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12

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Christof Hübner

Polymers - Opportunities and Risks II

Sustainability, Product Design and Processing

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The Handbook of Environmental Chemistry

Founded by Otto Hutzinger

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Volume 12

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Polymers – Opportunities and Risks II

Sustainability, Product Design and Processing

Volume Editors: Peter Eyerer · Martin Weller ·
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Aims and Scope

Since 1980, *The Handbook of Environmental Chemistry* has provided sound and solid knowledge about environmental topics from a chemical perspective. Presenting a wide spectrum of viewpoints and approaches, the series now covers topics such as local and global changes of natural environment and climate; anthropogenic impact on the environment; water, air and soil pollution; remediation and waste characterization; environmental contaminants; biogeochemistry; geoecology; chemical reactions and processes; chemical and biological transformations as well as physical transport of chemicals in the environment; or environmental modeling. A particular focus of the series lies on methodological advances in environmental analytical chemistry.

Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last three decades, as reflected in the more than 70 volumes of *The Handbook of Environmental Chemistry,* there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry,* the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of*

Environmental Chemistry provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Editors-in-Chief

Volume Preface

Polymers have achieved tremendous success since their first industrial applications. Today the worldwide production of polymers is about 260 Mio t/a entailing a huge number of employees working not only in production but also in the processing of polymers. A success story of such magnitude must now, however, be regarded in terms of environmental issues, which was not the case until the 1970s when pollution of the environment was focused on more and more by society in different parts of the world, today playing a very important role.

Against this background the *Handbook of Environmental Chemistry* will discuss the environmental aspects of the industrial use of polymers in two volumes called *Polymers – Opportunities and Risks I: General and Environmental Aspects* and *Polymers – Opportunities and Risks II: Sustainability, Product Design and Processing*. The scope of these volumes is to take a critical view on the chances and potential of polymers, recognizing their risks in reference to environmental issues arising from their production and application.

Because of the strong engineering background of the editors, the engineering view point is predominant throughout these volumes emphasizing the fact, that the processing of polymers and the service life of polymeric parts play – besides their production – a decisive role in view of their environmental impact. The field addressed is characterized by such diversity that two single volumes are just able to relate the most important aspects.

Following this mainly engineering view point, the first volume *Polymers – Opportunities and Risks I* is dedicated to the basics of the engineering of polymers (materials, processing, design, surface, use phase, recycling, depositing) – but always in view of the environmental impact.

In the second volume *Polymers – Opportunities and Risks II*, single aspects are regarded in more detail by means of examples. Our aim was to select examples that cover a broad range of topics of interest and of course we would be happy if we have succeeded in meeting the interests of the majority of readers.

Because of the complexity of the subject and the broadness of the covered topics, the production of these volumes took far longer than expected when we planned the project. We would like to thank Springer-Verlag for their help and active cooperation and the contributing authors for their patience in waiting for the publication of their contributions, quite a few of which are not published in their original form but were actualized in 2009. We would also like to thank Alexandra Wolf for her incredible commitment in helping with manuscript organization.

Peter Eyerer
Christof Hübner
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Volume Editors

Contents of Volume II

Contents of Volume I

Assessing the Sustainability of Polymer Products

Marc-Andree Wolf, Martin Baitz, and Johannes Kreissig

Abstract Sustainability of products is related to Life Cycle Thinking and Assessment. It is widely understood that environmentally preferable products cannot be simply defined by “Recyclable,” “natural,” “renewable resource based,” “biodegradable,” “chlorine free,” “reusable,” or “organic.” It is the product’s complete life cycle that must be environmentally preferable. Misconceptions still exist, particular on plastics. But looking closer there is no environmentally good or bad material, there are only good or bad applications of a material. This means consistent rules for sustainability assessment on a life cycle basis are important. Standard approaches already used in industry practice and can be complemented with further aspects. Tools are established, databases exist, and experts are have already formed networks. Further improving polymers for more sustainable products is hence a process that has already started, by consistently combining existing life cycle approaches, tools, and databases. Herein are summarized misconceptions, rules, standard approaches and needed additions, tools, databases, and experts related to the Sustainability of polymers.

Keywords Database, ISO 14040, Life cycle assessment, Software, Sustainability

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1 Introduction and Scope of Work

According to the findings of the Brundtland Commission "Sustainable development integrates economics and ecology in decision making and law making to protect the environment and to promote development." (...) "Sustainable development wants to achieve social equity between generations and within each generation." (...) "It meets the needs of the present without compromising the ability of future generations to meet their own needs."[1].

Since that time in the late 80ies of the 20th century the understanding of sustainability issues has constantly grown and much experience has been gained from case studies, systematic integration into companies' decision structure and – lately – policy making.

Examples of more advanced sustainability-oriented policy making on the European level are the Integrated Product Policy (IPP) with various activities coordinated under IPP, such as directives and framework directives that are going to adapt life-cycle thinking approaches, e.g. Directive on Energy-using Products (EuP), Integrated Pollution Prevention and Control (IPPC), End-of-Life Vehicle Directive (EoLV), Waste Electric and Electronic Equipment Directive (WEEE), and various other upcoming and environmentally motivated policies and directives. This has been taken up and brought in relationship to Waste with the Thematic Strategy on Waste and to Resources with the Thematic Strategy on the Sustainable Management of Natural Resources, both communication in 2005. In 2008 the Sustainable Consumption and Production (SIP) and the Sustainable Industrial Policy (SIP) Action Plans have reiterated and integrated these policies. Similar policies exist in e.g. Japan, China, Thailand and other countries. They all will form new, harmonized environmental boundary conditions for production and consumption in Europe and beyond. More information on European policies can be found at http://ec.europa.eu/environment/policy_en.htm.

The consideration of the life cycle of the system subject to legislation is a new trend that results in more reliable, long-term oriented and target-orientated policy making: The planning horizon for companies grows and at the same time the ways to improve products become much more flexible. Companies can largely choose the path to follow for improvement, instead of being only subject to fixed substance-by-substance emission limits.

One of the consequences of the experiences gained with life cycle-based assessments and of the consequent development of new policy instruments is a shift of the viewpoint from the material to the product: There is no ecologically good or bad material, but only more or less appropriate applications of a material. The study "LCA of PVC principally competing materials" on behalf of the European Commission showed, that this finding is also valid for PVC, which always had a rather bad environmental image [2] (downloadable at http://ec.europa.eu/enterprise/sectors/chemicals/documents/competitiveness/index_en.htm). Chances and Risks of Polymers depend on the specific application of a material and cannot be given on the level of the material itself. In further consequence the product-perspective is widened to the products' (and services') functions and further on to the consumer demand.

This work "Assessing the sustainability of polymer products" first takes the opportunity to inform about and explain popular misconceptions around polymeric materials and later provides solutions for evaluation of "sustainability" in a holistic perspective. Such an approach is urgently needed since past and present efforts often lead and still lead to environmental impairment instead of improvements – which can be seen in the examples given in the text on misconceptions below.

A comment about the scope of this work: Focus is placed on the environmental dimension of sustainability with one chapter addressing social aspects. Cost issues are dealt with in the other chapters of this book.

2 Popular Misconceptions About Polymers

2.1 "Polymers Are Environmentally Disadvantageous (and PVC Is the Worst)"

2.1.1 Misleading Assumptions, Explanations, and Examples

"Synthetic polymers waste the non-renewable resource crude oil" – Really?

→ Well below 5% of crude oil is used in the chemical industry (including polymer production). The resource crude oil (hydrocarbon chains) here is transformed into polymer products (hydrocarbon chains), rather than directly consumed for its energy content. The major part of the crude oil is used in the transport sector as fuels and for home heating purposes. Fuel applications consume the fuel, as the crude oil is irreversibly transformed from hydrocarbon chains dominant in the hydrocarbon to the gas carbon dioxide and water vapor. Of course, synthetic polymers are mainly built from crude oil and natural gas, whose production again requires a high energy input. Often however – besides the points mentioned – light weight polymer products save more energy than their production consumes: Lighter cars consume less gasoline. Various Life-cycle studies on polymers used in mobile applications like cars showed promising resource and energy-saving potential, if polymer solutions are applied accordingly. An achievable saving depends heavily on the chosen application. Depending on the specific situation and application solutions from polymers or from competitive materials like metals or inorganic materials are the most promising, while this on the other hand cannot be generalized per se [3–7].

→ Most polymers allow construction of long-living products with an advantageous use phase performance and that require less maintenance than many other materials: A study on wooden window frames vs. PVC/steel- and PA/aluminum-based ones showed clearly certain disadvantages of the wood-concept. Wooden window frames can have a less efficient isolation against energy losses during the use phase, a lower durability, and the need for regular application of surface coating for weather protection with consequent VOC emissions. The base material "wood" is not necessarily environmentally better, just because it is "natural." The best concept for that application was the PVC/steel concept with that of aluminum/PA being close. The performance of windows interacts strongly with the chosen building environment. Taking the wood example: it is a very good material for roof construction, where it clearly wins any comparison with polymers, due to its technical properties for that specific purpose. The "best" is hence dependent on the total system and is not primarily dependent on the kind of material [8, 9].

→ There is no automatism on the level of a material type, but the "environmental soundness" depends on the specific material application. For the example of PVC, the study "PVC and principally competing materials" (cited above) showed this fact.

2.1.2 Where the Misconception Is None

Production and use of polymer products is environmentally disadvantageous wherever other materials perform the same function with less impacton the environment. Which types of materials these may be again depends on the specific function. Depending on the polymer type between 25 and several 100s MJ of non-renewable energy resources are consumed for the production of 1 kg of polymer. In the polymer's end-of-life only a fraction of 15–50 MJ, which is embodied in the polymer can be recovered for example as electricity and steam from waste incineration plants. Furthermore, new incineration plants are able to recover quality hydrochloric acid from the chlorine content of the polymers (and of course other non-polymer chlorine inputs). The remainder is lost. Production of synthetic polymers indeed consumes a high amount of energy, of which only a share can be recovered. While polymers are not per se environmentally bad, but in contrast often the better material alternative, they nevertheless must not be wasted, of course.

Another aspect: Plastic waste laying in the landscape is often felt to be an environmental problem. This is partly true, but mainly an optical annoyance to human beings. To the environment the ugly waste does not mean a relevant harm. In the oceans however, plastic bags for example of PE seem to indeed often do harm to wild animals such as fish, turtles, and whales that swallow these long-lasting bags which for example block their digestion.

2.1.3 Conclusion

Overall, polymers offer many advantages over other materials – IF used in the right products where polymers can employ beneficial characteristics such as durability, light weight and flexibility as required for the specific function. Like all materials, however, polymers can also be used in a disadvantageous way.

2.2 "Polymers from Renewable Resources Are Always Good for the Environmen"

2.2.1 Misleading Assumptions, Explanations and Examples

"Renewable resources that grow in the field from solar energy are the right basis for polymers" – Really?

→ Fertilizers, pesticides, and farm machinery are required for modern agriculture. Their production and use again requires energy and causes emissions. Especially emissions of nitrate, ammonia and laughing gas contribute to eutrophication of rivers and groundwater and to global warming. Ammonia, is also released from manure – in especially high amounts. In the overall perspective, organic farming offers only slight (if any) advantage over conventional or integrated farming as also, for example [9] showed. All these emissions can be reduced by eco-optimized field management (which is not always identical to organic-farming practices), but certain relevant impacts are unavoidable. In an extensive study on developing high-quality polymers based upon such field crops such as wheat and corn it turned out that these were environmentally disadvantageous compared to the same polymers made from crude oil [10]. Next to emissions, which cannot be reduced substantially is the land use itself. Next to nitrate emissions, land use is the most relevant environmental impact caused by cropping. Presently per 1 kg of polymer about 2–20 kg wheat are consumed – depending on the polymer type and specific production route. This means that the production of each kg of polymer requires 2.5–25 m^2 to be cropped per year. For the average consumption of 100 kg plastics annually per average European citizen this means 250–2,500 m^2 of agricultural land cropped per year only for that purpose. The complete substitution of all 50 Mio t of polymers consumed in Western Europe would hence require roughly a cropping area of 500 × 500 km of best farmland at a high production level (assuming a very ambitious 5 kg wheat per kg polymer). The limits of producing polymers from renewable resources become obvious.

