-cylinder the most convenient approach is to avoid developing special solutions for that case. Instead, the elastic properties of this 'special cylinder' may be taken as very small compared with the rest of the cylinders, and then the solutions and conditions presented above may be used.

15.2.5 Determination of E_2 and ν_{23}

These two material constants of the composite may be determined when K_{23} and G_{23} are determined as described above. The expressions are:[1]

$$E_2 = \frac{1}{\dfrac{1}{4K_{23}} + \dfrac{1}{4G_{23}} + \dfrac{\nu_{12}^2}{E_1}} \qquad 15.38$$

$$\nu_{23} = \frac{E_2}{2G_{23}} - 1 \qquad 15.39$$

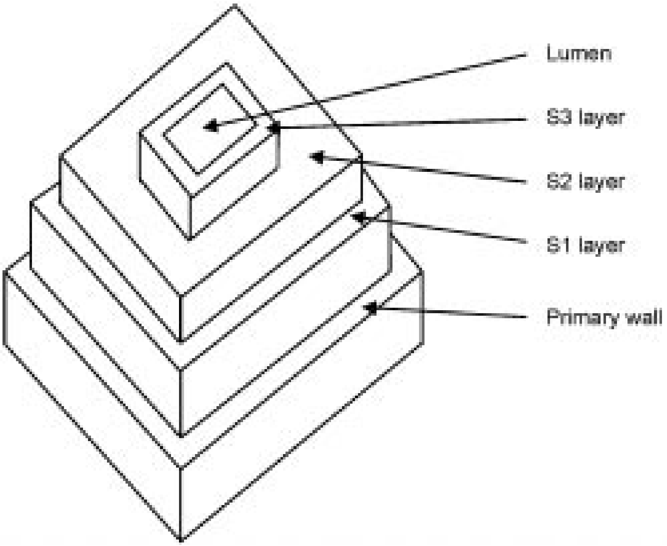
15.3 Ultrastructure-based multiscale modelling of fibre elastic properties

15.3.1 Geometrical features of the fibre ultrastructure

Direct experimental measurement of fibre properties by available techniques is very complex and for some properties, for example transverse shear, even impossible. Therefore an improved understanding of fibre behaviour and development of models able to predict the fibre properties as dependent on the fibre ultrastructure are of high priority. In this section we will consider in detail wood-fibres, while recognising that other natural fibres have the same basic features and constituents and, hence, the presented methods of analysis and observed trends are applicable to them also.

Visual inspection of fibre in the annual growth ring of a tree reveals a large variation in geometrical parameters of wood fibres (tracheids) when moving from the earlywood to the latewood region. The thickness of the fibre wall increases and the size of the cavity (lumen) decreases. The length of the softwood fibre is about 1–4 mm[8] and the diameter is 20–40 μm. Owing to the high length/diameter aspect ratio (about 100) these fibres in the context of the stress transfer in composites may be treated as long and continuous.

In spite of the large variation of geometrical parameters, the ultrastructure and chemical constituents of the fibre remain the same. The cell wall has a layered structure as shown in Fig. 15.6. The wall of the fibre is a laminate which consists of the middle lamella (binder layer between individual wood-fibres which in composites is partially or completely removed due to processing), the primary wall, which can be treated as a composite with random fibril orientation, and the secondary wall which consists of several 'unidirectional (UD) composite' layers (S1 – outer layer, S2 – middle layer, S3 – inner layer).



15.6 Schematic showing of the wood fibre ultrastructure.

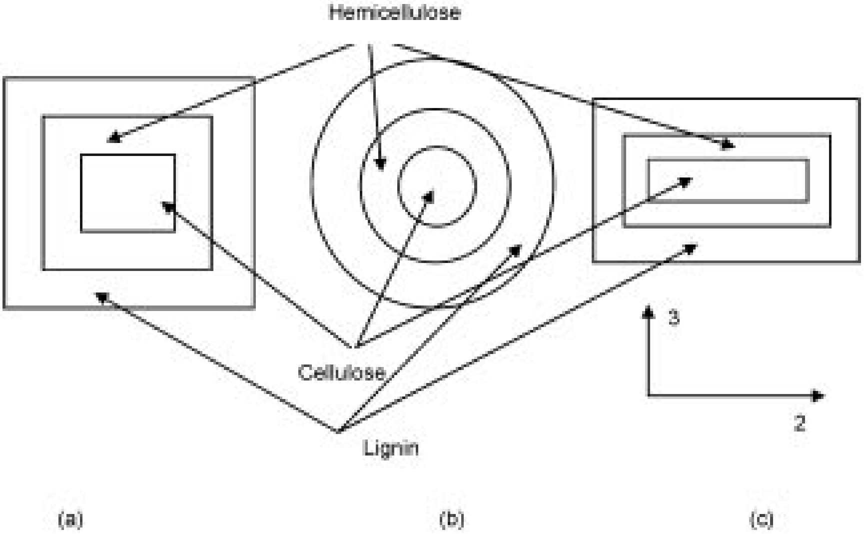
15.3.2 Elastic properties of a cell wall layer

Since the layers of the secondary wall are built of thread-like anisotropic units called microfibrils, they can be treated as UD composites. The microfibrils consist of cellulose chains, hemicellulose and lignin. The volume fractions of these chemical constituents are different in different cell wall layers but are essentially the same in the earlywood and in the latewood fibres. The values used in simulations presented in this section are given in Table 15.1.

Each of the secondary wall layers has a certain orientation of microfibrils. Hence, the elastic properties of a layer first have to be determined in its local material symmetry system of coordinates and then transformed to the global system related to the fibre axis. The geometrical configuration of microfibrils in the cell wall is not fully clear. However, a common assumption in modelling is that cellulose fibres are surrounded by hemicellulose material and this sub-block is embedded in a lignin matrix.[9] The most common realisation of these assumptions in the RVE is shown in Fig. 15.7.

Table 15.1 Volume fractions of constituents (%) at 12% average moisture content

Cell wall layer	Cellulose	Hemicellulose	Lignin
S2, S3	44.3	31.6	24.1
S1, primary, middle	18.0	17.4	64.6



15.7 Three simple models of the repeating element of the cell wall layer. Cross-sections: (a) Model A, square; (b) Model B, cylindrical; (c) Model C, rectangular.

In the assumed periodic structure the RVE is equal to the repeating element. Owing to the symmetry with respect to R and T directions the model in Fig. 15.7(a) results in equal elastic moduli in these two directions, $E_2 = E_3$. However, it is worth mentioning that square packing does *not* result in transverse isotropic material:[1] the transverse shear modulus G_{23} of this material does not follow the well-known $G_{23} = \frac{1}{2}E_2/(1 + \nu_{23})$ rule for isotropic materials. Therefore, the cylindrical assembly model in Fig. 15.7(b) is a better representation of a transverse isotropic material. Finally the model in Fig. 15.7(c) represents an orthotropic material and the degree of the anisotropy in the transverse (2,3)-plane can be varied by changing the length ratio in directions 2 and 3. Since the degree of the anisotropy on this scale is not known *a priori* and analytical solutions for this model are not available, this model is not used in the following discussion.

The transverse isotropic elastic properties of cellulose have been measured experimentally and also estimated theoretically.[10] The elastic modulus in the microfibril direction E_1^C is between 130 and 170 GPa, the transverse modulus $E_2^C \in [17; 27]$ GPa, the axial shear modulus $G_{12}^C \in [4.0; 5.0]$ GPa, the axial Poisson ratio $\nu_{12}^C \in [0.03; 0.2]$, the transverse Poisson ratio $\nu_{23}^C \in [0.48; 0.52]$. The variation in transverse isotropic elastic properties of hemicellulose is as large as for cellulose. Independent of the model used to calculate the properties of the cellulose + hemicellulose + lignin (C+H+L) system, this intrinsic uncertainty in input data leads to large variation and uncertainty in calculated averaged properties. Hence, the requirements to the model accuracy are not very high but the accuracy of the model has to be known. In this section in addition to the CCA model we will inspect simple engineering models and calculation schemes. They will be validated comparing with the results obtained using the concentric cylinder assembly model. In simulations we will use 'medium' properties of the constituents presented in Table 15.2. The upper index in Table 15.2 and in the following indicates the chemical constituent (k = C, H, L).

The averaged (homogenised) elastic properties of the S2 layer calculated according to the three-cylinder assembly model (Model B in Fig. 15.7) are presented in Table 15.3. Alternatively the CCA model averaging over the Model B geometry may also be performed using a two-step procedure. In the first step, the averaged properties of a sub-block of cellulose and hemicellulose cylinders are found. Then the averaged properties of the (C+H) sub-block are used as

Table 15.2 Elastic properties of constituents used in simulations

Constituent	E_1^k (GPa)	E_2^k (GPa)	G_{12}^k (GPa)	ν_{12}^k	ν_{23}^k
1 Cellulose	150.0	17.5	4.5	0.085 71	0.50
2 Hemicellulose	16.0	3.5	1.5	0.457 1	0.4
3 Lignin	2.75	2.75	1.034	0.33	0.33

Table 15.3 Elastic properties of S2 and S3 cell wall layers in material symmetry axes

Property	Model B	Model B (C + H) + L	Model B C + (H + L)	ROM models	Model A FEM
E_1 (GPa)	72.278	72.282	72.271	72.169	72.4
E_2 (GPa)	5.964	5.973	5.947	6.090	6.70
ν_{12}	0.243	0.243	0.244	0.262	0.242
G_{12} (GPa)	2.112	2.112	2.113	2.112	3.10
G_{23} (GPa)	2.056	2.060	2.049	2.260	1.36
ν_{23}	0.451	0.450	0.451	0.347	0.391

input data for the next CCA model where (C + H) sub-block is embedded in the lignin (L). The result of the homogenisation is named (C + H) + L in Table 15.3.

An alternative is to homogenise first the (H + L) sub-block and in the second step to consider a cellulose (L) cylinder embedded in an (H + L) cylinder. The result is denoted C + (H + L) in Table 15.3. This exercise was performed to evaluate the significance of geometrical details other than volume fractions. The results are very close, which proves that the sequence of the homogenisation is not important. This result indicates that the volume fractions are the main parameters and, hence, the 'rule of mixtures' (ROM) type of models, which ignore constituent geometry and account only for volume fractions, may have sufficient accuracy.