2.2.2 Where the Misconception Is None

Alongside the general possibilities of further developing the not yet mature technologies for polymer production from crops, there is one, more specific and promising option: The use of unused or poorly used by-products from the cropping of food – such as straw, stalks etc. – promises to result in more environmentally friendly polymers than those made from crude oil. If the land is cropped for harvesting e.g. grains for food, the by-products straw, stalks etc. are produced at (almost) no cost and can be used for polymer production. There is still a need for developing such technologies that biotechnologically and/or chemically transform the lignocellulosic biomass into polymers. This option of synthesis of highly specific polymers in microbiological reactors from starch or hydrolyzed cellulose is still under heavy development. It depends to a great extent on the polymers produced and possible subsequent chemical modification needed as well as on the separation technologies. The further development of these technologies requires e.g. enforced evolution principles and extensive strain selection and often also genetic modification. Such routes offer significant principal advantages that still have to be made available by research efforts. The only principle disadvantage is, that the total possible production volume is limited by the amount of food produced, as food by-products are used. One further aspect has to be considered in this context: While the potential for such production routes is still very high, for reasons of soil conservation a complete removal of all biomass would not be sustainable. Moreover there are other, existing uses for some of the by-products, such as bedding. Additionally, the upcoming competition with again different, new uses such as for synthetic diesel fuel from such renewable resources has also to be anticipated.

Another option is the extraction of highly specific plant components that can be used with minimal further processing. The number of such naturally occurring substances and the concentration in the plants is however limited. Examples are rubber and colophonium, while for these examples the present production is not very sustainable and is often worse than e.g. rubber production from synthetic resources.

2.2.3 Conclusion

Cropping renewables explicitly for polymer production is environmentally disadvantageous. The use of crops as feedstock can only be advantageous if the crops' by-products are used for producing polymers. Biotechnological production routes can potentially result in more environmentally friendly polymers. The assessment of renewable resources for use in polymers and other products has to be carried out in a case-specific manner [11].

2.3 *"Biodegradability of Polymers Is Good for the Environment"*

2.3.1 Misleading Assumptions, Explanations, and Examples

"Through biodegradation the plastics are naturally digested and do not pollute the environment" – Really?

→ Biodegradation of polymers releases (at least) the CO_2 stored in the polymer. If the polymer is instead incinerated , CO_2 would still be released , but useful electricity could be produced at the same time. Biodegradation methods such as composting hence waste the energy content stored in the polymers and only low-valued products (compost) are the result.

→ Plastic waste in the landscape is an aesthetic problem, only, as has already been stated above. Moreover, during biodegradation other components of the polymer compound are released: dyes, softeners, and stabilizers are often also used in biodegradable polymers and reach the environment. If the polymer is not degradable, in contrast, it remains intact long enough to be collected and recycled or disposed of properly. The same problem occurs in waste deposits: the biodegradable polymers decompose and release xenobiotics.

→ Biodegradation of plastics is a problem for mixed plastic waste recycling: the decaying polymers pollute the other plastic waste and consequently make recycling more difficult. Moreover, because of degradation, biodegradable polymers themselves are typically not recyclable at a high-quality level. They can only be recycled energetically or – at a maximum – on the raw material level.

→ Biodegradability of polymers means limited durability of the products made thereof especially in humid environments: For most applications biodegradability results in less durable, lower performance products. In order to make a polymer biodegradable, specific chemical and structural properties of the polymer and the polymer products are required, which further limits the fields of application.

2.3.2 Where the Misconception Is None

Biodegradable polymers have some – however very few – useful applications: wherever the degradation is an essential part of the products function (e.g. in certain medical applications, as collection bags for humid biowaste, whereever used plastic bags and bottles end up in the sea, etc.).

2.3.3 Conclusion

Biodegradability can be a very important requirement for certain applications and may be advantageous in selected applications. However, in most cases of mass product solutions the biodegradability of polymers is not an advantage. Biodegradability of polymers is in the majority of cases clearly environmentally disadvantageous from a life cycle perspective. Again it is a matter of using the most appropriate material for an application and not a general "good" or "bad" material question.

2.4 "Recycling of Polymers Is Always Good for the Environment"

2.4.1 Misleading Assumptions, Explanations, and Examples

"Recycling of polymers saves resources, since no new crude oil is required" – Really?

→ The technical quality of the recycled polymer is in most cases (at least slightly) lower than that of the primary material. This is due to polymer degradation by light, heat, water, mechanical stress etc. over often many years of use e.g. in cars, buildings etc. Products made of such recyclates can be less durable. Also the application fields for the recyclates are limited, since plastic formulations are very specific and contain up to 60% other substances such as fillers, softeners, stabilizers, pigments etc. The formulation of the secondary polymer can hence not be adjusted freely to meet the required specification. Products made from recycled polymers are also often heavier, since worse mechanical properties have to be counteracted by using more of the polymer. This is again a big disadvantage in mobile applications: it leads to higher fuel consumption of the car, bus, or train during the use phase. In summary recycled plastics are often environmentally disadvantageous compared to primary plastics. Consequently, even more crude oil and other resources may be required compared to producing and using primary polymers.

→ Contamination of the polymer parts to be recycled represents a problem: e.g. soiling and food remains in packaging result in either lower-quality recyclates or additional effort for recycling (e.g. washing). This means not only higher cost but also additional energy consumption and emissions. Similar problems occur in the recycling of clean but mixed plastic waste, which is often environmentally disadvantageous. In this case, better separation technologies can result in fewer impurities and thereby indirectly improve the environmental performance. Research efforts that point in this direction can improve the overall situation.

→ Any recycling process of used polymer products requires energy and produces emissions and typically waste water. Depending on the properties of the plastics to be recycled, the overall environmental balance can often be negative, i.e. the recycling of the plastics results in more environmental damage than the primary production would cause. This strongly depends on the plastic properties such as degree of ageing, soiling, the degree of impurities (like other polymers), composition and amount of additives (fillers, softeners, stabilizers, pigments etc.), the material's principal recyclability (e.g. duroplastics, thermoplastics, and fiber-reinforced composites are different here) as well as the effort for logistics in terms of transport energy and emissions. Generally it can be said, that most of the soiled mixed plastic waste, small to medium-sized parts of duroplastics and reinforced plastics as well as most small parts of thermoplastics are better incinerated with regeneration of the energy than recycled on the material level. Again, development of new separation and recycling technologies may alter this situation.

2.4.2 Where the Misconception Is None

In contrast to a large share of post-consumer polymer waste, polymer production waste is available without ageing, in defined composition and – if directly recyclable such as is the case for thermoplastics – available at the required location without logistic and cleaning efforts. Such recycling is almost always environmentally strongly advantageous. This is already state of the art in industry, since it also saves money. This can hold true for "clean" post-consumer waste of a short lifespan, too (like certain non-food packaging waste).

Advantageous is also the material recycling of similar types of post-consumer polymer waste with limited ageing, available in large parts, without impurities, only lightly soiled etc. PVC cable waste is such an example. Practical feasible recycling methods exist and are operated to recycle PVC from cable waste sources while also recovering the copper, which is the main driver and guarantees appropriate amounts to be collected. An advantage approach leads to material recycling due to selective dissolution or feedstock recycling with hydrolysis and pyrolysis. This method shows the best environmental performance among the presently available technologies. It is followed by the feedstock recycling processes, being slightly advantageous compared to incineration with energy and chlorine recovery. Of course all options perform much better than landfilling [12].

In a study on the material recycling of PUR foam dispensers used in the building industry, collection and recycling shows clear environmental advantages over the incineration or disposal of the typically only partly emptied dispensers, as a recent study shows [13].

However, the cost for this type of recycling is high and economically depends on legal settings that require the recycling. Such a situation exists for high-quality recycling of waste fuel tanks from cars: supercritical extraction of migrated fuel and subsequent material recycling showed environmental advantages, while the recycling is very costly [14].

2.4.3 Conclusion

Recycling offers the chance to reduce resource consumption and emissions. It is however not always advantageous: soiled mixed plastic waste is better incinerated than recycled. The environmental and cost side of recycling also depends on the development of better separation and cleaning technologies that increase the number of cases, where recycling is environmentally and often also economically advantageous. A general answer cannot be given: The specific product to be recycled and other aspects (such as logistics) are decisive and have to be considered. Other options alongside material recycling such as raw material recycling and energetic recovery should also be considered and the cost for the different opportunities should be included (see Fig. 1). A general statement that can be made is: Useful Recycling

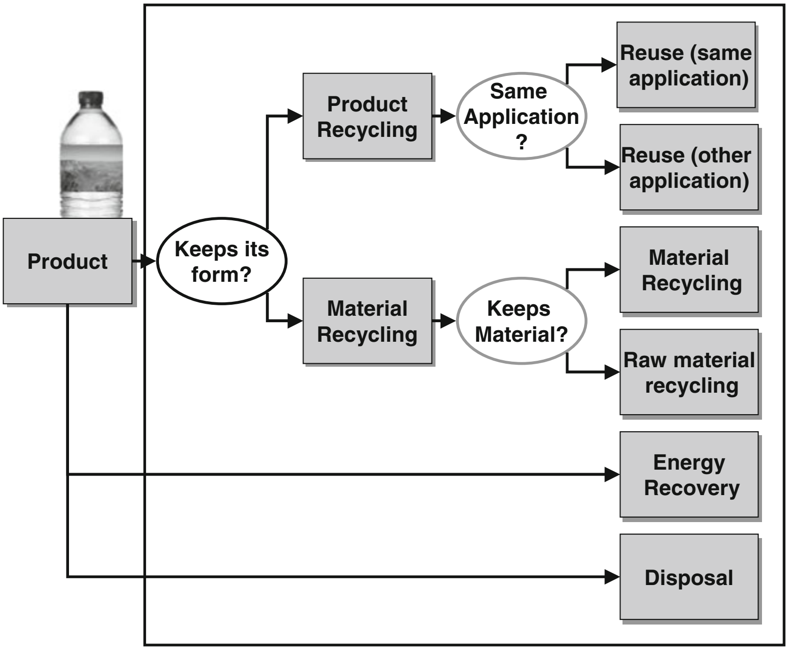

Fig. 1 Principal end-of-life alternatives for after-use polymer products

needs certain available mass streams. If the available mass stream of polymer waste is too small (even if extremely pure) the recycling strategy will not work.

Disposal (and also composting) are always the poorest options; this has already been explained above. These examples also illustrate why current EU waste legislation foresees the possibility to deviate from the waste hierarchy (i.e. avoidance, reuse, recycling, energy recovery, land-filling) by showing advantages of specific end-of-life treatments applying Life Cycle Assessment.

2.5 "Light-Weight Vehicles Are Always Good for the Environment"

2.5.1 Misleading Assumptions, Explanations, and Examples

Weight saving means fuel saving and since the use phase is environmentally most important for a vehicle's life cycle, weight saving is always good." – Really?

→ The change from steel-based car chassis to those made of carbon-fiber reinforced compounds is often named as an example for the success of the factor-four principle developed by the Wuppertal Institute (see http://www.wupperinst.org/FactorFour/). However, the environmental impact resulting from production of the carbon-fiber chassis is not considered in that case: it is in the same range as the amount of fuel saved due to the lighter weight of the car. Carbon-fiber production is very energy consuming and results in a high amount of emissions. If the production of the carbon-fiber chassis is analyzed to an adequate degree of detail (regarding also specific production emissions) the life cycle of carbon-fiber chassis tends to show that the weight advantage is compensated by the disadvantage during chassis production. Furthermore, the recyclability of carbon-fiber reinforced compounds is often extremely limited, which lowers the end-of-life advantages, since steel can be recycled very efficiently.

2.5.2 Where the Misconception Is None

The above short "list" of only one example illustrates that in most cases the light-weight approach is a good approach in mobile applications. If for example a metal part is substituted by a polymer part, the production of the polymer part often may require more primary energy than the old part, but at the same time saves primary energy due to fuel savings. On a net basis light-weight construction in vehicles is hence often environmentally advantageous. Figure 2 illustrates this with results of a study on air-intake manifolds for a gasoline-driven car. The figure illustrates that even in light-weight construction an important link between the technical boundaries, the intended application, and the desired environmental improvement exists, if the life cycle is considered [15].