The simplest model for axial modulus is the rule of mixtures which follows from the iso-strain assumption in the axial direction:

$$E_1 = \sum_{k=1}^{3} V_k E_1^k = V_C E_1^C + V_H E_1^H + V_L E_1^L \qquad 15.40$$

In this model all transverse stresses caused by different Poisson contractions are neglected.

From the iso-strain model and free transverse contraction follows the rule of mixtures for the axial Poisson ratio:

$$\nu_{12} = \sum_{k=1}^{3} V_k \nu_{12}^k = V_C \nu_{12}^C + V_H \nu_{12}^H + V_L \nu_{12}^L \qquad 15.41$$

In this model the transverse contraction of each phase is considered as free, which for a concentric cylinder assembly is not entirely true.

Fairly accurate predictions for the transverse modulus E_2 and for the axial shear modulus G_{12} of composites may be obtained using Halpin–Tsai expressions. These expressions were obtained for two-phase composites as the best fit to numerical results for square and rectangular repeating elements. Therefore they cannot be applied directly to Model B and need to be adjusted for cylindrical RVE and for three-component systems. For circular fibres in square repeating elements the suggested parameter ξ values are 2 for transverse modulus and 1 for shear modulus. To find this parameter in Halpin–Tsai equations as the best fit to numerical results following from the CCA model, we applied it to results for glass fibre/epoxy composites ($V_f = 0.5$). The best fit to transverse modulus data was obtained using $\xi = 1.155$ and for shear modulus using $\xi = 1.0$. These values are used in calculations for cell wall layers in this section.

A two-step procedure is used for the three-phase material. First the Halpin–Tsai equations are applied for the cellulose/hemicellulose sub-block to calculate the averaged properties:

$$E_2^{\mathrm{C+H}} = E_2^{\mathrm{H}} \frac{1 + \xi \eta_{\mathrm{C+H}} V_{\mathrm{C/(C+H)}}}{1 - \eta_{\mathrm{C+H}} V_{\mathrm{C/(C+H)}}} \qquad \eta_{\mathrm{C+H}} = \frac{\dfrac{E_2^{\mathrm{C}}}{E_2^{\mathrm{H}}} - 1}{\dfrac{E_2^{\mathrm{C}}}{E_2^{\mathrm{H}}} + \xi} \qquad \xi = 1.155 \tag{15.42}$$

$$G_{12}^{\mathrm{C+H}} = G_{12}^{\mathrm{H}} \frac{1 + \xi \eta_{\mathrm{C+H}} V_{\mathrm{C/(C+H)}}}{1 - \eta_{\mathrm{C+H}} V_{\mathrm{C/(C+H)}}} \qquad \eta_{\mathrm{C+H}} = \frac{\dfrac{G_{12}^{\mathrm{C}}}{G_{12}^{\mathrm{H}}} - 1}{\dfrac{G_{12}^{\mathrm{C}}}{G_{12}^{\mathrm{H}}} + \xi} \qquad \xi = 1.0 \tag{15.43}$$

In (15.42) and (15.43) $V_{\mathrm{C/(C+H)}}$ is the volume fraction of the cellulose in the (C + H) sub-block.

In the next step the (C + H) sub-block is embedded in lignin and the average properties of the (C + H + L) composite are calculated:

$$E_2 = E_2^{\mathrm{L}} \frac{1 + \xi \eta V_{\mathrm{(C+H)}}}{1 - \eta V_{\mathrm{(C+H)}}} \qquad \eta = \frac{\dfrac{E_2^{\mathrm{C+H}}}{E_2^{\mathrm{L}}} - 1}{\dfrac{E_2^{\mathrm{C+H}}}{E_2^{\mathrm{L}}} + \xi} \qquad \xi = 1.155 \tag{15.44}$$

$$G_{12} = G_{12}^{\mathrm{L}} \frac{1 + \xi \eta V_{\mathrm{(C+H)}}}{1 - \eta V_{\mathrm{(C+H)}}} \qquad \eta = \frac{\dfrac{G_{12}^{\mathrm{C+H}}}{G_{12}^{\mathrm{L}}} - 1}{\dfrac{G_{12}^{\mathrm{C+H}}}{G_{12}^{\mathrm{L}}} + \xi} \qquad \xi = 1.0 \tag{15.45}$$

In (15.44) and (15.45) $V_{\mathrm{(C+H)}}$ is the volume fraction of the cellulose/hemicellulose sub-block in the C + H + L composite.

The transverse Poisson ratio of the composite is calculated using the simple empirical expression suggested by Philippidis and Theocaris:[11]

$$\nu_{23} = \nu_{12} \frac{1 - \nu_{21}}{1 - \nu_{12}} \qquad \nu_{21} = \nu_{12} \frac{E_2}{E_1} \tag{15.46}$$

Table 15.4 Elastic properties of S1 and primary (considered as UD) fibre wall layers in material symmetry axes

Property	Model B	ROM models	Model A FEM
E_1 (GPa)	31.616	31.561	31.7
E_2 (GPa)	3.926	3.814	4.19
ν_{12}	0.298	0.308	0.299
G_{12} (GPa)	1.394	1.394	1.84
G_{23} (GPa)	1.343	1.335	0.959
ν_{23}	0.462	0.429	0.435

Finally the shear modulus in the plane of transverse isotropy may be calculated as:

$$G_{23} = \frac{E_2}{2(1 + \nu_{23})} \qquad 15.47$$

The elastic properties of the cell wall layers, calculated according to (15.40)–(15.47) are presented in Tables 15.3 and 15.4 in the 'ROM models' columns. The accuracy of axial modulus, transverse modulus and axial (in-plane) shear modulus as compared with the concentric cylinder assembly model solution is excellent. The deviations are less than 0.2%, 3% and 0.01%, respectively. The rule of mixtures for the axial (in-plane) Poisson ratio leads to less than 8% overestimation (the error is largest in the S2 layer case). The transverse shear modulus is determined with less than 10% error for S2 layer and 1% error for S1 layer. The low accuracy of the out-of-plane Poisson ratio is related to the accuracy of the used empirical expression (15.46).

Keeping in mind the large uncertainty in input data, the accuracy obtained using the above ROM models is sufficient and they may be successfully used instead of the concentric cylinder assembly or finite element modelling (FEM). FEM results using Model A in Fig. 15.7 are also presented in Tables 15.3 and 15.4. As expected the axial modulus and the axial Poisson ratio are in excellent agreement with Model B. Transverse and shear moduli according to Model A and Model B are rather different. The difference in transverse modulus reaches 10% for the S2 layer (much smaller for the S1 layer). The shear modulus values differ by almost 50%. These results are not surprising and are coherent with differences in numerical results for fibre composites using hexagonal and square unit cells. Comparing the G_{23} and E_2 values, it is obvious that the square unit cell does not represent transverse isotropic material. The demonstrated difference between the results of the CCA model and FEM and the uncertainty in the choice of the best model configuration is one more argument for the suitability of the presented ROM models.

In the following section, calculating the average elastic properties of the fibre wall, we will briefly address the sensitivity of the fibre wall properties with respect to the variation of the properties presented in Tables 15.3 and 15.4.

15.3.3 Elastic properties of the fibre wall

As described above, the wall of the fibre is a multidirectional laminate with lay-up [P, S1, S2, S3]. The relative layer thicknesses which are not shown in this laminate code can be found in Table 15.5. The layer thickness ratios are rather different in earlywood and in latewood fibres; in particular the S2 layer is much thicker in the latewood. The fibril orientation angle in the layer with respect to the fibre axis is also given in Table 15.5. The middle layer is not included in the laminate as it is assumed that it has been removed during processing. It can be included as an additional layer if necessary.

The in-plane elastic constants of the fibre wall may be calculated using CLT. The calculation steps to obtain the stiffness matrix of the fibre wall (laminate) are briefly explained below.

1. Using the elastic constants obtained in Section 15.3.2, calculate the stiffness matrix of the *k*th fibre wall layer in its symmetry axis:

$$Q_{11}^k = \frac{E_1^k}{1-\nu_{12}^k\nu_{21}^k} \quad Q_{22}^k = \frac{E_2^k}{1-\nu_{12}^k\nu_{21}^k} \quad Q_{12}^k = \frac{\nu_{12}^k E_2^k}{1-\nu_{12}^k\nu_{21}^k} \quad Q_{66}^k = G_{12}^k \tag{15.48}$$

In (15.48) $\nu_{21}^k = \nu_{12}^k\,(E_2^k/E_1^k)$ is the minor Poisson ratio of the layer.

2. Recalculate the stiffness matrix Q_{ij}^k of the *k*th layer to the coordinate system of the fibre (the obtained stiffness matrix is denoted $\bar{Q}_{ij}^k$):

$$\bar{Q}_{11}^k = Q_{11}^k m^4 + Q_{22}^k n^4 + Q_{12}^k 2m^2n^2 + Q_{66}^k 4m^2n^2 \tag{15.49}$$

$$\bar{Q}_{22}^k = Q_{11}^k n^4 + Q_{22}^k m^4 + Q_{12}^k 2m^2n^2 + Q_{66}^k 4m^2n^2 \tag{15.50}$$

$$\bar{Q}_{12}^k = m^2n^2\left(Q_{11}^k + Q_{22}^k - 4Q_{66}^k\right) + Q_{12}^k(m^4 + n^4) \tag{15.51}$$

$$\bar{Q}_{66}^k = m^2n^2\left(Q_{11}^k - 2Q_{12}^k + Q_{22}^k\right) + Q_{66}^k(m^2 - n^2)^2 \tag{15.52}$$

$$\bar{Q}_{16}^k = m^3n\left(Q_{11}^k - Q_{12}^k\right) + n^3m\left(Q_{12}^k - Q_{22}^k\right) - Q_{66}^k 2mn\left(m^2 - n^2\right) \tag{15.53}$$

$$\bar{Q}_{26}^k = mn^3\left(Q_{11}^k - Q_{12}^k\right) + nm^3\left(Q_{12}^k - Q_{22}^k\right) + Q_{66}^k 2mn\left(m^2 - n^2\right) \tag{15.54}$$

Table 15.5 Geometrical parameters of layers in the wood fibre wall[8,12,13]

Cell wall layer	Earlywood		Latewood	
	Thickness h_k (μm)	Microfibril angle θ_k	Thickness h_k (μm)	Microfibril angle θ_k
P	0.1	Random	0.1	Random
S1	0.2	±(50–70)	0.3	±(50–70)
S2	1.4	10–40	4.0	0–30
S3	0.03	60–90	0.04	60–90

In (15.49) to (15.54), $m = \cos\theta_k$, $n = \sin\theta_k$.

The P-layer has random fibril orientation and therefore it is an isotropic material. The stiffness matrix of this layer may be calculated using properties of the earlier calculated UD fibril material (see Table 15.4):

$$\bar{Q}_{11}^{P} = \bar{Q}_{22}^{P} = \tfrac{1}{8}\left(3Q_{11}^{UD} + 3Q_{22}^{UD} + 2Q_{12}^{UD} + 4Q_{66}^{UD}\right) \tag{15.55}$$

$$\bar{Q}_{12}^{P} = \tfrac{1}{8}\left(Q_{11}^{UD} + Q_{22}^{UD} + 6Q_{12}^{UD} - 4Q_{66}^{UD}\right) \tag{15.56}$$

$$\bar{Q}_{66}^{P} = \tfrac{1}{8}\left(Q_{11}^{UD} + Q_{22}^{UD} - 2Q_{12}^{UD} + 4Q_{66}^{UD}\right) \tag{15.57}$$

$$\bar{Q}_{16}^{P} = \bar{Q}_{26}^{P} = 0 \tag{15.58}$$

3. Calculate the extensional stiffness matrix A_{ij} of the fibre wall (laminate)

$$A_{ij} = \sum_k \bar{Q}_{ij}^{k} h_k \quad i,j = 1,2,6 \tag{15.59}$$

For the fibre wall [P, S1, S2, S3]

$$A_{ij} = \bar{Q}_{ij}^{P} h_P + \bar{Q}_{ij}^{S1} h_{S1} + \bar{Q}_{ij}^{S2} h_{S2} + \bar{Q}_{ij}^{S3} h_{S3} \quad i,j = 1,2,6 \tag{15.60}$$

For example, $A_{11} = \bar{Q}_{11}^{P} h_P + \bar{Q}_{11}^{S1} h_{S1} + \bar{Q}_{11}^{S2} h_{S2} + \bar{Q}_{11}^{S3} h_{S3}$.

4. Determine in-plane elastic constants of the fibre wall. Since the laminate is asymmetric, the coupling stiffness matrix is non-zero which generally speaking means that axial load would lead to curvatures. However, owing to the cylindrical geometry of the fibre local curvature changes are not possible. Hence the stress–strain relationship for the fibre wall is:

$$\begin{Bmatrix} \sigma_z \\ \sigma_\phi \\ \sigma_{z\phi} \end{Bmatrix} = \frac{1}{h}\begin{bmatrix} A_{11} & A_{12} & A_{16} \\ A_{12} & A_{22} & A_{26} \\ A_{16} & A_{26} & A_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_z \\ \epsilon_\phi \\ \epsilon_{z\phi} \end{Bmatrix} \tag{15.61}$$

In (15.61) h is the thickness of the fibre wall:

$$h = h_P + h_{S1} + h_{S2} + h_{S3} \tag{15.62}$$

From (8.61) it follows that the compliance matrix $[S]$ of the fibre wall is:

$$[S] = h[A]^{-1} \tag{15.63}$$

and the elastic constants of the fibre wall may be calculated using relationships:

$$E_z = \frac{1}{S_{11}} \quad E_\phi = \frac{1}{S_{22}} \quad G_{z\phi} = \frac{1}{S_{66}} \quad \nu_{z\phi} = -\frac{S_{12}}{S_{11}} \tag{15.64}$$

The normal stress–shear coupling constants can also be obtained but they are not analysed in this work.

The obtained expressions are used to analyse the effect of fibril orientation on elastic properties of wood fibres. Since the S1 and S3 layers are rather thin

Table 15.6 In-plane elastic properties of wood fibre wall, S2 angle 10°

Property	Earlywood		Latewood	
	Model B	ROM models	Model B	ROM models
E_z (GPa)	36.49	36.43	37.27	37.23
E_ϕ (GPa)	7.96	8.04	7.05	7.13
$\nu_{z\phi}$	0.676	0.680	0.63	0.64
$G_{z\phi}$ (GPa)	2.85	2.84	2.61	2.61

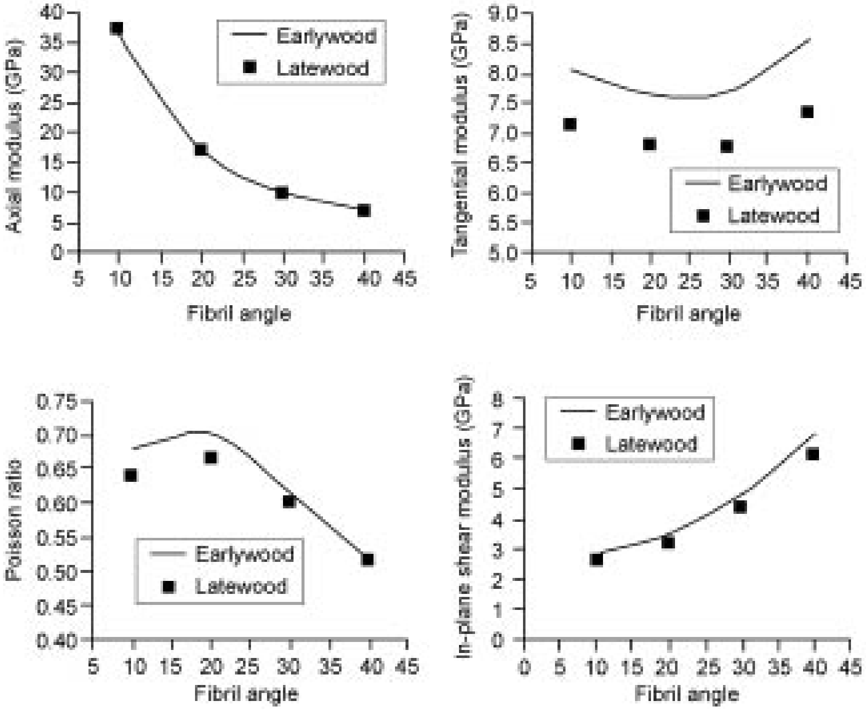
compared with the S2 layer, the fibril angle in the S2 layer is most important. Therefore, in simulations fixed values for fibril angles in S1 and S3 layers (−60° and −75°, respectively) are used, leaving the fibril angle in the S2 layer as the only parameter and considering the earlywood and the latewood separately.

First we will inspect the sensitivity of the calculated fibre wall properties with respect to the model used to determine the single layer properties. Input data from Model B and ROM models given in Tables 15.3 and 15.4 are used to calculate the elastic constants presented in Table 15.6 for earlywood and latewood fibres. Results are presented for $\theta_{S2} = 10°$. They show that using ROM models instead of the CCA model to obtain input data for the laminate theory leads to almost identical values of fibre wall elastic properties.

Therefore all the following results are calculated using input data for layer properties obtained by ROM models. The dependence of the fibre wall's elastic properties on the fibril orientation angle in the S2 layer is shown in Fig. 15.8. Surprisingly the axial modulus of the earlywood fibre wall is not much smaller than the modulus of the latewood fibre wall. It is because in the considered example the S2 layer in the earlywood is quite thick: significantly thicker than the rest of layers. Owing to the high volume fraction of this layer, the fibre wall modulus is dominated by S2 properties and any further increase of S2 thickness in the latewood does not lead to significant changes. The difference would be much larger for a thin S2 layer in the earlywood.

The tangential modulus and shear modulus of the latewood fibre wall are low. This trend was also observed by Persson[10] performing numerical analysis using FEM. The tangential modulus is about 10–20% higher than the transverse modulus of the S2 layer and it does not change significantly with the fibril angle change.

The elastic properties presented above were calculated from the laminate compliance matrix, which means that they were determined according to definitions: through strain components as response to applied uniaxial stress states. The fibre wall's elastic properties measured in these tests and their apparent properties when embedded in composites may differ. For example, defining the axial modulus of the fibre, stress is applied in the fibre direction. Owing to the helical fibril orientation (resulting in non-zero terms A_{16} and A_{26}),



15.8 In-plane elastic properties of the wood fibre wall versus the microfibril angle in the S2 layer.

shear strain $\gamma_{z\phi}$ occurs in the fibre and it will rotate. If in the test the fibre ends are clamped, the rotation is partially or completely prevented and in the limit $\gamma_{z\phi} = 0$. Because of this constraint the apparent modulus determined as the axial stress and strain ratio is considerably higher than the true value. It is also similar in fibre composites where the surrounding resin and other fibres restrict the rotation. Hence, in this chapter where the rotational effects are not explicitly included in the composite scale model, the apparent modulus corresponding to 'non-rotation' conditions is even more relevant than the true modulus.

The apparent modulus (axial stress versus axial strain ratio) in the limiting case $\gamma_{z\phi} = 0$ can be calculated using CLT. The value of the apparent elastic modulus may be obtained from the A-matrix simply assuming $A_{16} = 0$ and $A_{26} = 0$. The apparent elastic properties of the earlywood and latewood fibres under condition $\gamma_{z\phi} = 0$ are presented in Table 15.7. They may be compared with the true elastic constants presented in Table 15.6.