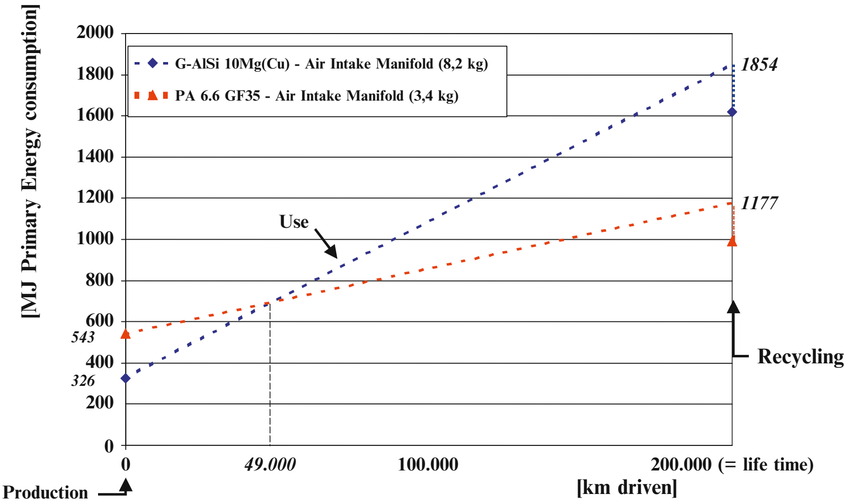

Fig. 2 Primary energy consumption within the life cycle of two air intake manifolds made of different materials in a gasoline driven car

The following detailed conclusions were derived for the air-intake manifold:

- Polymer variants show often higher energy consumption in production
- The metal variants may have technical disadvantages during utilization
- The metal variant has a better recycling potential
- Polymer and metal variants show individual improvement potentials
- These improvement potentials lay in different technologies (Polymer: Polyamide routes, Adipic acid – Hexamethylenediamine, lost core/twin shell, Aluminum: Form of anode (only of interest at primary production), cleaning step during recycling, recycling material percentage)

2.5.3 Conclusion

With few exceptions weight reduction of parts in mobile applications is good. However, the carbon-fiber example shows: the situation can only be judged for the concrete case and application.

2.6 Over all conclusions

There is no technically good or bad material, the same as there is no generally cheap or expensive material – such judgments always depend on the intended applications: While stainless steel is a technically very suitable material for reactors in the chemical industry and nice looking and durable in exterior building applications, nobody would consider it good for clothing or as a wind screen, of course. Gold is expensive, but still the cheapest material for contacts in electronic products.

The same is true for the environmental performance of materials: There is no “eco-material.” It always depends on the specific application, on the function to be performed, and on the alternatives of competing materials that are available.

The conclusions can hence be summarized in one short sentence:

“There is no environmentally good or bad material, there are only good or bad applications of a material.”

The question of how to systematically assess material alternatives in specific application cases, has not been answered so far. The next chapter will help with this and provides an introduction on how to assess the overall effects on the environment in such cases. The life cycle based methods and tools that will be presented are already in use by a number of leading companies to support realizeation of the possibilities of polymers (and many other materials) while minimizing the risks involved.

3 Rules for Sustainability Assessment

Sustainability and life-cycle thinking are linked today [16]. A suitable approach for a sustainability assessment that provides reliable decision support has to obey the following eight rules:

- Perform the analysis of material alternatives on an engineering basis. This avoids misleading “solutions,” that are technically impossible or disadvantageous.
- Compare on the level of products which perform the same function. This avoids “comparing apples with peas,” i.e. ensures, that only things are compared, that are actually comparable.
- Consider the complete life cycle of the products. This avoids the shifting of burdens among the life cycle phases raw material extraction, production, use, and end-of-life of the product. It avoids for example, that some energy might be saved during production while much energy is wasted during the use phase.
- Include all three safeguard objects “Man,” “Environment,” “Economy.” This avoids the shifting of burdens among man, environment, and economic interests of companies or countries.
- Include all relevant effects on the safeguard objects. This avoids the shifting of burdens among problem fields, e.g. for the safeguard object “Environment” it has to be avoided, that a small reduction in acidifying emissions is outweighed by much higher emissions that contribute to global warming or vice versa.
- Consider the marketability of alternatives. This avoids solutions, which cannot be sold on the market and have hence no improvement impact: Only environmentally advantageous products that actually substitute less environmentally friendly products in large amounts result in a real improvement.
- Carry out the analysis in parallel to product or process development. This allows decision support to be effectively provided when changes can still be made:

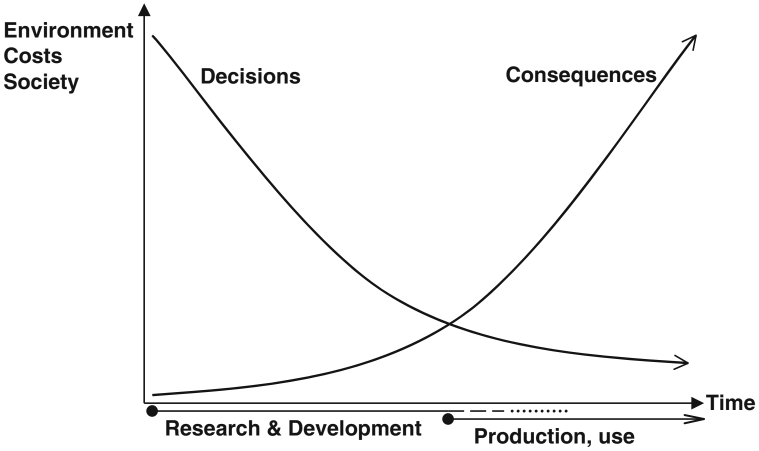

Fig. 3 Only early decision support can be effective decision support

during advance development and development of products, processes and technologies. When production is running or a product has already been produced, relevant changes can no longer be implemented. This means: only early decision support is useful decision support (see also Fig. 3).

- And finally: Do not confuse approaches or strategies with targets. This avoids misconceptions such as those listed exemplarily above. “Use renewable resources” or “recycling of the product” is only an approach, but does not guarantee an actual improvement – often to the contrary: Only the product-specific assessment of the alternatives gives reliable guidance. Such a reliable assessment always requires the consideration of ALL the above-named rules.

4 Tool-Box for Sustainability Assessment of Polymer Products

4.1 Overview

Sustainability assessment requires a case-specific combination of tools, methods, and data around ecological, economic, and social chances and risks.

Since an assessment on the level of the material is not complete, an assessment on the level of products is required, which covers all life cycle phases, i.e. production, use and end-of-life. Such a Life Cycle Sustainability Assessment (LCS) should be the core of an assessment, while it has to be completed by a variety of other tools, which address e.g. compliance with local emission limits and consumer protection regulations. Legal compliance requires other efforts than an overall sustainability assessment. Since compliance is an issue companies have to deal with anyway and many different tools and methods are developed and used, this topic is excluded here.

The following subsections will focus on the environmental assessment along the life cycle of products. Some aspects of cost aspects and social sustainability will briefly be addressed as well. Especially regarding social aspects, several approaches have already been presented by different research groups. However, methods are still under development. It can be expected that reliable life cycle decision support in social working environment issues will be available and practice-proven from about 2010 or 2011 onwards.

Life cycle modeling and sustainability assessment support companies in the following areas:

- Calculate the Carbon footprint of your product, or event
- Finding solutions within design alternatives like answers to questions of material or process choice
- Carry out environmental benchmark studies of technologies and energy-efficiency studies
- Evaluate cost-effectiveness of environmental measures and/or directing efforts to most effective ones
- Calculate green house gas balances as support to emission trading schemes
- Support Environmental Management Systems (ISO 14001 and EMAS II support)
- Support Sustainability Reporting following GRI guidelines
- Support life cycle based labeling schemes such as the European environmental label (see e.g. http://www.bau-umwelt.com, and EC Mandate M350 of the European Commission)
- Provide Environmental Product Declarations (EPDs) for B2B communication of Life Cycle Effects of intermediate materials and parts
- Identify social aspects that require special attention – also in-house but especially those induced by the companies' economic activities along the products' life cycles such as via material supply and disposal of its products
- Identify existing weak-points within the supply chain as well as optimization potentials, e.g. how much SO_2 emissions are released and what possibilities exist to reduce them
- Support stakeholder communication
- Support argumentation with authorities
- Be prepared for upcoming regulations and support strategic decisions linked to these (e.g. lead-free stabilizers, meet future recycling quota, solvent-free coating, Directives of Energy-consuming Products and others, etc.)
- Link environmental monitoring and material-flow based strategic cost risk analysis. For example, what aggregated production cost potential might be related to CO_2 emissions along the life cycle of a product? What is the influence of the oil price on my product price?
- It depends on the specific situation and materials / products in focus where a life cycle study is of highest value

While the sustainability assessment of products requires a consistent approach independently of which materials the products are made, polymers require special attention in some issues. These will briefly be tackled in the next section before moving to the generally required approach.

4.2 Polymer Products and the Chemical Industry

Products of the chemical industry constitute the basis of many goods required for our daily needs. Plastics are characterized by a wide range of properties, e.g. their flexibility, insulation, and light weight. The comparison among materials from an ecological point of view requires an extensive approach on the product or process level. This is offered by a Life Cycle Assessment (LCA). In the same way, effective optimization potentials in the production or application can be identified with this enhanced view. The challenges from a life cycle perspective of processes and products from the chemical and plastic industry can be highlighted as:

- The high diversity of substances and highly integrated production sites require large amounts of data in order to allow the evaluation of their environmental effects.
- Extensive knowledge about technologies and routes of production of chemical substances are needed for making statements about the environmental impact of these substances.
- For the comparison of different technologies and routes for a product and the assessment of ecological weak-points it is necessary to understand the configuration of the processes and to have knowledge about the unit operations they consist of.
- Plastic products are made of tailor-made polymer compounds that involve a variety of relevant contributors such as flame retardants, softeners, and stabilizers. Data on real compound formulations is required.
- Recycling of polymers is somewhat restricted compared to that of metals, as polymers age after long use. Also the material separation of mixed plastics at the level of the polymeric compound is more difficult than it is for most metals. The feasibility of recycling, the quality of the recyclates, and the allocation of environmental impacts towards the recyclates is therefore more difficult.

Experience gained over the past 20 years makes life cycle studies of polymer products for experienced life cycle experts nowadays as easy as for most materials.

The following three subsections present the three inter-linked methods Life Cycle Assessment, Life Cycle Engineering (LCE), and Life Cycle Sustainability. LCA will be introduced first since it is subject to an ISO standard and forms the “classical” core of life cycle studies. The further developments towards LCE and LCS are addressed in the following sections. Links to further reading and other information sources will be given in the text and in the list of references.

5 Life Cycle Assessment According to ISO 14040 ff[1]

5.1 Introduction

For many years, the environmental assessment of materials, processes, and products took place in a rather isolated, non-quantitative manner. Simple, often only qualitative indicators on the content of potentially toxic compounds in products or on the water consumption of processes were used. However, it turned out, that effects have to be quantified and that all relevant impacts and not just some have to be considered. This integrated assessment was completed after the insight was gained, that the complete life cycle of the products has to be considered.

With the Life Cycle Assessment method developed from the late 1980s of the twentieth century, it has become possible to assess the overall environmental impacts caused by products or product systems. With the help of LCA, parts, components, complete products as well as technologies and processes of any type, material, purpose and in any industry can be investigated and possibilities for an ecological optimization can be identified.

An important foundation has been set in the international standard series ISO 14040 ff, which was developed by the end of the 1990s [17–20]. The main three standards 14041, 14042, and 14043 have recently been very slightly revised and summarized to a new standard 14044 which is available since 2006.

Basic principles have been described in these standards which need to be heeded when conducting an LCA. The abstract rules contained within the standard must be transformed into concrete single steps for each respective case. On the other hand, there are common aspects that require special attention in specific industrial sectors. A guideline for conducting inventory analysis e.g. in the construction materials industry already exists [21–23]. These guidelines help building materials manufacturers to carry out inventory analysis for their respective production processes in accordance with the requirements of the standard. Since the guideline guarantees a uniform application of LCA for all sectors of the construction materials industry, the results of different studies can be used for further analyses of building components and buildings. This guideline was developed within the framework of the research project “Life Cycle Assessment of Construction Materials and Buildings.”. The Institute of Polymer Testing (IKP, with the work now continued by the LBP), the Institute of Construction Materials (IWB) at the University of Stuttgart (Germany), as well as a large number of enterprises and associations in the field of the building material industry, building contractors, and suppliers of technical equipment took part in this project.

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[1] Under the International Reference Life Cycle Data System (ILCD), a further specified practice guidance to the ISO 14040 series standards is currently being developed. This is co-lead by the European Commission’s Joint Research Centre (JRC) and consulted with a number of national LCA projects and industry associations worldwide. For more information see chapter 8.3 “Latest developments” and related www links.