The apparent elastic modulus E_z^* is almost by 50% higher than the real modulus: if the fibre rotation is not allowed it becomes much stiffer. This effect using FE analysis was studied by Neagu *et al.*[4]

The dependence of the apparent elastic fibre wall's properties on the fibril

Table 15.7 Apparent in-plane elastic properties of fibre wall, S2 angle 10°

Property	Earlywood		Latewood	
	Model B	ROM models	Model B	ROM models
E_z^* (GPa)	55.51	55.40	60.86	60.73
E_ϕ^* (GPa)	8.85	8.93	7.46	7.56
$\nu_{z\phi}^*$	0.426	0.434	0.479	0.488
$G_{z\phi}^*$ (GPa)	4.46	4.45	4.29	4.28

orientation angle in S2 layer is shown in Table 15.8. The results presented there should be analysed in comparison with the true elastic properties presented in Fig. 15.8. The apparent axial modulus of the cell wall is always higher. The apparent tangential modulus is quite close to the real modulus, the apparent Poisson ratio is significantly smaller and the apparent in-plane shear modulus is much higher.

The out-of-plane elastic properties of one fibre wall layer are very uncertain. Depending on the assumptions made, the layer material may be transverse isotropic or generally orthotropic. Models for out-of-plane properties of a random layer (P layer) are not available. Hence, at the current stage, when experimental data of these properties are not available, the development of sophisticated models for out-of plane fibre wall properties is pointless. Simple expressions based on constant stress or constant strain assumptions are sufficient.

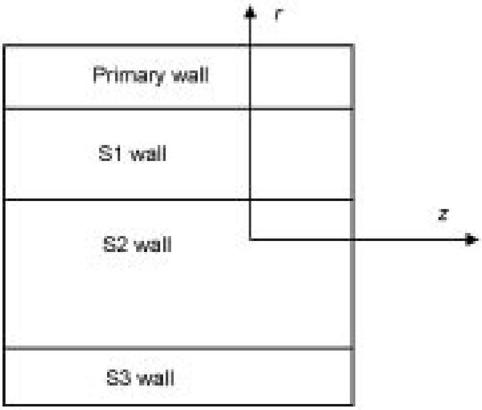
The calculation expressions can be obtained considering the 1,3-section of the laminate shown in Fig. 15.9. The radial modulus of this laminated structure is defined under uniaxial loading in the r-direction. The geometrical configuration corresponds to assumptions used in the constant stress model leading to:

$$\frac{1}{E_r} = \sum_k \frac{V_k}{E_r^k} \qquad 15.65$$

In (15.65) V_k is the volume fraction of the k layer defined as:

Table 15.8 Effect of microfibril angle in S2 on apparent in-plane elastic properties of wood fibre wall

Property	Earlywood				Latewood			
	10°	20°	30°	40°	10°	20°	30°	40°
E_z^* (GPa)	55.40	41.93	24.00	11.68	60.73	44.87	24.19	11.17
E_ϕ^* (GPa)	8.93	8.54	8.13	8.53	7.56	7.22	6.91	7.45
$\nu_{z\phi}^*$	0.434	0.813	1.011	0.853	0.488	0.972	1.173	0.935
$G_{z\phi}^*$ (GPa)	4.45	8.47	13.04	16.02	4.28	8.76	13.84	17.16



15.9 Cross-section of the fibre wall.

$$V_k = \frac{h_k}{h} \tag{15.66}$$

The constant stress model can be used also to calculate the shear moduli G_{zr} and $G_{r\phi}$:

$$\frac{1}{G_{zr}} = \sum_k \frac{V_k}{G^k_{zr}} \qquad \frac{1}{G_{r\phi}} = \sum_k \frac{V_k}{G^k_{r\phi}} \tag{15.67}$$

The out-of-plane Poisson ratios can be estimated using constant strain assumption in z-direction and for each layer assuming free contraction in the r-direction:

$$\nu_{zr} = \sum_k V_k \nu^k_{zr} \qquad \nu_{\phi r} = \sum_k V_k \nu^k_{\phi r} \tag{15.68}$$

The out-of-plane elastic properties of wood fibre wall with in-plane properties presented in Table 15.6 as 'ROM models' are given in Table 15.9. The elastic properties of layers in the global coordinate system E^k_r, G^k_{zr}, $G^k_{r\phi}$, ν^k_{zr}, $\nu^k_{\phi r}$ were calculated using 3D stiffness transformation expressions.[14] The out-of-plane

Table 15.9 Out-of-plane elastic properties of wood fibre wall, S2 angle 10°

Property	Earlywood True/apparent	Latewood True/apparent
E_r (GPa)	5.52/5.61	5.78/5.85
G_{zr} (GPa)	1.93/1.93	2.02/2.02
$G_{\phi r}$ (GPa)	2.03/2.03	2.13/2.13
ν_{zr}	0.224/0.186	0.323/0.168
$\nu_{\phi r}$	0.319/0.291	0.323/0.309

Table 15.10 Effect of the microfibril orientation in S2 on the out-of-plane fibre wall properties

Property	Earlywood				Latewood			
	10°	20°	30°	40°	10°	20°	30°	40°
E_r (GPa)	5.61	5.67	5.81	5.97	5.85	5.93	6.09	6.29
G_{zr} (GPa)	1.93	1.94	1.95	1.97	2.02	2.03	2.04	2.06
$G_{\phi r}$ (GPa)	2.03	2.02	2.01	1.99	2.13	2.12	2.11	2.09
ν_{zr}	0.186	0.0011	−0.048	0.056	0.168	−0.039	−0.093	0.023
$\nu_{\phi r}$	0.291	0.263	0.2119	0.128	0.309	0.279	0.221	0.128

properties of the in-plane isotropic P layer were assumed equal to the properties of the corresponding aligned (UD) material.

Apparent elastic constants corresponding to the case when the fibre rotation is prohibited are also presented. As expected, the out-of-plane elastic moduli of the fibre wall are in between the range of corresponding layer properties. The apparent out-of-plane properties in the 'no-rotation' case are rather close to the true properties except Poisson ratios. The sensitivity of the natural fibre composite properties with respect to out-of-plane constants will be addressed in the next session. The apparent out-of-plane elastic properties' dependence on microfibril orientation angle in the S2 layer is given in Table 15.10. The dependence, except for Poisson ratios, is weak.

In this section we have calculated the fibre wall elastic constants. The fibre properties may be calculated using these constants and the fibre geometry. For example the fibre axial modulus may be evaluated using the volume fraction of the fibre wall in the fibre (including lumen):

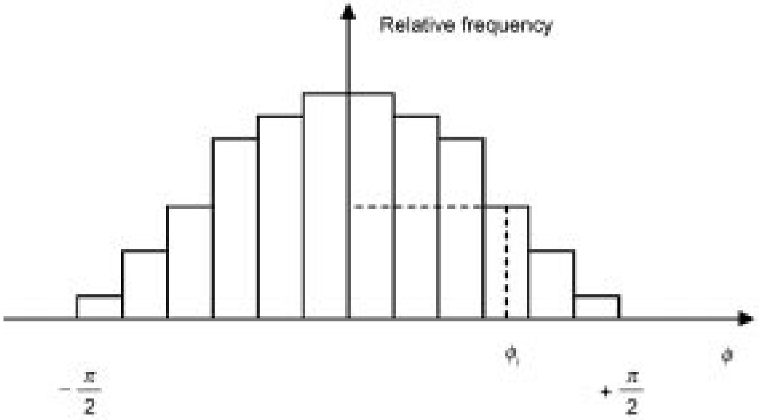
$$E_z^{\text{fibre}} = E_z \frac{r_1^2}{r_N^2} \qquad 15.69$$

In (15.69) r_1 is the internal and r_N is the external radius of the fibre wall; see Fig. 15.2.

15.4 Elastic properties of natural-fibre composites

15.4.1 Composites with in-plane fibre orientation distribution

Fibres in natural-fibre composites are usually not aligned. In the following analysis we assume that all fibres have an in-plane orientation: the fibre axis is parallel to the mid-plane of the composite plate. This assumption is justified if the fibre length is larger than the thickness of the composite plate. A certain in-plane orientation of fibres may be characterised by its relative frequency. The whole fibre orientation angle region $\phi \in [-\pi/2; +\pi/2]$ may be divided in sub-regions of size $\Delta\phi$ and the relative number of fibres with an orientation in the



15.10 An example of symmetric distribution of the relative frequency of fibre orientation distribution.

given region may be counted. Details regarding the experimental techniques used may be found in Neagu *et al.*[15] The result of the counting may be represented as the relative orientation frequency distribution function (also called the fibre orientation distribution function). An example of a distribution symmetric with respect to the 0-direction is shown in Fig. 15.10. Symmetric distributions result in orthotropic macro-properties of the composite.

According to definition the orientation distribution function $f(\phi_i)$ multiplied by $\Delta\phi$ is the probability that the fibre orientation angle is between $\phi_i - (\Delta\phi/2)$ and $\phi_i + (\Delta\phi/2)$. Obviously:

$$\sum_i f(\phi_i)\Delta\phi = 1 \qquad 15.70$$

In a case of infinitesimally small sub-regions (15.70) may be written as:

$$\int_{-\pi/2}^{+\pi/2} f(\phi)\,\mathrm{d}\phi = 1 \qquad 15.71$$

The experimentally obtained $f(\phi_i)$ values can be fitted by Fourier series expansion, which in a symmetric case can be written as:

$$f(\phi) = \frac{1}{\pi}\sum_{n=0}^{\infty} a_n \cos 2n\theta \qquad 15.72$$

Usually two to four terms in (15.72) give sufficient accuracy. To satisfy (15.72) $a_0 = 1$ and the rest of coefficients is determined in a fitting procedure.

If the fibre orientation in the composite is in-plane random, all orientations are represented equally and:

$$f(\phi) = \frac{1}{\pi} \qquad 15.73$$

The effective stiffness matrix of a composite with a given in-plane fibre orientation distribution function $f(\phi)$ may be calculated using the 'laminate analogy' approach.[16,17] In this approach the composite is replaced by an effective layered structure which is obtained virtually separating all fibres with a given orientation $\phi \in [\phi_i - \mathrm{d}\phi/2, \phi_i + \mathrm{d}\phi/2]$ from the rest of the composite and building a UD layer with this fibre orientation. The fibre volume fraction in this layer is the same as the average volume fraction in the composite. Elastic properties modelling of these aligned (UD) composites is performed in Section 15.4.2. The relative thickness of the virtual UD layer in the laminate is equal to the probability of this orientation $f(\phi_i)\mathrm{d}\phi$. In this way an effective laminate is designed with an infinite number of layers with different orientations.