Also in other industries, such as the automotive industry, chemical industry, basic materials industry etc. and more recently the electronics industry, LCA is in practical use in-house in the context of product development, technological decisions, for strategic planning and marketing. Leading companies and associations such as ABB, Airbus, Alcan, Alcoa, Alsecco, Alusuisse, Anglo Platinum, Arcelor, Armstrong Building Products, Atochem, Audi, Autoliv, BASF, Baufritz, Bayer, Behr, BFH, Bizerba, BLZ, BMW, Bosch, BV Baustoffe, Steine und Erden, BV Gips, BVP Porenbeton Informations-GmbH, CeramTec, Chrysler, Ciba, Ciba Specialty Chemicals, Conti Temic microelectronic GmbH, Continental, Curamik, Daimler, EVONIK Degussa, Degussa Metals Catalysts Cerdec, Delphi, Deutsche Bahn AG, Deutsche Gesellschaft für Holzforschung (DGfH), DOW Chemicals, DSM, DuPont, Dürr, EBARA, Eisenmann, Enichem, ExNorm, Falconbridge, Faurecia, Fiat, Ford, FV Bims, General Motors, GEP, Grundfos, HeidelbergCement, Hilti, Hoechst, Honda, Hüls, International Iron & Steel Institute (IISI), ISOVER, Isuzu, JEITA (Japan Electronics and Information Technology Industries Association), Johnson Controls, Junkers, Kronospan, LG Electronics, Mann+Hummel, MCC, Mitsubishi, Motorola, Nissan, NKL, Nokia, Norsk Hydro, Opel, Porsche, Posco, PPG Industries, PSA, PT Timah, Renault, Rockwool, Samancor, Schwörer, Siemens, Sollac, Solvay, Sony, Stiftung Initiative Mehrweg (SIM), STO, Temic, Tenax, ThyssenKrupp, Toyota, TRW, Umicore, Ursa, Vaillant, Valeo, VDO, Vetrotex, Viessmann, Vinyl2010, Volkswagen, Volvo, WeberHaus, Wilo, Wörwag, Xella, ZF use LCA in decision support, often with in-house experts and on a regular basis.

The same holds true for governmental institutions at national and international level of which many use LCA as an assessment tool in projects and increasingly consider life cycle aspects in legislation, as was briefly pointed out and illustrated in the introduction to this work. Further reading on Life Cycle Assessment in practice can be found e.g. in [3, 24].

5.2 *Overview*

Life Cycle Assessment is a suitable tool for analyzing and assessing the environmental impacts that are caused through production, use, and disposal of products or product systems (as well as services) for specific applications. LCA itself does often not produce clear-cut straightforward assertions but helps in decision making by making complex issues transparent and by aggregating large amounts of data to a few indicators. The standard ISO 14040 defines an LCA as follows:

“LCA is the compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle.”

The concept of an LCA is mainly concerned with the following basic aspects:

- The observation of the whole life cycle of a product – from raw material acquisition, processing, and production to its use, recycling, and disposal including all transportation and storage steps.

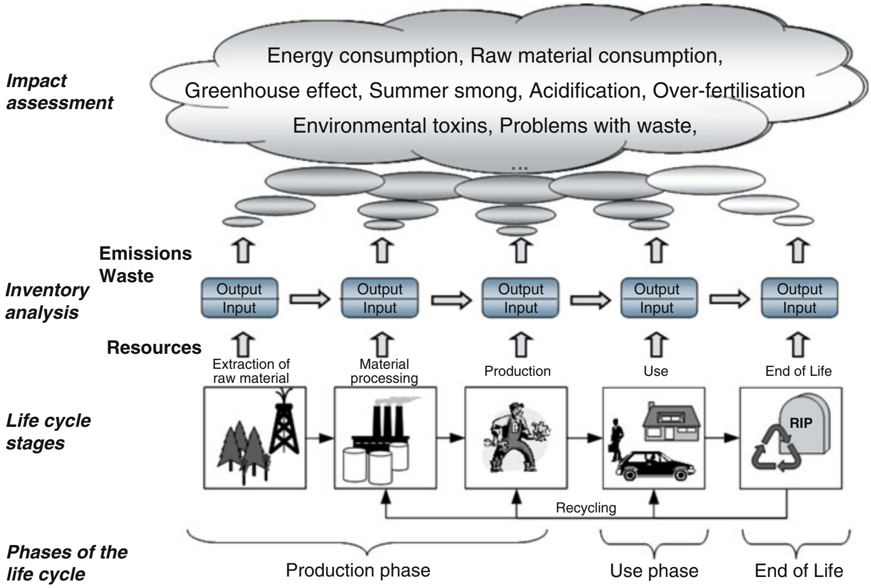

Fig. 4 Life Cycle Assessment of products

- The coverage of all those impacts on the environment, such as raw material and energy consumption, use of land (input flows), emissions to air, water, and land, as well as waste (output flows) associated with the life cycle.
- Aggregation and assessment of these impacts in view of the possible effects on the environment with the aim of assisting environment-oriented decisions.

Figure 4 gives a schematic, graphical overview of Life Cycle Assessment.

According to ISO 14040 the application fields of an LCA can assist the user in (see Fig. 5):

- Identifying opportunities to improve the environmental aspects of products at various points in their life cycle.
- Decision making in industry, governmental, or non-governmental organizations (e.g. strategic planning, priority setting, product or process design or redesign).
- Selecting the relevant indicators of environmental performance, including measurement techniques as well as in marketing (e.g. an environmental claim, eco-labeling scheme, or environmental product declaration).

An LCA is organized into the following phases goal and scope definition, inventory analysis, impact assessment, and interpretation as shown in Fig. 5. The figure identifies the reciprocal influences of the individual phases and therefore shows the iterative character of an LCA. The application and the framework of the LCA have been separated to show that an application or a decision is not

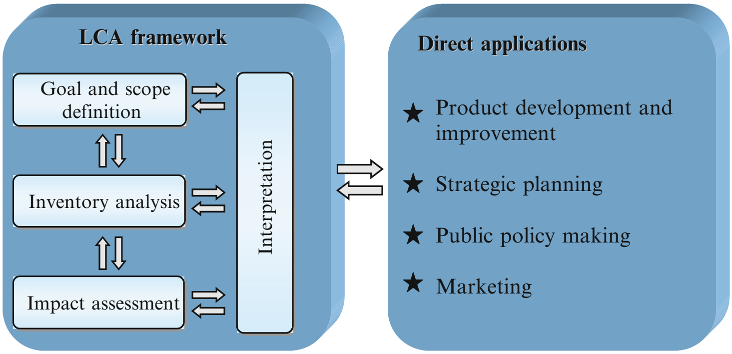

Fig. 5 Phases of an LCA

automatically given through the results of an LCA study. The responsibility for an appropriate application of LCI data remains with the user, it cannot be taken on by the client or the practitioner of an LCA study. The single phases of an LCA have been described in the following sections.

It must be emphasized that whilst the following points are to facilitate the understanding of an LCA, knowing the original content of the standard ISO 14040 is absolutely necessary in carrying out an LCA study which conforms to the ISO. Moreover, as for most tasks and especially for the complex issue LCA, experience is indispensable for effectively and efficiently carrying out an LCA, avoiding errors and producing reliable results.

However, even an LCA cannot cover all interactions with the environment. In this case, other tools must be used to fully observe the environmental impacts. LCO "only" can form a powerful and broad component in the tools used for environmental management and product development.

5.3 *Goal and Scope*

The definition of the goal of an LCA study is of central importance, since the results are related to the respective question. The following points must be documented in the goal definition:

- Intended application
- Reasons for carrying out the study
- Intended audience

Following the requirements established in ISO 14040, goals for studies can be:

- Weak-points analysis in the production for optimization of processes
- Accompanying assessment in the development of new materials for specific applications

- Accompanying assessment in the development of new or improved technologies with specific functions or system specification
- Decision-making assistance in marketing e.g. by comparison of a company's product with a benchmark (e.g. BAT, competitor's product, alternative production route, made of different material etc.)
- The optimization of a component or part
- The optimization of a complete product

Further goals of such a study could be:

- Assistance of strategic decisions
- Recognition of possible influences of the social and political context
- Identification of consequences resulting from political measures (e.g. in energy policy)

Defining the scope contains, in essence, the following points:

- System description
- Fundamental procedures
- Data requirements

These will be explained in more detail in the following subsections:

5.4 System Description

The system description contains an analysis of the system with a description and a transparent presentation (e.g. flow charts; see example in Fig. 6).

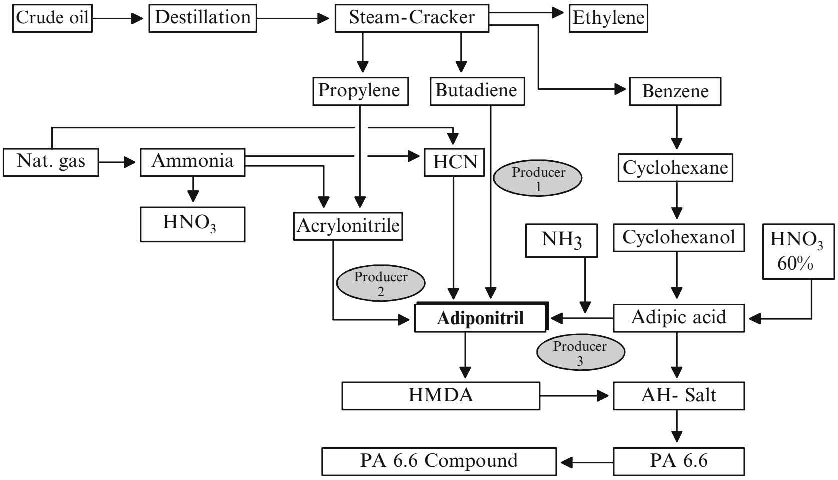

Fig. 6 Simplified cradle-to-gate system for a PA 6.6 Compound

An important step in the system description is the definition of the functional unit[2]. The spatial and temporal system boundaries are then defined (space and time under observation).

5.5 Fundamental Procedures

Defining and documenting the fundamental procedures is important when conducting an LCA. That includes basic rules as well as specific issues. These could be, for example, the desired level of detail and depth or the choice of impact categories within the study. The application of cut-off criteria (for input and output flows) which allow the exclusion of insignificant contributions is to be described. If a system produces several products the input and output flows have to be allocated to each product. These allocation procedures must also be shown.

5.6 Data Requirements

The data quality and consistency has a significant influence on the LCA results. Depending on the goal and the required precision for decision support, the requirements are to be formulated on the quality of data (e.g. on its precision, completeness, and representativeness). In this context, the sources of the data (of the LCA to be carried out) have to be named and the used data base with reference to the upstream processes (e.g. electricity production and production of basic materials etc.) should be documented. Any assumptions made, e.g. any estimations, should also be mentioned.

5.7 Life Cycle Inventory Analysis

Meaningful data of technical products and the life cycles behind them can only be obtained if the appropriate technical understanding and expert knowledge of the data collectors is ensured. Studies often lack especially in this regard. The main purpose of an inventory analysis in the context of data collection consists of the identification and quantification of the relevant input and output flows over the whole life cycle of a product. With these, one must also count, among others, the use of resources and the use of land, raw materials, fabricated products,

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[2] The functional unit specifies the function of the product system being studied and its efficiency. It serves as a reference for the established environmental impacts.

auxiliary materials, energy carriers, and electricity (input). Emissions to air, water and land as well as waste and by-products (output) must also be recorded in an inventory analysis. Only by covering the whole life cycle is it ascertained that no environmental burdens have been shifted to other life phases and therefore not taken into account. After the actual data collection, the product flows, i.e. those input flows under observation which cannot be directly taken from the crust of the earth, must be connected with the respective upstream process LCI data. This upstream chain is identical with the supply chain. This means that all the necessary expenditure needed in providing the input flows (e.g. in the production processes or transportation) must also be taken into consideration on entering the system. Appropriate cut-off criteria are to be defined in order to on the one hand ensure, that relevant data are compiled or collected but on the other hand to also limit the effort to the required minimum (Fig. 7).

Data calculation is likewise a component of an inventory analysis. The question of allocation is here especially of importance. An allocation should always be carried out when dealing with systems involving multiple products (e.g. electricity and steam as by-products from a power plant). It is then important to define a key to allocate the environmental burdens of the production to the individual product, since in a specific case we require only the data of e.g. electricity production, but have to exclude the share which is linked to the steam production. This requirement of carrying out an allocation of the environmental burdens also applies for recycling. The most appropriate allocation key is typically the market value of the co-products, but e.g. the energy content and others are also in use, depending on the specific situation.

Some comments are made in the following on the different recycling types and possible allocation solutions to be applied:

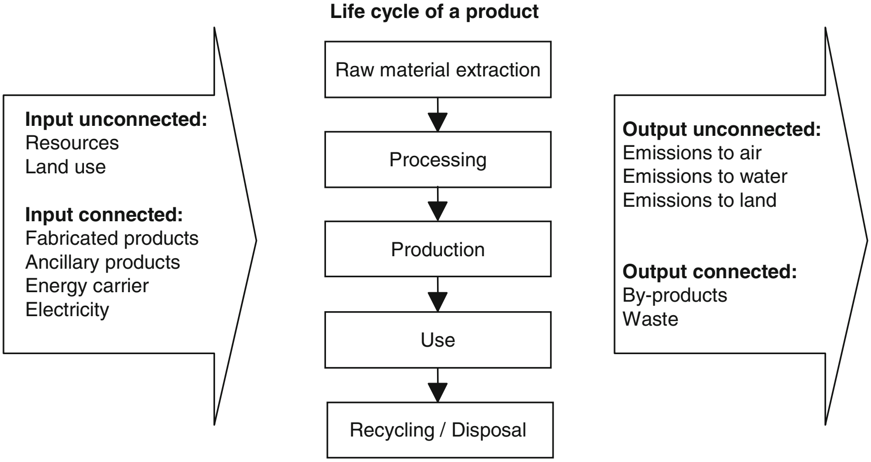

Fig. 7 Examples of input and output flows in the life cycle of a product

5.7.1 Closed Loop Recycling

With respect to the assessment method closed loop recycling represents the easiest way of calculating benefits/burdens. Closed loop recycling means that parts or materials will be used again in the same product. Especially for materials it also would mean a re-melting or re-granulating of materials and the application in exactly the same product type. No down-cycling or undefined dispersion of materials or parts in the market takes place. Thus, a calculation of benefits could take place by reducing the demanded primary materials and parts during the manufacturing phase of one life cycle by the amount of recycled mass of materials or parts during the end-of-life of the same life cycle. Certainly, in addition the burdens to gain these recycling fractions, i.e. the environmental effects of the recycling process, have to be calculated.

Often the processes to gain recycled materials cause lower impacts than the production of virgin materials and, thus, the benefits from recycling are reflected in the assessment of closed loop recycling. If a material is down-cycled, e.g. thermoplastics or fibers in reinforced polymers, it could not be used again for the same application. A calculation of these recycling benefits leads to open loop recycling.

5.7.2 Open Loop Recycling

Closed loop recycling normally is an exception of the recycling activities. It may take place for re-used parts or for material recycling loops during manufacture, e.g. the re-granulation of sprues of molded plastic parts. But it is not guaranteed that recycled material fractions from post-consumer waste will circulate always for the same product type. Normally, gained materials from recycling are dispersed in the market and will lead to various nondefined products. This becomes even clearer when looking at energy recovery from thermal recycling. In these cases, the benefit of the waste (if recycled) has to be calculated; various approaches are still used for this purpose, while harmonization is underway.

5.7.3 Allocation in Life Cycle Cascades

Various allocation methods are generally applied in LCA. Basically, the allocation method does not calculate benefits for recycling or gained recycled materials or products for the life cycle under consideration. The idea of the allocation in recycling is to distribute burdens that arise in the primary life cycle to other life cycles, which benefit from the first one. Thus, the environmental impacts are decreased from processes that turn out in one life cycle but provide functions to future life cycles of other products.

The influence due to the choice of the allocation method is significant. The result of environmental assessment differs also by the considered life cycle (primary, secondary, . . .). The principal problem of allocation is, therefore, the decision for the allocation rules and the considered life cycle.

5.7.4 System Expansion

In case of system expansion, other than in allocation, “benefits” attributed by usable secondary products or materials are calculated, which represent the saved environmental impact in another life cycle of the product. Quantification of these benefits depends primarily on the quality of the secondary product and the definition of its application.

It is presumed that the gained secondary material substitutes primary material. Therefore, the burdens of the processing of primary materials can be subtracted from the first life cycle, which leads to a decrease of the environmental impact.

However, the criteria used for this method is not unitary. The criteria have to be defined by the examiner. A debatable point of this method is how to count and measure the quality of the secondary product compared to the primary product

The use of system expansion is recommended in ISO 14041. However, also the implementation of allocation is allowed, which has to be considered a wise decision since allocation is considered more appropriate in most cases. Therefore, the choice of method has to be made case-by-case, unless a harmonization under the ISO standard is achieved.

5.7.5 Checklist for Inventory and Life Cycle Modeling

In addition to this, a uniform process of working is needed for data collection and calculation, which should be clearly illustrated. The concrete proceedings in the form of checklists specified for the production of products in enterprises of the basic materials industry are listed exemplarily as:

- Determination of reference unit
- Sketch of flow charts
- Interface setting between the unit processes[3]
- Qualitative determination of inputs and outputs
- Quantitative determination of inputs and outputs
- Documentation of the type of data survey
- Inventory data collection in the plant
- Inventory data collection of transport
- Calculation of the inventory plus primary chains

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[3] Unit processes allow the partitioning of inputs and outputs to each process step. Unit processes may consist of one or several processes up to a whole production site.

5.8 Life Cycle Impact Assessment

5.8.1 Overview

The impact assessment is carried out on the basis of the inventory data. The data is categorized in impact categories according to its potential impact on the environment. These categories describe the potential environmental impacts and not the actual effects, since the real effects depend on broader parameters that are not registered by an LCA. This includes, for example, spatial and temporal parameters since an assertion over actual environmental impacts is connected with where and when the emissions, which have been added up, have actually been released. A detailed site-specific modeling of releases to the environment is used in Environmental Risk Assessment, which is the principal methodological basis also for impact assessment models in LCA, but works on a location-specific context and requires a considerably higher data input.

Such an impact category is, for instance, the well-known Global Warming Potential. All emissions that produce a potential contribution to the greenhouse effect are assigned to this category. The most well-known emission in this category, due to the current discussion, is carbon dioxide. However, also other substances contribute to Global Warming such as methane, laughing gas, and SF6, for example.

In classifying the inventory data according to their potential environmental impacts, an aggregation of typically several hundred elementary flows to a maximum of ten impact categories (see more below) takes place. Out of these principally involved impact categories, typically only two to four relevant ones can be identified; which ones these are depends on the specific case. The amount of the data is therefore considerably reduced and the results can better be interpreted by referring directly to the environmental impacts. Since the inventory data is related to the functional unit of the analyzed product or process, this relation also exists in life cycle impact assessment. These results and data obtained from the impact assessment are used together with the inventory results in the interpretation phase of an LCA. Next to coming to the various impact categories such as global warming, acidification etc. also a further calculation of actual damages in terms of harm to human beings and changes in Ecosystems is carried out in some methods. These "end-point" methods have the aim to provide a scientific basis for calculation of better and more directly comparable effects. The before mentioned "mid-point" methods require weighting factors, which help to assess the relative relevancy among the impact categories.

5.8.2 Details

The standard ISO 14042 divides the phases of the impact assessment into mandatory and optional elements.

The mandatory elements are:

- Choice of impact categories,
- Classification, and
- Characterization.

The optional elements are:

- Normalization,
- Grouping,
- Weighting, and
- Data quality analysis.

5.8.3 Choice of Impact Categories

The first step within the framework of an impact analysis is the choice of impact categories in connection with the scope and goal definition. The choice of impact categories to be considered depends on the specific case and will not be explained here in detail. Generally the included impact categories have to be relevant for the analyzed process or product, e.g. the Summer Smog formation is relevant for processes dealing with organic solvents, while Global Warming is relevant where carbon-based energy carriers are incinerated.

5.8.4 Classification

Classification comes next, where the inventory data is assigned to categories according to their impact. For instance, carbon dioxide emissions contribute to the greenhouse effect. If a substance contributes to several impact categories, it has to be taken into account, in all of these categories. Such a case is, for example, nitrogen oxides which are both the cause of eutrophication and acidification in lakes and soil as well as of health impacts to human beings which are exposed to the substance in the air.

5.8.5 Characterization

Classification is followed closely by characterization: To every substance is assigned a potential impact in the impact category under study. The potential impact of a substance is set in relation to a dominant factor in the category. The reference unit for example. the greenhouse potential is 1 kg carbon dioxide. The values which result from it are described as impact factors. For instance, the emission of 1 kg of methane which has a stronger greenhouse effect corresponds to the emission of 24.5 kg CO_2; methane therefore gets the equivalent value of 24.5 kg CO_2 per kg of methane allocated. After multiplying the emissions by the impact factors they are added to the respective impact category and summed up to a total. Emissions and the respective impact factors used internationally are found in [25].

The inventory data and the classified and characterized results are the ecological profile of the product or product system under study. These profiles may be used as modules for the life cycle assessment of subsequent products, for which these products are input of goods (e.g. LCI data of a steel production analysis are the basis for an LCA of a car made of tailored blanks such as building material profiles, for example, may be used to analyze buildings). A prerequisite for this is however that the methods and background data used for the modeling of the systems are identical.

5.8.6 Normalization

The optional element called normalization places the contribution of a product system in relation to the contribution of a region such as a country or continent or an average citizen of such a region. In this way the significance of the contribution of a product to an impact category can be shown. The normalized results show accordingly to which environmental problem field the system under study contributes most. This, however, does not provide any assertions on whether one impact category is more important than the other from an ecological point of view. Information and data on normalization can be found in the LCA guide [25].

5.8.7 Grouping

Within grouping each impact category may be assigned to a group (e.g. subdividing impact categories into regional, local, and global groups) or in terms of a sequence of impact categories which have been established according to their (subjective) significance. This does not imply that the results of different impact categories may be transformed into one indicator, in other words, the grouping still does not imply an aggregation of data.

5.8.8 Weighting

Weighting, on the other hand, aims at an aggregation of impact categories. The relative relevancy of the environmental problem field Global Warming is weighted against that of Acidification, for example. What needs to be taken into consideration is that a weighting of such different environmental impacts is based on values and therefore cannot be attributed to scientific knowledge. In special cases however, the impact assessment results can be further aggregated in an evaluation. A prerequisite for this is that the impact assessment results maintain their transparency and accuracy and that the data before weighting is available. Practice experience however shows, that often a better decision support can be given on the level of the impact categories and / or normalized results. Weighting can however help to identify the dominant two to four impact categories. A “blind” interpretation based upon a total aggregation to one single environmental indicator is not allowed in comparative studies according to ISO 14040 ff.

Some impact method systems further calculate the actual (expected) impact of the environmental problem fields, e.g. how many people can be expected to die due to rising sea level due to global warming. This step has the advantage of making the problem fields more comparable, as only the effects are compared, which can be measured in the same unit (here: number of dead people). The disadvantage is the very high uncertainty that lies behind such calculations, which strongly lowers the value of the numbers. The same holds true for methods that calculate the impacts in costs, e.g. Euro impact due to increased health costs or damage to forests. Moreover, also for such “end-point” methods weighting is required: among the safeguard objects man, nature, and resources, for example.

5.8.9 Data Quality Analysis

As a last step the standard deals with data quality analysis. This step should support the validity of the analysis. Methods for more reliable data quality analysis are a present focus of research and international harmonization.

5.8.10 Choice of Impact Categories

In the standard ISO/DIS 14042 no standard impact categories are defined for application. The requirements for the choice of impact categories are however set. These are for example:

- Conformance with the goal definition
- Comprehensive choice of environmental issues in relation to the product
- Clear citation of sources
- Explanation and description of the categories and working mechanisms
- Arguments for choice

Over and above this, recommendations as to choice are given for example:

- International acceptance of the impact categories
- Avoidance of “double counting” of the same impacts in several categories (e.g. by erroneously taking into consideration the impacts “acidification” and “proton input” in separate categories)

An interdisciplinary expert group (SETAC-Europe[4]) has developed recommendations for the best available models for impact categories. The choice of the

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[4] Society of Environmental Toxicology and Chemistry.