The stiffness matrix of the composite using this model is equal to the extensional stiffness matrix of the effective laminate and can be written as:

$$Q_{ij}^{\mathrm{comp}} = \sum_{k=1}^{\infty} \frac{t_k}{h} \bar{Q}_{ij}^{k}(\phi_k) = \sum_{k=1}^{\infty} \bar{Q}_{ij}^{k}(\phi_k) f(\phi_k)\mathrm{d}\phi \qquad 15.74$$

In (15.74) summation may be replaced by integration, leading to the following expression for composite stiffness matrix elements:

$$Q_{ij}^{\mathrm{comp}} = \int_{-\pi/2}^{+\pi/2} \bar{Q}_{ij}(\phi) f(\phi)\mathrm{d}\phi \qquad 15.75$$

The stiffness matrix $\bar{Q}_{ij}$ of a UD layer with orientation ϕ may be obtained from elastic properties of the layer in its material symmetry axes using (15.49)–(15.54). The orientation angle denoted by θ_k in (15.49)–(15.54) has to be replaced by ϕ and Q_{ij}^{k} is the stiffness matrix Q_{ij}^{a} of the aligned composite analysed in detail in Section 15.4.2.

The in-plane engineering constants of the composite may be calculated in two steps. First the composite compliance matrix is calculated by inversion of the stiffness matrix as:

$$[S^{\mathrm{comp}}] = [Q^{\mathrm{comp}}]^{-1} \qquad 15.76$$

Then the composite elastic constants are found as:

$$E_1^{\mathrm{comp}} = \frac{1}{S_{11}^{\mathrm{comp}}} \quad E_s^{\mathrm{comp}} = \frac{1}{S_{22}^{\mathrm{comp}}} \quad \nu_{12}^{\mathrm{comp}} = -\frac{S_{12}^{\mathrm{comp}}}{S_{11}^{\mathrm{comp}}} \quad G_{12}^{\mathrm{comp}} = \frac{1}{S_{66}^{\mathrm{comp}}} \qquad 15.77$$

15.4.2 Aligned fibre composites

The first step in analysing composites containing fibres oriented in different directions is to consider an artificial aligned composite with the same fibre content. Since the fibres have in-plane alignment and the fibre length to diameter ratio is large, the concentric cylinder assembly model developed in Section 15.2 can be used to calculate the elastic properties of this composite.

The cell wall properties, to be used in the cylinder assembly model, require special discussion. The fibre wall due to helical structure of the fibre wall layers is not balanced and therefore a coupling between tension and torsion exists (for example, free fibre rotation occurs in uniaxial tension). The CCA model presented in Section 15.2 is valid for orthotropic phases in the cylindrical coordinates with no coupling terms entering expressions.

In Section 15.3 the fibre wall elastic constants were calculated for two cases: (a) allowing free fibre rotation (this case defines the 'true' properties) and (b) not allowing the rotation, which leads to usually higher 'apparent' properties. In the composite the fibre rotation is rather limited. The fibre is embedded in the resin, which is supported by averaged transverse isotropic composite and the rotation at the assembly boundary is zero. In order to obtain an adequate fibre representation in this 'non-rotational' case the 'apparent 'properties of the fibre wall corresponding to this loading case are more appropriate than the 'true' properties. The apparent elastic fibre wall constants are given in Tables 15.7 to 15.10. Certainly, in future the accuracy of the use of 'apparent' properties in the 'non-rotational' model have to be addressed by solving the problem in an accurate formulation, where the extent of rotation of the fibre in the composite is part of the solution.

The resin properties used in numerical simulations, see Table 15.11, are as for typical epoxy resins. The out of-plane properties of the fibre wall were calculated using rather rough assumptions: (a) on the microfibril level (calculating fibre wall layer properties) the use of the concentric cylinder assembly model implies that the layers are transverse isotropic; and (b) calculating the fibre wall properties we used thin laminate theory and evaluated the out-of-plane properties of the laminate (fibre wall) using simple engineering formulas. Therefore we start with performing parametric analysis, varying the out-of-plane properties of the fibre wall to evaluate the possible error in composite properties introduced by these simplifications. Fibre wall properties from Table 15.9 were considered as 'nominal' values. In the following calculation, one property at a time was varied to see the effect on composite elastic properties. As shown in Table 15.12 in the earlywood case with a filled lumen, changing the radial modulus from 5.61 to 5 GPa, the composite changes were negligible; on changing the Poisson ratio ν_{zr} from 0.186 to 0.1, only the Poisson ratio ν_{12} changed by 3%. Change of

Table 15.11 Resin elastic properties used in simulations

E_m (GPa)	ν_m	G_m (GPa)
3.0	0.35	1.111

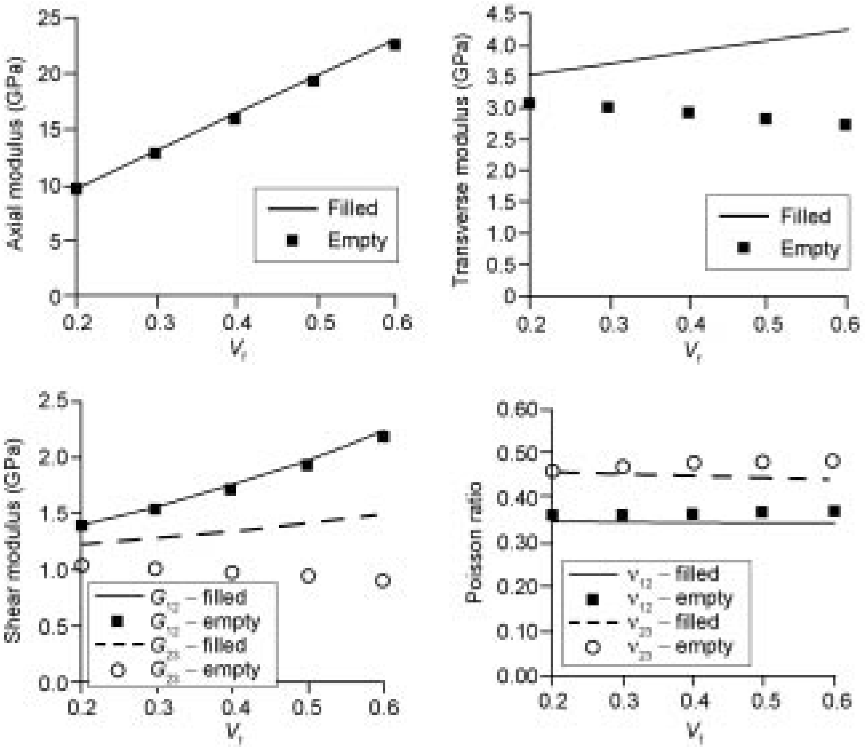
Table 15.12 Sensitivity of aligned composite properties with respect to out-of-plane properties of the fibre wall. Earlywood fibre with filled lumen $V_{\text{fiber}} = 0.4$, $V_{\text{lumen}} = 0.36$

Property	Nominal properties	$E_r = 5\,\text{GPa}$	$\nu_{zr} = 0.1$	$\nu_{\phi r} = 0.2$	$G_{zr} = 1.7\,\text{GPa}$	$G_{r\phi} = 1.8\,\text{GPa}$
E_1 (GPa)	16.44	16.44	16.44	16.44	16.44	16.4
E_2 (GPa)	3.90	3.87	3.90	3.89	3.90	3.85
G_{12} (GPa)	1.76	1.76	1.76	1.76	1.77	1.76
ν_{12}	0.345	0.345	0.334	0.344	0.345	0.345
G_{23} (GPa)	1.34	1.34	1.34	1.35	1.34	1.32
ν_{23}	0.454	0.448	0.455	0.443	0.454	0.460

other properties resulted in less than 2% changes in composite properties. The numerical values are different if the lumen is empty but the sensitivity to the fibre wall out-of-plane properties is as low as in the filled lumen case. These results and similar results for the latewood fibre reinforced composite lead to the conclusion that the accuracy of the models used to determine the fibre wall out-of-plane properties is sufficient. The calculated differences are smaller than the accuracy of the available experimental techniques and they are much smaller than the variation of material properties owing to the statistical nature of the material.

The dependence of the earlywood fibre composite elastic properties on the fibre volume fraction V_f are shown in Fig. 15.11. Calculations are performed using nominal fibre wall properties. The elastic properties of composites with empty lumen and composites with lumen filled with resin are different. For a composite axial modulus according to Fig. 15.11 this difference is very small, because E_1 is a property dominated by the stiff fibre wall and the slightly larger total amount of resin when the lumen is filled does not much alter the axial modulus.

The transverse modulus of the composite E_2 strongly depends on the resin properties and usually modestly increases with increasing content of fibres (assuming their transverse modulus is larger than the resin modulus). This trend is confirmed in Fig. 15.11. If the lumen is empty the composite transverse modulus decreases with the increase in fibre content: increasing fibre content also increases the volume fraction of the empty domain, $V_{\text{empty}} = V_f V_{\text{lumen}}$ which does not contribute to the composite modulus. Generally speaking, we have two competitive mechanisms with increasing fibre content: (a) the contribution of the fibre wall increases or (b) the volume with zero contribution (all lumens) increases. The outcome and, hence, the resultant trend depends on the transverse fibre modulus and resin modulus ratio and on the volume fraction of the lumen. In the empty lumen case in Fig. 15.11 the composite transverse modulus is lower than the resin modulus.