Table 1 Impact categories which assess environmental impact

Impact category/ aggregated inventory data	Source	Short description	Examples
Depletion of resources	[24]	Non-sustainable raw material use	Petroleum or ore extraction
Greenhouse warming potential (GWP)	[43–45]	Emissions to air which influence the temperature of the atmosphere	CO_2, CH_4
Ozone depletion potential (ODP)	[46–48]	Emissions to air which deplete the stratospheric ozone layer	CFCs
Acidification potential (AP)	[24,48,49]	Emissions to air which cause acid rain	NO_X, SO_2, HCI, HF
Eutrophication potential (EP)	[24,48,49]	Eutrophication of lakes, rivers and soil	P and N compounds
Photochemical ozone creation potential (POCP)	[50–56]	Emissions to air which lead to ozone production in the lower troposphere (close to ground level)	Hydrocarbons
Human toxicity potential (HTP)	[57–60]	Emissions to land, air and water which are harmful to human health	Heavy metals and dioxins
Ecotoxicity potentials (AETP and TETP)	[57–60]	Emissions to land, air and water, which harm and disturb ecosystems	Heavy metals, acids, etc.
Land use	[28,29]	Duration and type of man-made occupation and change of land	Area used for crop production, raw material extraction, etc.

impact categories should generally aim at sustainable development, preserving resources, the global protection of the eco-sphere, protecting human health, and the stability of the ecosystems. Comparative LCAs lead to different results depending on the choice of impact categories under study, which have to be justified in the goal definition.

In accordance with the above-mentioned aspects, the impact categories and their respective source have been listed in Table 1.

The methodology of impact assessment for some environmental impacts is still under scientific development. This applies especially for the toxicity potential (HTP, AETP, TEPT). The impact models and methods for these and their use in decision making has partly been recalled recently also by developers of the methods [26]. Land use is also still under development while of high relevancy e.g. for polymers or energy carriers made from renewable resources.

The following impact categories, which have been approved internationally, are considered to be important and of higher robustness when conducting LCAs:

- Global Warming Potential (GWP) in kg CO_2-Equivalent
- Acidification Potential (AP) in kg SO_2-Equivalent

- Eutrophication Potential (EP) in kg PO_4-Equivalent
- Photochemical Ozone Creation Potential (POCP) in kg C_2H_4-Equivalent
- Ozone Depletion Potential (ODP) in kg CFC 11-Equivalent

Resource depletion is another "impact" of importance here. Resource depletion is presently accounted for as extraction of primary energy (for energetic resources) and/or according to the surplus energy concept (for both energetic and material resources).

Resources are further separated into renewable and nonrenewable. Fossil fuels like coal, petroleum, and natural gas belong to the nonrenewable energy carriers. In the renewable energy, we find, for example, water and wind energy but also those from renewable raw materials. The expenditure specification in primary energy (PE) in megajoules (MJ), which is divided into renewable and nonrenewable energy carriers, represents a common aggregation of energetically used resources. In addition, the use of secondary energy carriers has to be separately documented.

5.8.11 Waste

While often waste is considered an impact category, waste treatment and dumping is indeed part of the technical system and should be integrated into the system under study. Its environmental effects are assigned to the known impact categories including land use. If this is not possible, the waste can be documented in groups such as: overburden, ore processing residues, household waste, and hazardous waste. Such waste mass information is often also of interest as it provides another, technical indicator pointing to the use of waste deposits.

5.8.12 Description of the Most Relevant Impact Categories

In the following subsections, the proposed impact categories and their definition as well as the basic impact mechanisms and effects will be described in detail. Information on other impact categories such as the toxicity categories can be found in the CML-2001 table in [27] or further in the original sources listed in Table 1. Land use is briefly described here, but in more detail in [28].

5.8.13 Global Warming Potential (GWP)

The mechanisms of the greenhouse effect can be observed on a smaller scale in a car, in living rooms, or as the name indicates in greenhouses: The incoming short-wave sunlight can penetrate the glass almost unhampered and is transformed into long-wave infrared radiation when coming into contact with nontransparent elements or objects found in the room. The long-wave infrared radiation cannot leave the room unhampered since it is absorbed by the glass and partly released again into the room. The occurring radiation energy input is therefore greater than that energy, which is leaving the room. This leads to an increase in the room's temperature.

What has been described here can also be observed on a global scale. The occurring short-wave sun radiation comes into contact with the earth's surface and is partly absorbed (which directly leads to warming) and emitted as infrared radiation. The reflected part is absorbed in the troposphere[5] by greenhouse gases[6] and is radiated again in every direction, so that it is partly radiated back to earth. This leads to a further warming.

Without the natural greenhouse effect the temperature would fall to about 18°C below zero. Life as we know it, would be inconceivable, since the average temperature on earth is now about 15°C.

In addition to the natural greenhouse effect, there is also an anthropogenic effect due to human activity. Greenhouse gases that are considered to be released anthropogenically are, for example, carbon dioxide, methane, and CFCs. The estimated contributions of gases relevant to the anthropogenic greenhouse effect are listed in Table 2.

An increase in temperature on the earth's surface can lead to serious changes. One such example would be the increased melting of the polar ice caps which is associated with a rise in sea level, whilst a change in the distribution of rainfall would lead to a shift in vegetation zones. The consequences have not been completely assessed. The fact is that presently an increase of about 1°C per 100 years in the earth's surface temperature is observed. It is no longer a real controversy that this tendency was caused by the anthropogenic greenhouse effect – natural fluctuations

Table 2 Climatic gases which contribute to the anthropogenic greenhouse effect

	Proportion of additional greenhouse gases (%)	Increase of concentration per year (%)	The most important anthropogenic sources
Carbon dioxide (CO_2)	50	0.5	Combustion of fossil fuels, deforestation
Methane (CH_4)	19	1	Rice cultivation, cattle breeding, waste, fossil fuels
Fluorine–chlorine–hydrocarbons (CFCs)	17	5	Aerosol/propellants, cooling, cleaning, fire suppressants, foaming agents
Tropospheric ozone (O_3)	8	0.5	Nitrogen oxide and hydrocarbons emissions
Nitrous oxide (N_2O)	6	0.3	Eutrophication, deforestation, biomass combustion

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[5] Troposphere: Lower part of the atmosphere up to about a height of 10 km.

[6] Gases with a strong absorption band in the range of infrared (IR) light are called greenhouse gases [43]. Water steam and carbon dioxide are typical examples.

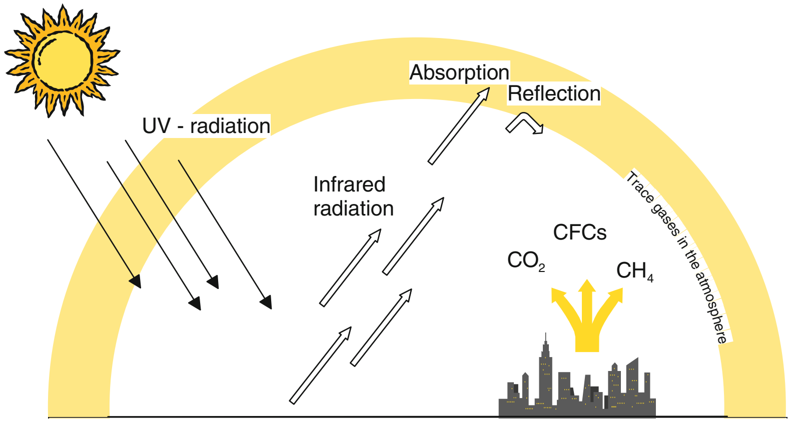

Fig. 8 Anthropogenic greenhouse effect – schematic illustration

however might contribute to it. Figure 8 shows the most important mechanisms of an anthropogenic greenhouse effect.

The greenhouse potential is calculated in carbon dioxide equivalents (CO_2-Eq.) This means that the greenhouse potential of an emission is given in relation to CO_2. Since the length of stay of a gas in the atmosphere must be included in the calculation, the time horizon under observation must always be given. This is usually given in relation to 100 years. In evaluating the greenhouse effect, it should be taken into consideration that the effects are global and of a long duration.

5.8.14 Ozone Depletion Potential (ODP)

Ozone is created when oxygen molecules are irradiated with short-wave UV-light. This leads to the building of the so-called ozone layer in the stratosphere (15–50 km of height). Under the pressure at sea level this shield would have a thickness of only 3 mm ozone. In spite of its minimal concentration, the ozone layer is important for life on earth. Ozone absorbs the short-wave UV-radiation and releases it without any direction in longer wavelengths. Only a part of the UV-radiation reaches the earth protecting life against cancer and mutagenic effects in chromosomes.

Anthropogenic emissions cause the depletion of the ozone. This is generally known through reports on the hole in the ozone layer. Although these reports referred only to the Antarctica area, ozone depletion is now also discernible to a lower degree on the mid-latitudes (e.g. Europe).

The substances which have a depleting effect on the ozone can be grouped essentially into two. These are fluorine–chlorinehydrocarbons (CFCs) and nitrogen oxide (NO_X). Figure 9 shows the essential aspects of ozone depletion.

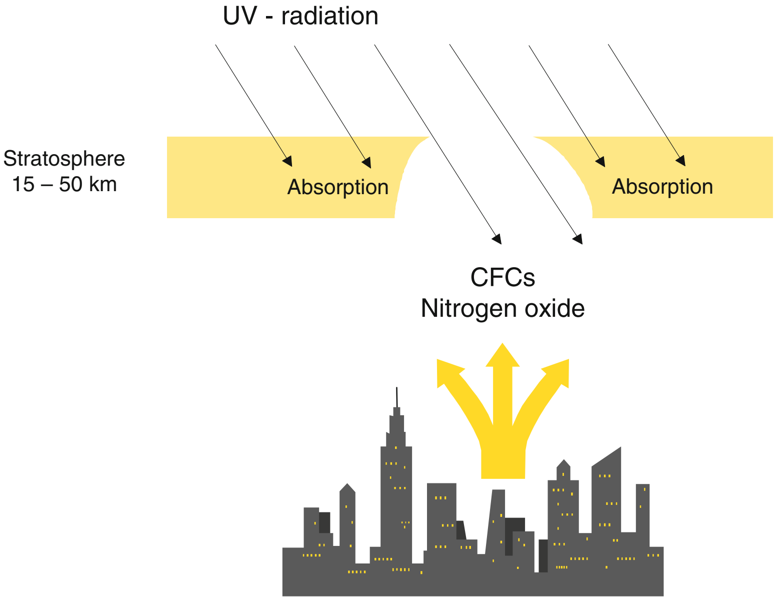

Fig. 9 Ozone depletion – schematic illustration

The sensitivity of man, animals and plants to UV-B and UV-A radiation is of special importance. Possible effects are, for example, growth changes or a decrease in harvest crops (photosynthesis disruption), tumor indications (skin cancer and eye diseases) and the decrease of sea plankton, which would affect the food chain. One side-effect of ozone depletion is the warming up of the earth's surface.

In calculating the ozone depletion potential, the anthropogenically released halogenated hydrocarbons, which can destroy many ozone molecules, are first of all recorded. The so-called ozone-damaging potentials (ODP: Ozone Depletion Potential) result from calculating different ozone relevant substances. This is done by calculating, first of all, a scenario of a fixed quantity of emissions of a CFC reference (CFC 11). This results in an equilibrium state of a total ozone reduction. The same scenario is considered for each substance under study whereby CFC 11 is replaced by the quantity of the substance. This leads to the ozone depletion potential for each respective substance, which is given in CFC 11 equivalents. An evaluation of the ozone depletion potential should take into consideration the long-term, global, and partly irreversible effects. After the ban of those substances that severely affect the ozone layer in many countries world-wide during the 1990s, the emissions went down considerably; some countries still produce these substances however. Also, the action of these substances will continue for several tens of years, since they slowly migrate into the troposphere continuing to destroy the ozone layer.

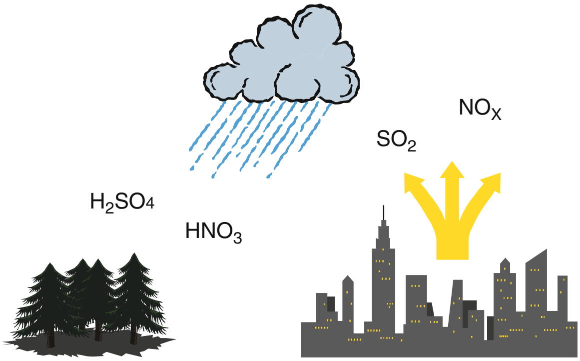

Fig. 10 Acidification – schematic illustration

5.8.15 Acidification Potential (AP)

The acidification of soils and waters arises predominantly through the transformation of air pollutants into acids. This leads to a decrease of the pH-value of rainwater and fog from 5.6 to 4 and below. Sulfur dioxide and nitrogen oxide and their respective acids (H_2SO_4 and HNO_3) produce relevant contributions. Damage occurs to ecosystems, of which the dying of forests is the most well-known while e.g. Sweden has more severe problems with dying lakes. This can lead to direct or indirect damage (nutrients being washed out of soils, an increased solubility of metals into the ground). Also buildings and building materials become damaged. Examples of this are metals and natural stones which are exposed to accelerated corrosion and dissolution (Fig. 10).