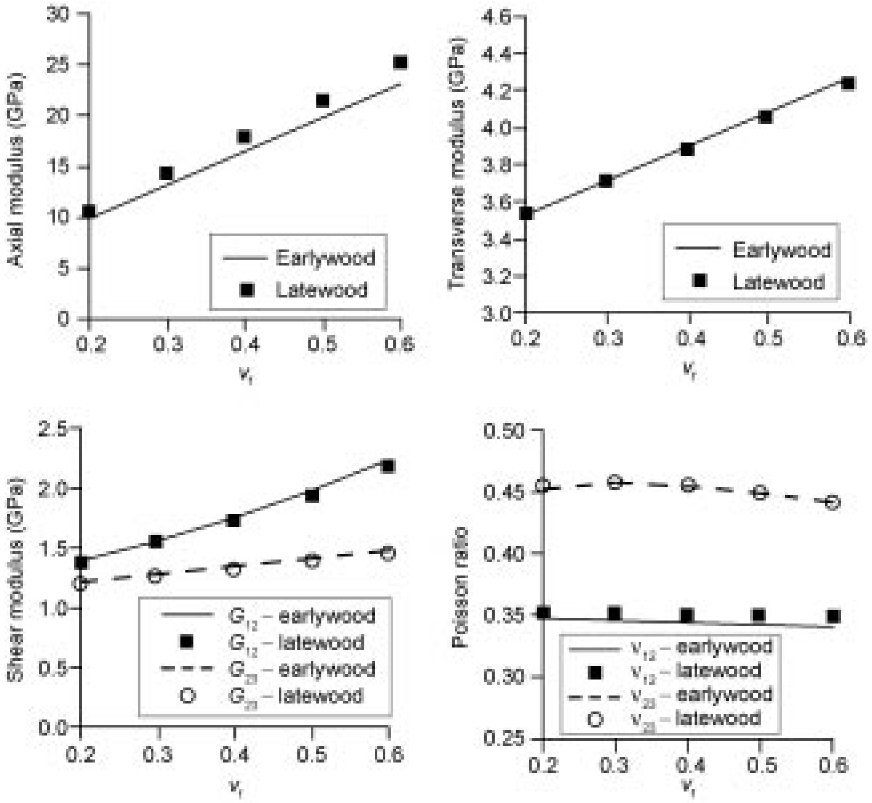


15.11 Elastic properties of aligned earlywood composite. Fibres with $V_{\text{lumen}} = 0.36$. Fibril orientation angle in S2 is $\theta = 10°$.

The in-plane shear modulus of the composite is practically the same for filled and empty lumen composites and increases with the fibre content. If the lumen is filled, the out-of-plane shear modulus G_{23} is larger than the resin shear modulus and increases with fibre content, whereas in the empty lumen case it is lower than the resin modulus and slightly decreases with increasing fibre content. The reason for that may be the same as for the transverse modulus change.

The Poisson ratio values are slightly lower for composites with filled lumen. The change with increasing fibre content for the constituent properties combination is negligible. The in-plane ratio ν_{12} is in the range usually measured for long fibre composites. Also the out-of-plane Poisson ratio ν_{23} values are as usually assumed for artificial fibre composites (experimental data are seldom available).

In Fig. 15.12 the described trends for the aligned earlywood composite are compared with latewood composite. All trends are the same and the numerical values, except the axial modulus, are fairly similar. As discussed above this is because in this particular case the S2 layer in the earlywood was rather thick and therefore the earlywood and latewood fibre wall properties are similar. For

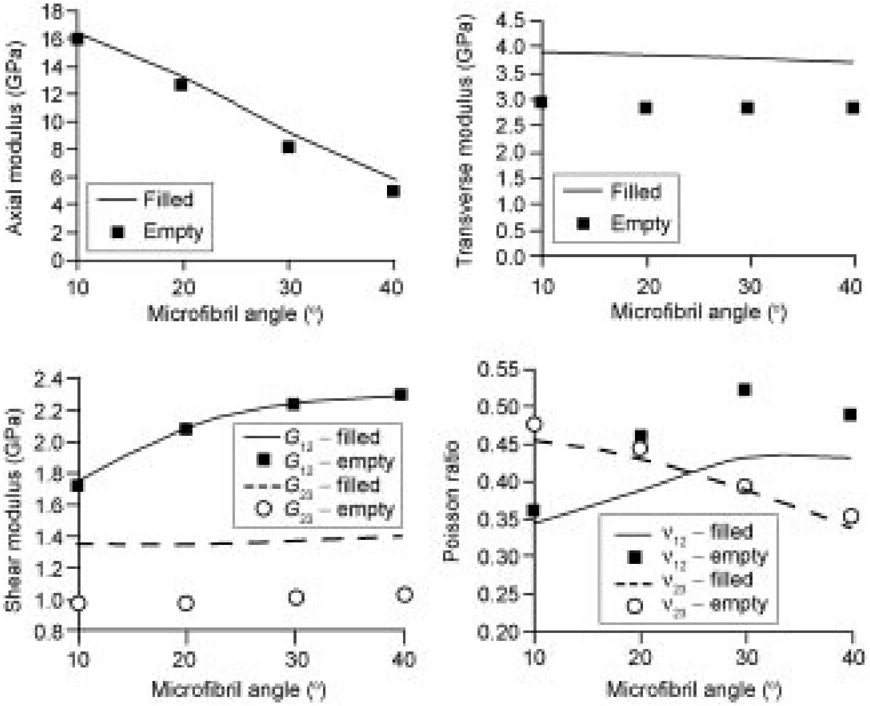


15.12 Elastic properties of aligned earlywood and latewood fibre composites with filled lumen. Fibres with $V_{\text{lumen}} = 0.36$. Fibril orientation angle in S2 is $\theta = 10°$.

earlywood fibres with thinner S2 layer the fibre wall properties may be significantly different.

From results presented in Figs 15.11 and 15.12 we see that, using fibres with 10° microfibril orientation in the S2 layer, the axial modulus of the composite is rather high and it may be increased several times by increasing the fibre content. The remaining elastic moduli are fairly low and they are improved with increasing fibre content only if the lumen is filled with resin.

When analysing the fibre reinforcing efficiency we have to compare the effect of increasing fibre content with the improvement obtained by using fibres with selected orientation of microfibrils in the S2 layer. In Fig. 15.13 the elastic properties – microfibril angle relationships – are shown for an earlywood fibre composite with $V_f = 0.4$. On changing the microfibril angle from 10° to 40° the composite axial modulus is reduced four times. This result demonstrates that choice of fibres with small microfibril orientation angle in S2 is as important for composite axial modulus improvement as an increase of the fibre volume



15.13 Elastic properties of aligned earlywood composite as a function of microfibril angle in S2 layer. Fibres with $V_{\text{lumen}} = 0.36$. Fibre volume fraction $V_f = 0.4$.

fraction. Resin in the lumen does not increase the axial modulus significantly.

The transverse modulus and the out-of-plane shear modulus are almost unaffected by the changing orientation angle. The in-plane shear modulus G_{12} increases with increasing microfibril orientation angle. The numerical value is independent of the lumen filling. The in-plane Poisson ratio of the composite increases to an angle of about 30°.

The calculated engineering constants of the aligned composite may be used to obtain the stiffness matrix Q^a_{ij}, which has to be used to calculate the stiffness of a composite characterised by a given fibre orientation distribution, see (15.75):

$$Q^a_{11} = \frac{E_1}{1-\nu_{12}\nu_{21}} \quad Q^a_{22} = \frac{E_2}{1-\nu_{12}\nu_{21}} \quad Q^a_{12} = \frac{\nu_{12}E_2}{1-\nu_{12}\nu_{21}} \quad Q^a_{66} = G_{12}$$

15.78

15.4.3 Random composites

In composites with random in-plane orientation distribution of fibres the distribution function $f(\phi)$ is constant and is given by (15.73). In this case the integration in (15.75) has been performed analytically,[17] leading to:

$$\begin{aligned} Q_{11}^{\text{comp}} &= Q_{22}^{\text{comp}} = \tfrac{1}{8}\left(3Q_{11}^{a} + 3Q_{22}^{a} + 2Q_{12}^{a} + 4Q_{66}^{a}\right) \\ Q_{12}^{\text{comp}} &= \tfrac{1}{8}\left(Q_{11}^{a} + Q_{22}^{a} + 6Q_{12}^{a} - 4Q_{66}^{a}\right) \\ Q_{66}^{\text{comp}} &= \tfrac{1}{8}\left(Q_{11}^{a} + Q_{22}^{a} - 2Q_{12}^{a} + 4Q_{66}^{a}\right) \end{aligned} \qquad 15.79$$

The properties Q_{ij}^{a} of the corresponding aligned composite are calculated using (15.78).

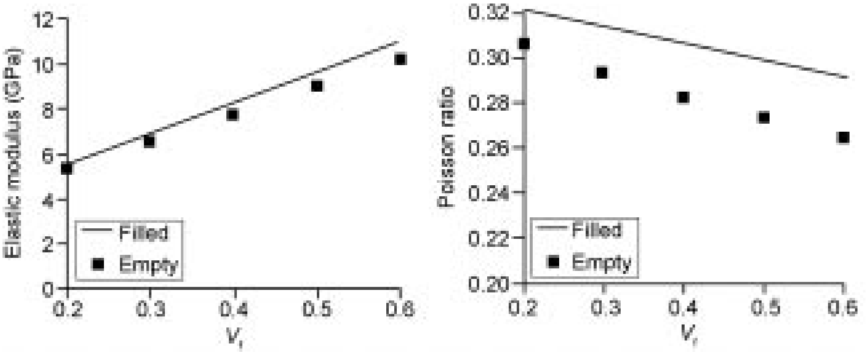
The in-plane elastic constants of the in-plane isotropic material follow from:

$$\nu^{\text{comp}} = \frac{Q_{12}^{\text{comp}}}{Q_{11}^{\text{comp}}} \quad G^{\text{comp}} = Q_{66}^{\text{comp}} \quad E^{\text{comp}} = 2G^{\text{comp}}(1 + \nu^{\text{comp}}) \qquad 15.80$$

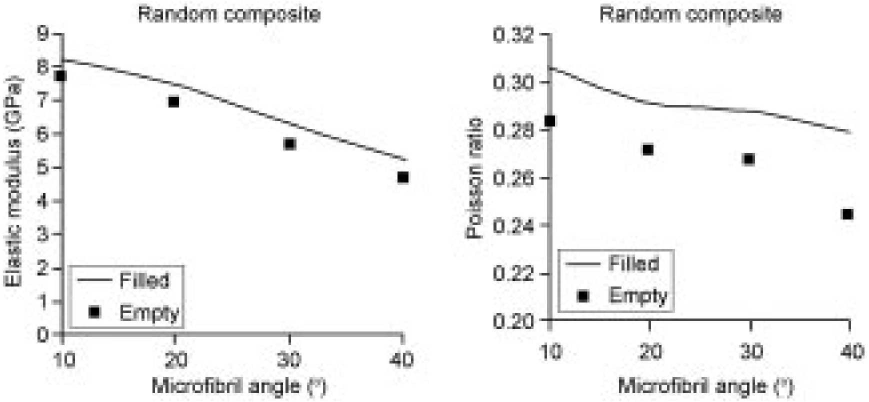
The above expressions and the elastic properties of the corresponding aligned earlywood composite obtained in Section 15.4.2 were used to calculate the dependence of the elastic properties of the random composite on the fibre volume fraction in the composite. Results are shown in Fig. 15.14. Changing V_f from 0.2 to 0.6 increased the elastic modulus about two times. As expected the modulus of the composite with empty lumen ($V_{lumen} = 0.36$) is slightly lower. The Poisson ratio, which is larger in the filled lumen case, decreased with increasing fibre content and the slope of this trend is similar in both cases.

The dependence of composite properties on the microfibril angle in the S2 layer of the fibre was studied varying it between 10° and 40° and keeping the rest of the parameters unchanged. The results of this study for fibre content $V_f = 0.4$ are presented in Fig. 15.15. The microfibril angle in S2 has as strong effect on the random composite modulus as the fibre volume fraction: the modulus changes almost two times. The Poisson ratio of the random composite reduces with increasing microfibril angle.

Different fibres in the composite may have very different microfibril orientation angles. If both the variation range and the relative amount of fibres with a certain microfibril angle are known, the laminate analogy can be used to



15.14 Elastic properties of earlywood fibre composites with random fibre orientation distribution versus fibre volume fraction. The microfibril angle in S2 layer is 10°. The volume content of the lumen in the fibre $V_{\text{lumen}} = 0.36$.



15.15 Elastic properties of earlywood fibre composite with random fibre orientation distribution versus microfibril orientation angle in S2 layer. The fibre volume content $V_f = 0.4$, volume content of the lumen in the fibre $V_{\text{lumen}} = 0.36$.

calculate the average properties of this composite. A virtual laminate is built of in-plane isotropic layers. Each layer is a random composite reinforced with fibres of certain microfibril orientation in S2 layer and the layer properties are calculated as described above. The thickness of the layer in the laminate corresponds to the relative amount of fibres of this microfibril orientation.

15.5 Moisture expansion of natural-fibre composites

Free hygro-expansion of materials is a well-known phenomenon. Moisture absorption leads to an increase in moisture weight content in the material and to dimensional changes (swelling). In the linear elasticity of orthotropic materials, these dimensional changes are assumed to be proportional to the moisture content change. Three different constant coefficients of proportionality, called swelling or moisture expansion coefficients, characterise the relative dimensional changes in three directions of the material symmetry:

$$\beta_k^H = \frac{\epsilon_k^H}{\Delta M} \qquad k = 1, 2, 3 \qquad 15.81$$

Here ϵ_k^H is free swelling strain in the k-direction due to moisture weight content change by ΔM.

Composite materials contain multiple connected phases with different swelling coefficients and different moisture contents. The free (unconstrained) average swelling of the composite is the result of internal force balance and depends on the microstructure of the composite and hygro-elastic properties of constituents. In the context of the multiscale analysis used in this chapter we can say that by performing micromechanics analysis on one scale we obtain average properties which serve as input moisture expansion coefficients for the next scale analysis.

Analysing the swelling of the cellulose/hemicellulose/lignin system we calculate average moisture expansion coefficients of all fibre wall layers. Since each layer is a UD composite containing microfibrils, we can generalise the CCA model described in detail in Section 15.2 to account for moisture expansion. Fibre wall layers are building blocks in the fibre wall and therefore laminate theory with moisture expansion terms is the right tool to calculate average fibre wall properties. On the next scale we consider aligned natural fibre composites containing filled with resin or empty lumen, cylindrical fibre wall and the resin block surrounding it. This system may be analysed using the CCA model with moisture terms. Finally, moisture expansion of composites with certain fibre orientation distribution may be analysed using laminate analogy.

In this section we will briefly describe the moisture expansion analysis using the CCA model and laminate theory, and present some numerical examples for fibre wall layers and aligned composites. The CCA model will be used on two scales: (a) to determine the moisture expansion coefficients of the fibre wall layer and (b) to calculate the moisture expansion coefficients of the aligned natural fibre composite. The only difference with the material model used in Section 15.2 and given by (15.2) is that free moisture expansion terms are added to the elastic stress–strain relationship:

$$\sigma_i = C_{ij}\left(\epsilon_j - \beta_j^H \Delta M\right) \qquad 15.82$$

Performing the same derivations as in Section 15.2 one can easily see that the expressions for radial displacement, radial and axial stress which were previously given by (15.11)–(15.13) have to be slightly modified. The $\psi_k \epsilon_{10} r$ term in (15.11) has to be replaced by:

$$\psi_k \epsilon_{10} r - H_k^* \Delta M_k r \qquad 15.83$$

The $\phi_k \epsilon_{10}$ term in (15.12) has to be replaced by:

$$\phi_k \epsilon_{10} - H_k^r \Delta M_k \qquad 15.84$$

In (15.13) the $g_k \epsilon_{10}$ term has to be replaced by:

$$g_k \epsilon_{10} - H_k^1 \Delta M_k \qquad 15.85$$

In (15.83)–(15.85)

$$H^* = \frac{1}{C_{22} - C_{23}}\left[(C_{13} - C_{12})\beta_1^H + (C_{23} - C_{22})\beta_r^H + (C_{33} - C_{23})\beta_\theta^H\right]$$

15.86

$$H_r = C_{12}\beta_1^H + C_{22}\beta_r^H + C_{23}\beta_\theta^H + (C_{22} + C_{23})H^* \qquad 15.87$$

$$H_1 = C_{11}\beta_1^H + C_{12}\beta_r^H + C_{13}\beta_\theta^H + (C_{12} + C_{13})H^* \qquad 15.88$$

For transversely isotropic material

$$H^* = 0 \tag{15.89}$$

In (15.83)–(15.85) ΔM_k is the moisture weight content in the kth constituent, which is not known and has to be determined experimentally or from moisture diffusion models. It is input data for the present analysis.

The stress and displacement expressions (15.11)–(15.13) modified with terms (15.83)–(15.85) have to satisfy continuity conditions on interfaces. The outer boundary $r = r_N$ is stress free. The strain ϵ_{10} in direction 1 is constant and its value in the case of free expansion must result in zero average stress in direction 1. With these boundary conditions the strain ϵ_{10} is the free moisture expansion strain of the assembly in direction 1:

$$\epsilon_1^{H-\text{assembly}} = \epsilon_{10} \tag{15.90}$$

The radial displacement on the boundary $r = r_N$ is free and can be used to calculate the radial and tangential free moisture expansion strains of the assembly:

$$\epsilon_r^{H-\text{assembly}} = \epsilon_\theta^{H-\text{assembly}} = \frac{u_n(r_N)}{r_N} \tag{15.91}$$

A convenient procedure for solving is to use ϵ_{10} as a numerical parameter, solve the problem and calculate the average axial force using (15.21). Then the parameter ϵ_{10} is changed until zero force (with required accuracy) is obtained. The moisture expansion coefficients follow from (15.81):

$$\beta_1^H = \frac{\epsilon_1^{H-\text{assembly}}}{\Delta M_{\text{assembly}}} \qquad \beta_2^H = \beta_3^H = \frac{\epsilon^{H-\text{assembly}}}{\Delta M_{\text{assembly}}} \tag{15.92}$$

The average moisture content of the analysed assembly $\Delta M_{\text{assembly}}$ obeys the rule of mixtures:

$$\Delta M_{\text{assembly}} = \sum_k \Delta M_k \frac{\rho_k}{\rho_{\text{assembly}}} V_k \tag{15.93}$$

$$\rho_{\text{assembly}} = \sum_k \rho_k V_k \tag{15.94}$$

As a first example we calculate the moisture expansion coefficients of the S2 and S1 layers in the fibre wall. The geometrical parameters and elastic properties of cellulose, hemicellulose and lignin are given in Tables 15.1 and 15.2. The used moisture expansion coefficients of these constituents are given in Table 15.13. It was assumed that the moisture content in the hemicellulose is 2.6 times larger than in lignin[10] and that cellulose is not absorbing water. The last assumption, although appropriate for the crystalline part of the cellulose, may not be true for the amorphous part. Correction for that would lead to non-zero value of the moisture content and of the average (effective) moisture expansion coefficient of the cellulose.

Table 15.13 Moisture expansion coefficients of constituents

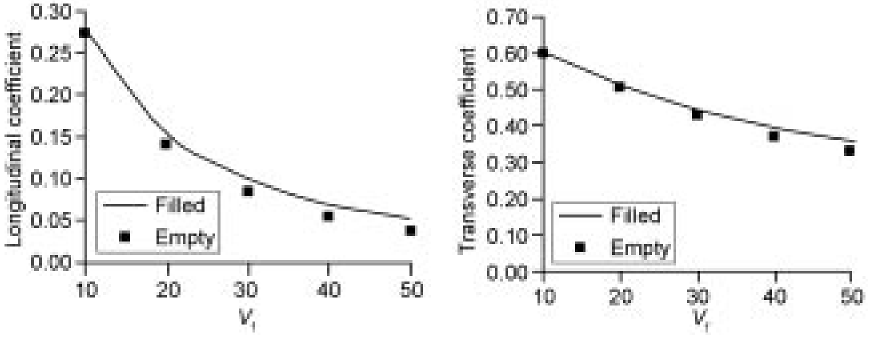
Property	Cellulose	Hemicellulose	Lignin
β_1^H	0	0	0.333
β_2^H	0	0.5	0.333
β_3^H	0	0.5	0.333

To calculate using (15.93) the average moisture content, the density of the cellulose was taken as 1.55, of the hemicellulose 1.49 and of the lignin 1.40 g/cm^3. For S2 layer the calculated moisture expansion coefficients in axial and transverse directions are 0.007 66 and 0.440 respectively. For S1 layer they are 0.022 and 0.440.