The acidification potential is given in sulfur dioxide equivalents (SO_2-Eq.). The acidification potential is described as the ability of certain substances to build and release H^+-ions. Certain emissions can also be considered to have an acidification potential, if the given S-, N-, and halogen atoms are set in proportion to the molecular mass of the emission. In evaluating acidification it should be taken into consideration that although it refers to a global problem, the effects, however, may differ regionally.

Because of the strong improvement of power plants in Western European countries and (technically induced) reduced sulfur content in fuels for cars and trucks, the emission especially of SO_2 has decreased dramatically. However, NOx is still emitted in large amounts also in Europe (and more so e.g. in the US) and the pre-damaged situation of lakes and forests require that further attention be paid to the acidification problem.

5.8.16 Eutrophication Potential (EP)

Eutrophication is the enrichment of nutrients in the environment. Often, aquatic and terrestic Eutrophication are differentiated. Air pollutants, waste water, and fertilization in agriculture contribute to this effect. This results in an accelerated algae growth in waters, which in turn, prevents sunlight from reaching the lower layers. This then leads to a decreased photosynthesis associated with a lower oxygen production in these layers. Oxygen is needed for the depletion of the large amounts of dead algae. Both effects cause a decreased oxygen concentration in the water which can finally lead to fish dying and to an anaerobic decomposition. This leads to disturbance or even destruction of the eco-system.

In terrestic ecosystems, eutrophication also results in changes of the composition of the bio-coenosis: especially rare plants and animals vanish. Also the stability of the eco-system can be lowered.

Eutrophication also results in increased nitrate content in ground water through leaching processes. Nitrate then reaches drinking water. The conversion product nitride is toxic; especially to small children. Some sources of eutrophication are shown in Fig. 11.

The eutrophication potential is calculated in phosphate-equivalents (PO_4-Eq). As in the acidification potential one must also be aware of the fact that when it comes to the eutrophication potential, the effects differ regionally.

5.8.17 Photochemical Ozone Creation Potential (POCP)

Whilst the ozone has a protective function in the stratosphere, it is classified as an unhealthy and plant-damaging trace gas at ground level. Photochemical ozone formation in the lower troposphere, which is also referred to as summer smog, damages the vegetation and certain materials. High concentrations of ozone are toxic to humans.

Sun radiation and the presence of nitrogen oxides and hydrocarbons lead through complex chemical reactions to aggressive reaction products. Ozone is the most important reaction product. Nitrogen oxides alone do not cause high ozone

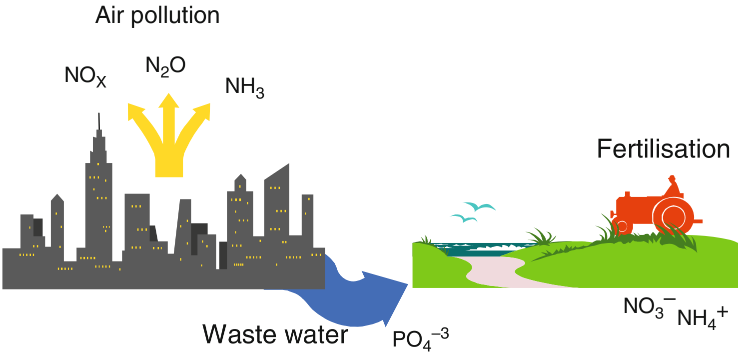

Fig. 11 Main sources of eutrophication– schematic illustration

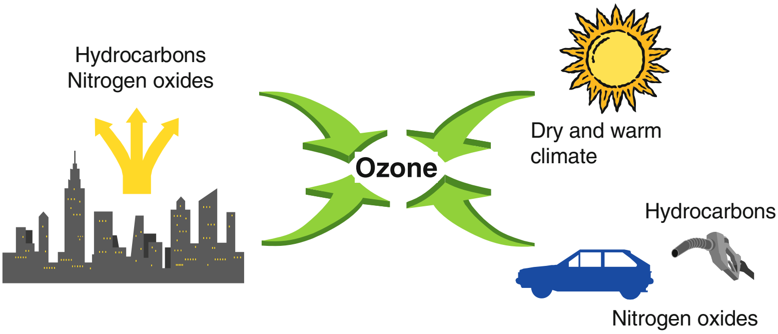

Fig. 12 Ozone creation at ground level– schematic illustration

concentration levels. Hydrocarbons must be present. Hydrocarbon emissions are released when dealing with petrol (storage, unloading, refueling etc.) or in connection with solvents or in the case of an incomplete combustion. Ozone concentration occurs in high temperatures, low air humidity, low air exchange, as well as high hydrocarbon concentrations. Since the presence of CO (usually from traffic) reduces the formed ozone to CO_2 and O_2, the highest ozone concentration does not often occur in the immediate area of the source. It occurs after some transport through the air rather in clean air areas (e.g. forests) and in areas where CO is hardly present. The photochemical ozone creation potential is referred to in ethylene-equivalents (C_2H_4-Eq.) in LCAs. In an evaluation it must be taken into account that the actual ozone concentration levels depend on the type of weather. Similarly, ozone formation must be analyed on a local scale (Fig. 12).

5.8.18 Land Use

LCA is addressing a variety of environmental problem fields from the perspective of the product's life cycle. If dealing with products based upon renewable resources, the land use of the cropping phase is of especially high relevance. Unfortunately the development of methodologies for including land use in LCA is still largely in its scientific stage. A basic approach followed today is the hemeroby approach based upon the works of [29]. The specific hemeroby approach employed considers two land use aspects: land conversion (e.g. from forest to agricultural area) and land occupation (e.g. use of a certain area of industrial land for a certain time period). In any product based upon renewable resources, cropping is known to be by far the most relevant land use type, while other land uses, such as industrial area, land transport area and others are of minor importance. Nevertheless, the latter should be addressed as well in order to provide a more complete picture; for products based upon nonrenewable resources they are the only contributors, moreover. The following processes typically contribute considerably to land use, in order of decreasing overall relevancy, which however will vary case by case:

- Agricultural cropping processes
- Forestry
- Surface mining
- Surface transport
- Storage and conversion in production plants

More advanced approaches, including the one under development at IKP, based upon the PhD thesis in [28], are not ready and have not been sufficiently tested so far for concrete decision support.

5.9 Life Cycle Interpretation

5.9.1 Overview

Within the framework of an evaluation, the results from the impact assessment and the inventory analysis are analyzed and conclusions and recommendations are established. A further aspect is the transparent presentation of the LCA results. The standard ISO 14043 comprises three interpretation elements:

- Identification of the significant issues
- Evaluation which considers completeness, sensitivity, and consistency checks
- Conclusions, recommendations, and reporting of the significant issues

5.9.2 Significant Issues

In order to determine the significant issues the main contributions of each impact category have to be identified ("Which emissions and/or which processes are dominant according to which category?"). The relevant inventory data which cannot be recorded through impact categories must also be integrated into the study. Following the scope definition the main contributions can be assigned to the individual process step, individual life phases, and the entire life cycle. Together with these results, the significant issues can now be established, since it is now also clear which processes or life phases are dominant.

5.9.3 Evaluation of Results

To evaluate the results according to the standard a completeness check a sensitivity check and a consistency check of the identified processes or life phases must be carried out. Completeness is checked by the mass and energy data analysis. Sensitivity is determined by calculating scenarios of different processes or different parameters. The effects of the different assumptions on the total result show the sensitivity. It must be ensured that all necessary information and data relevant to the interpretation are available and complete. It is also important to check to what extent uncertainties – for example through the estimation of data due to data gaps – may influence the result. These uncertainties may be determined by the calculation of a minimal–maximal range which reflects the possible extreme cases and the effects on the total results. The consistency check should ensure that the procedure is consistent with the goal and scope definition and that the methodology and rules have been accurately applied.

5.9.4 Conclusions and Recommendations

The third phase contains the conclusions, the recommendations, and the presentation of results. The relation between the interpretation phase and the other phases of LCA are illustrated in Fig. 5.

6 Life Cycle Engineering (LCE)

6.1 Introduction

Simply spoken, LCE is the extension of LCA by cost data and follows an engineering-based approach that brings LCA closer to the R&D decision support.

When LCA was developed in the 1980s, it came from an environmentalist background, i.e. often the technical understanding was not sufficient, and no attention was given to cost effects of measures and/or market requirements. Starting with this situation, the Life Cycle Engineering approach and similar eco-efficiency approaches and Produktlinienanalyse have been developed from the late 1980s onwards.

6.2 Approach

All these approaches such as LCA, LCE, and Eco-Efficiency base upon the same product model. The product model, i.e. the value added-chain (= supply chain) of a product plus its use phase and end-of-life, is the “backbone” of any product life cycle study. Elementary flows, i.e. mainly resources withdrawn from the environment and emissions released to the environment, are linked to this backbone in the LCA.

In LCE, cost data is additionally linked to this same backbone. Depending on the perspective of the contractor of the study, this cost data covers only specific processes. For example, for a polymer processor there is no need for a detailed cost model of crude oil production. He might however want to sell use phase cost advantages to his customers, which is why the use phase (e.g. fuel costs saved due to a light-weight approach in omnibus parts) becomes part of the cost model. Such a total cost of ownership (TCO) approach is then modeled consistently with the LCA model. To include disposal costs can be another step, which is interesting whenever take-back legislation is an issue. Other cost data of interest is upcoming cost for CO_2 emission certificates. Such additional cost factors, that also occur upstream, e.g. in crude oil processing, will affect future polymer prices, which is why a polymer processing company will be interested in modeling such upstream price effects as well. This can only be done if an adequate production life cycle model is available, that covers all relevant CO_2 emission sources in upstream processes.

Next to cost issues, LCE also puts a stronger focus on technical aspects. First of all, practice relevant decision support coming from LCA studies has to make sure, that the investigated alternatives are technically feasible. A better modeling of the product life cycle with technical requirements and material specifications supports this aspect. Past studies often lacked such expertise and approach, which is why its effect on real world products was limited. Secondly, design alternatives often result in other, indirect product changes. For example, changing from a metal-base die-cast air-intake manifold to an injection-molded polymer-based solution results in changes of the mounting elements, too. Such effects can only by included if the required engineering understanding is available. This avoids invalid results of LCA studies. Finally, the embedding of LCA into the R&D process significantly increases the relevancy of decision support: only early R&D support can be considered for changes of the product and production, which is why fast and still reliable LCA studies are a must. Comparison of already existing products have only minor effects, since only limited general conclusions can be considered for future product design (see Fig. 3).

Figure 13 shows the LCE scheme.

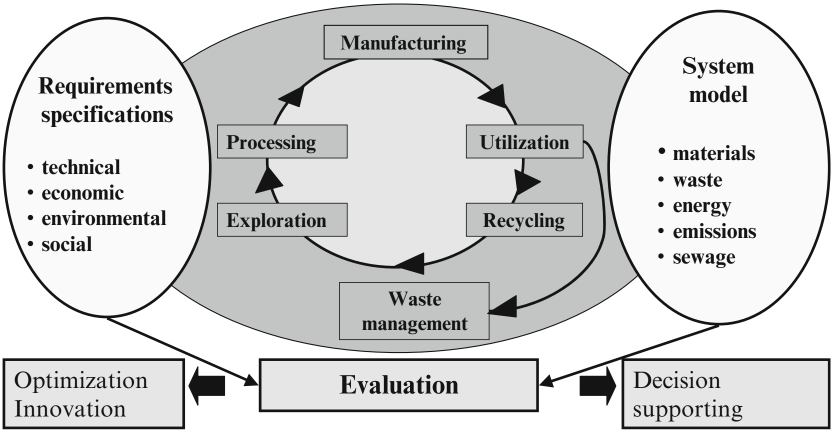

Fig. 13 Life Cycle Engineering scheme

6.3 Applications

Benefit for industry of LCE case studies

General

- Quantitative data on economic effects of environmentally motivated design alternatives for processes, products, or systems become available

Internal

- Environmental improvement potential of new technical solutions is quantified within complete life cycle of products by scenario simulation (specific weak-points known; new technologies)
- Better focus of effort in terms of money and other resources on optimization potentials within the process chain can be achieved; flow-related risks
- Strategic risks from environmental issues which are related with economic risks can be detected
- Motivation of employees is improved

External

- Advantage on the market in comparison with competitors
- Provides consistent information on environmental product performance and total cost of ownership implications
- Supports easier, fact-based communication with share holders and stake holders including public authorities and policy makers
- Provides reliable facts for communication with the general public and for marketing (both B2B and B2C)

By far most industry-based LCE studies are not publicly available, since they are confidential, of course. Some examples of LCE studies are however found in [12,30–34].