As a second example we calculate the swelling coefficients of earlywood fibre composite with varying fibre content. The lumen occupies 36% of the fibre volume. The microfibril orientation angle in the S2 layer is 20. The fibre wall elastic properties are given in Tables 15.8 and 15.10. The resin properties are given in Table 15.11.

The moisture content in the fibre wall was assumed to be six times higher than in the resin. The resin density is 1.3 and the fibre wall density is 1.5 g/cm^3. The fibre wall has $\beta_z^H = 0.008$, $\beta_\phi^H = \beta_r^H = 0.2$. The isotropic resin has swelling coefficient 0.7. Figure 15.16 shows the composite moisture expansion coefficients versus fibre volume fraction.

The axial moisture expansion coefficient of the aligned composite is low and decreases with fibre content. This coefficient is mainly governed by the low axial moisture expansion coefficient and high axial modulus of the fibre. However, the axial modulus is not infinitely high and the large resin expansion in the transverse direction applies radial tension to the fibre. The Poisson effect leads to fibre shrinkage in the axial direction. The combination of these two



15.16 Moisture expansion coefficients of composite reinforced with earlywood fibres versus the fiber volume fraction. Volume fraction of the lumen in the fibre is 36% and it may be empty or filled with resin.

effects (axial expansion governed by fibre properties and radial constraint) may lead to a smaller axial moisture expansion of the composite than of the fibre. The radial interaction is stronger if the lumen is filled. The transverse moisture expansion is much larger and reduces with fibre content.

As discussed above, the fibre wall can be considered as a laminate. The composite with certain in-plane fibre orientation distribution can also be analysed considering it as a laminate with an infinite number of layers. The governing in-plane equation of the classical laminate theory for free moisture expansion is:

$$\begin{Bmatrix} N_1^H \\ N_2^H \\ N_{12}^H \end{Bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{16} \\ A_{12} & A_{22} & A_{26} \\ A_{16} & A_{26} & A_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_1^H \\ \epsilon_2^H \\ \gamma_{12}^H \end{Bmatrix} \qquad 15.95$$

Here $[A]$ is the extensional stiffness matrix of the laminate defined by (15.59) and with $\bar{Q}_{ij}^k$ given by (15.49)–(15.54). Expressions for the 'force' $\{N^H\}$ in (15.95) written in a vector form are as follows:

$$\{N^H\} = \sum_k \Delta M_k h_k [\bar{Q}]_k \{\bar{\beta}^H\}_k \qquad 15.96$$

Here $\{\bar{\beta}^H\}_k$ is the moisture expansion coefficient vector of the kth constituent in the global system of coordinates:

$$\begin{aligned} &\bar{\beta}_1^H = m^2\beta_1^H + n^2\beta_2^H \qquad \bar{\beta}_2^H = n^2\beta_1^H + m^2\beta_2^H \\ &\bar{\beta}_{12}^H = 2(\beta_1^H - \beta_2^H)mn \qquad m = \cos\theta, \quad n = \sin\theta \end{aligned} \qquad 15.97$$

Since $\{N^H\}$ is known, the laminate strains may be found from (15.95). For the laminate these strains are free moisture expansion strains and, hence, the laminate moisture expansion coefficients can be calculated as:

$$\beta_1^{H-\mathrm{LAM}} = \frac{\epsilon_1^H}{\Delta M_{\mathrm{LAM}}} \qquad \beta_2^{H-\mathrm{LAM}} = \frac{\epsilon_2^H}{\Delta M_{\mathrm{LAM}}} \qquad \beta_{12}^{H-\mathrm{LAM}} = \frac{\gamma_{12}^H}{\Delta M_{\mathrm{LAM}}} \qquad 15.98$$

The average moisture content in the laminate ΔM_{LAM} may be calculated using expressions like (15.93) and (15.94).

15.6 Concluding remarks

A multiscale approach to model hygro-elastic properties of natural fibre has been described in this chapter. Two basic models were described and used on several scales. One of them is the N-concentric cylinder assembly model suitable for average properties of composites with aligned constituents. The second is classical laminate theory, whose efficiency for analysing thin layered structures is well recognised.

One of the main conclusions from the application examples is that the selection of fibres with low microfibril orientation angles in the S2 layer may be as beneficial for the composite properties as an increase of the fibre content. Modified simple models based on constant strain or constant stress assumptions were suggested to calculate elastic properties fibre wall layers. Their accuracy was proven by comparing with concentric cylinder assembly results.

Several problems, which are the subject of an ongoing investigation, have not been covered in this chapter. For example, if the fibre wall layer thickness becomes comparable with the fibre radius, the classical laminate theory for fibre wall properties is not applicable and the two-step averaging used (first the laminate theory to obtain the fibre wall properties and than the concentric cylinder assembly to treat the fibre wall in the resin) has to be replaced by one averaging step on the more complex *N*-cylinder assembly where each fibre wall layer is recognised.

To estimate the effect of the fibre rotation in the resin due to the helical ultrastructure of the fibre, more detailed analysis of the *N*-cylinder assembly with generally anisotropic cylinders has to be performed. Finally it has to be recognised that natural fibres and resins are inelastic time-dependent materials and viscoelastic (non-linear) and viscoplastic properties have to be included in models.

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Appendix 15.1 Constitutive model of an orthotropic material

$$\begin{cases} \sigma_1 = C_{11}\epsilon_1 + C_{12}\epsilon_r + C_{13}\epsilon_\theta & \sigma_{r\theta} = C_{44}\gamma_{r\theta} \\ \sigma_r = C_{12}\epsilon_1 + C_{22}\epsilon_r + C_{23}\epsilon_\theta & \sigma_{1\theta} = C_{55}\gamma_{1\theta} \\ \sigma_\theta = C_{13}\epsilon_1 + C_{23}\epsilon_r + C_{23}\epsilon_\theta & \sigma_{1r} = C_{66}\gamma_{1r} \end{cases} \qquad \text{A15.1}$$

The compliance matrix $[S]$ is defined as

$$[S] = \begin{bmatrix} \frac{1}{E_1} & -\frac{\nu_{1r}}{E_1} & -\frac{\nu_{1\theta}}{E_1} & 0 & 0 & 0 \\ -\frac{\nu_{1r}}{E_1} & \frac{1}{E_r} & -\frac{\nu_{r\theta}}{E_r} & 0 & 0 & 0 \\ -\frac{\nu_{1\theta}}{E_1} & -\frac{\nu_{r\theta}}{E_r} & \frac{1}{E_\theta} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G_{r\theta}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G_{1\theta}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G_{1r}} \end{bmatrix} \qquad \text{A15.2}$$

$$[C] = [S]^{-1} \qquad \text{A15.3}$$

For transversally isotropic material:

$$E_r = E_\theta = E_T, \nu_{1r} = \nu_{1\theta} = \nu_{LT}, G_{1r} = G_{1\theta} = G_{1T}$$
$$C_{12} = C_{13}, C_{22} = C_{33}, C_{55} = C_{66}, C_{44} = G_{r\theta} = \tfrac{1}{2}(C_{22} - C_{23}) \qquad \text{A15.4}$$

The last relationship in (A15.4) is identical to $G_{r\theta} = \dfrac{E_T}{2(1 + \nu_{r\theta}))}$ which is well known for isotropic materials.

Appendix 15.2 Elastic parameters in solution for orthotropic material

$$\alpha^2 = \frac{C_{33}}{C_{22}} \qquad \text{A15.5}$$

$$\psi = \frac{C_{13} - C_{12}}{C_{22}} \frac{1}{1 - \alpha^2} \qquad \text{A15.6}$$

For isotropic material $\psi = 0$ and $\alpha = 1$.

$$\beta = C_{22}\alpha + C_{23} \qquad \text{A15.7}$$

$$\gamma = C_{23} - C_{22}\alpha \qquad \text{A15.8}$$

$$\begin{aligned} g &= C_{11} + (C_{12} + C_{13})\psi \\ f &= C_{12}\alpha + C_{13} \\ h &= C_{13} - C_{12}\alpha \\ \phi &= C_{12} + (C_{22} + C_{23})\psi \end{aligned} \qquad \text{A15.9}$$

$$a^2 = \frac{C_{55}}{C_{66}} \qquad \text{A15.10}$$

For an isotropic material $a = 1$.

Constants λ_i used in Section 15.2.4 are defined by the following expressions:

$$\lambda_{1,2}^2 = -p - \sqrt{p^2 - q} \qquad \lambda_{3,4}^2 = -p + \sqrt{p^2 - q} \qquad \text{A15.11}$$

where

$$p = \frac{4(C_{23}^2 - C_{22}C_{33}) + G_{r\theta}(8C_{23} - C_{22} - C_{33})}{2G_{r\theta}C_{22}} \qquad q = 9\frac{C_{33}}{C_{22}} \qquad \text{A15.12}$$

For an isotropic phase (A15.11)–(A15.13) turn to

$$\lambda_1 = 1 \quad \lambda_2 = -1 \quad \lambda_3 = 3 \quad \lambda_4 = -4 \qquad \text{A15.13}$$

Expressions for constants b_i are

$$b_i = -\frac{C_{22}\lambda_i^2 - 4G_{r\theta} - C_{33}}{2[G_{r\theta} + C_{33} - \lambda_i(C_{23} + G_{r\theta})]} \qquad \text{A15.14}$$

For an isotropic material

$$b_1 = 1 \quad b_2 = \frac{G_{r\theta}}{C_{22}} \quad b_3 = -\frac{G_{r\theta} - 2C_{22}}{C_{22} - 2G_{r\theta}} \quad b_4 = -1 \qquad \text{A15.15}$$

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