6.4 Conclusions

Fostering the development from LCA towards LCE both improves reliability of LCA results and allows one to simultaneously provide relevant cost figures on design alternatives.

7 Life Cycle Sustainability (LCS)

7.1 Introduction

While LCE introduced cost data to LCA and improved the engineering side of LCAs, LCS is an extension of LCE with social working environment aspects, the

Life Cycle Working Environment (LCWE). It is hence the consequent further development addressing for the first time all three columns of sustainability (i.e. environment, economy, and society) in one joined approach.

7.2 *Approach*

The modern LCS approach was developed in parallel by several institutes in the second half of the 1990s (e.g. [35–37]). Preceding work on social life cycle issues in France ("social balances" in the 1970s) and Germany (as part of the "Produktlinienanalyse" in the 1980s) did not have many applications in practice and vanished almost completely, although they were important predecessors of LCS.

The method Life Cycle Working Environment covers the amount of human work, the qualificational profile of work, accidents and often work-related diseases and the humanity of work (e.g. childwork, equal remuneration for women etc.). The specific indicators used and the approach to link the data to processes differ still significantly among the institutions. Table 3 shows the parameters included in the method developed in 1999 by the main author of this chapter at the IKP, Stuttgart, Germany (meanwhile renamed LBP Stuttgart). More on the method can be found in [38] and [39]. The methodology is made available in a professional software tool for LCA and LCE [40] and a database is in preparation.

Figure 14 shows the systematic inclusion of social aspects into the Life Cycle Sustainability approach at IKP. The original name LCWT (WT for "Working Time") was changed to LCWE.

Figure 15 shows how data collection on the level of the process is consequently extended from product and elementary flows as in LCA by cost and social process data.

Figure 16 shows the most suited systematic procedure for a full and integrated Life Cycle Sustainability Assessment. Please note, that not all aspects have to be addressed for all life cycle phases: Technological aspects are typically only relevant in the foreground system (here: production). In the next step, only those solutions that turn out to be technically feasible are evaluated from the cost side, typically covering the foreground system and e.g. the use phase if cost-relevant implications occur. In order to keep the effort limited, cost estimations often help to rule out several alternatives. The full life cycle assessment is done for the remaining alternatives and along the complete life cycle. Extensive, actual and high quality background databases minimize the effort for collecting new data. This can thereby often be limited to the foreground system plus use phase and end-of-life. Again, experience-based simplifications help to minimize the effort for the LCA. It has to be stressed however, that such simplification is only meaningful if extended experience for similar products and processes already exists. Otherwise simplification will lead to unreliable results. As the last step (or in parallel to the environmental evaluation) the social implications are analyzed. Here again the complete

Table 3 Social aspects in the working environment considered in the Life Cycle Working Environment methodology developed at IKP

“Qualified working time (QWT)”
Establishment of qualified jobs and support of socio-economic welfare
• Duration of work (= base indicator)
• Qualificational profile of work
• Training/Qualification on the job
• (Contract duration, Protection against dismissal)[a]
• (Minimum wages)[a]
“Health and safety of working time (HSWT)”
Protection of human health
• Lethal accidents
• Non-lethal accidents
• Working conditions (noise, dust, heat, cold, contact with irritating or unhealthy substances, odour, etc.)
• (Job-related diseases)[a]
“Humanity of working time (HWT)”
Humanity and flexibility of working conditions
• Worst forms of child labour
• Child labour
• Forced labour
• Discrimination (regarding access to job independently of sex, origin, religion, colour, race, disablement etc.)
• Equal remuneration for men and women
• Actual share of women work (general and in management)
• Right to organise in trade unions
• Right to collectively bargain
• (Daily and weekly working time, breaks)[a]
• (Flexibility of working time)[a]
• (Participation and career opportunities)[a]
• (Satisfaction of employees)[a]

[a] These indicators are still under discussion (if it is possible to include them although they do not fully meet the criteria for indicator-selection set up)

life cycle has to be considered. The best design alternatives are then the basis for R&D decision support. Depending on the specific case, the decision support might already clearly point to an alternative; otherwise the models are detailed a little more to come to reliable decision support.

Such a Life Cycle Sustainability study can only be carried out in parallel to R&D if sufficient experience is available to provide both fast AND reliable feedback to product or process developers, of course.

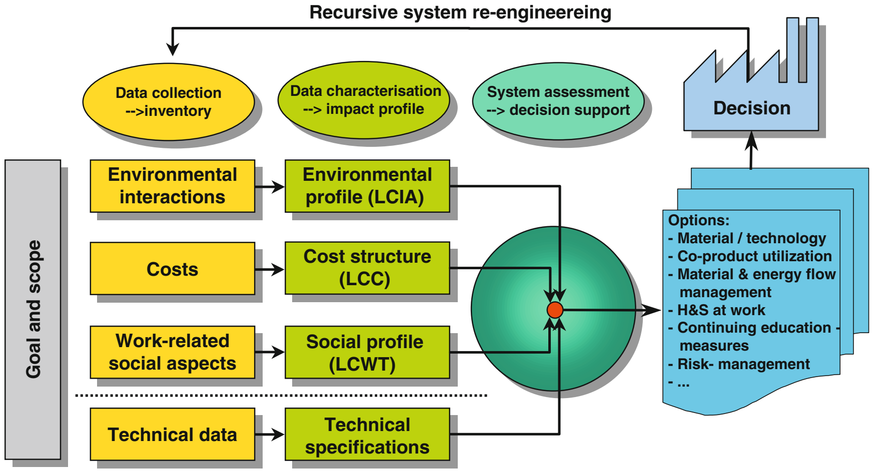

Fig. 14 Life Cycle Sustainability of products according to approach developed at IKP

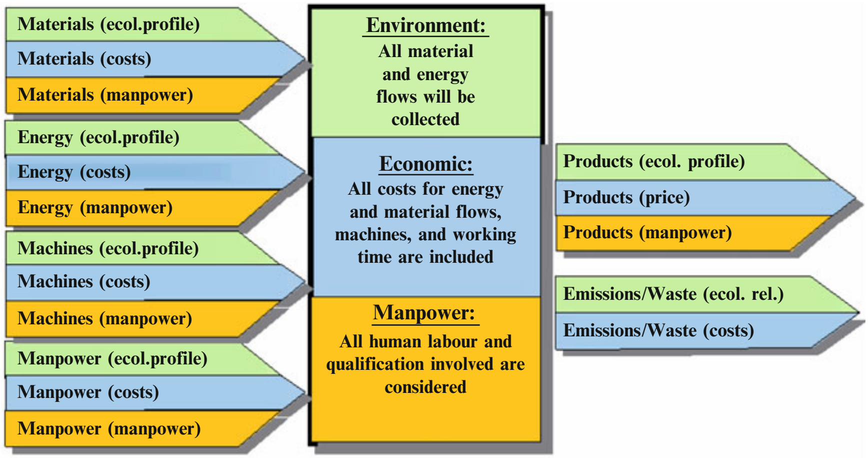

Fig. 15 Data collection on level of the unit process for complete Life Cycle Sustainability Assessment

7.3 Applications

Similarly as LCE, LCS offers consistent decision support in a large variety of tasks, involving environmental, cost, and social implications along the life cycle of products. Again, the specific application of the approach depends on the product or process in question and many boundary conditions.

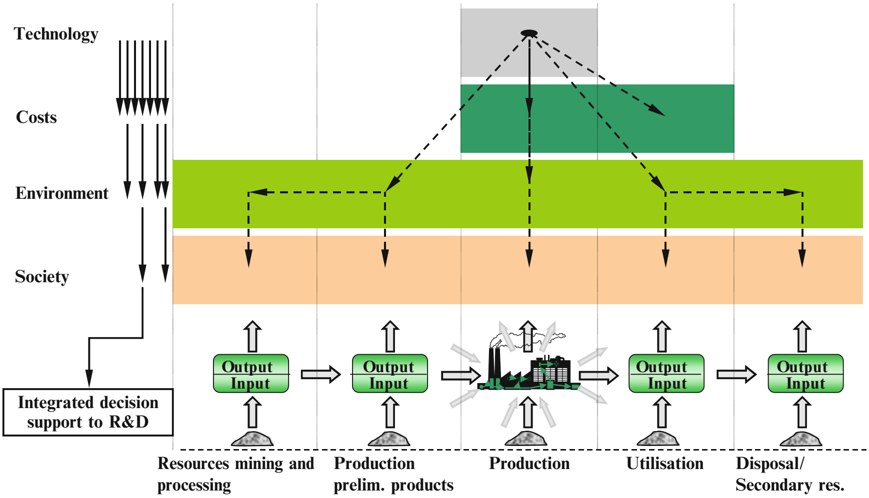

Fig. 16 Stepwise procedure of narrowing down design alternatives – from technological alternatives to most sustainable solutions

7.4 Conclusions

As a consequent further development of LCA and LCE, LCS is expected to become the basis for future integrated sustainability decision support on the level of products / services and processes. It is a tool, developed for use in industry, but is expected to find application in policy making, too.

The new sub-method LCWE for the social working environment aspects has the following status: Based upon the various methods several case studies have been completed and the first, basic LCWE databases have been made available by some research groups. Presently, several large companies are evaluating some of the different LCWE methods for practicability. It has to be stressed however, that further practice experience has to be gained, before the inclusion of such LCWE results into the decision-making process in industry can be recommended.

8 Experts, Tools, and Data for LCA, LCE and LCS

8.1 Experts

When planning to carry out LCA, LCE, or LCS studies for decision support in industry or policy making, experts with the respective experience are required. While many large companies have in-house experts or expert groups for LCA or LCE, Competency is also bought in on a case-by-case basis. This depends on various aspects, such as company size, type of products/services delivered, width and depths of product profile, LCA-situation at business customers, competitive situation, legal situation, visibility to end-consumers etc.

Since Life Cycle Studies are a rather complex issue, both efficiency and reliability of decision support strongly depend on specific experience gained in past work. It is strongly advised to benefit from experience gained in past studies.

Among the experienced LCA / LCE experts is a large group with a specific link to polymers, which is also the (former) home of the authors of this work: Developed out of initial industry projects at the Institute for Polymer Testing and Polymer Science (IKP) at Stuttgart University (Germany), the department Life Cycle Engineering (LCE, German “GaBi”) was founded by Prof. Dr.-Ing. Peter Eyerer in 1989. This team and its work is now being continued as part of the LBP, Stuttgart University. The interdisciplinary team of currently ten full-time academic staff provides independent ecological, economic, and technical decision support along the life cycle of products, processes, and services. Far over 100 industry and research projects were carried out world-wide, to date. The LBP-GaBi group forms – together with its spin-off company PE International GmbH, which is located in the same building – the world’s largest working group in the field of Life Cycle Assessment and Life Cycle Engineering.

In addition to research and consulting work, LBP-GaBi develops comprehensive but user-friendly software solutions and databases for use in industry practice, research, and consultancy in the field of sustainability.

LBP-GaBi provides decision support on various system levels from processes through process-chains, products, and service-systems to production sites and supply-chains as well as at the regional level. Solutions to specific tasks have been worked out in bilateral and multiclient industry and research projects for far over 200 customers.

More information can be found at http://www.lbpgabi.uni-stuttgart.de/ and www.pe-international.com.

8.2 Tools and Data

A neutral and detailed characterisation of LCA experts, software and databases globally is available at the European Commission’s Joint Research Centre “LCA Resources Directory” accessible via http://lct.jrc.ec.europa.eu.

One of the globally leading LCA/LCE software tools is the GaBi Software- and Database-System. It has been developed in an on-going and customer-oriented process jointly by LBP, University of Stuttgart and PE International GmbH since 1992. GaBi is used especially by in-house expert groups in many leading companies and associations for its efficient work support and extended, high-quality databases as well as by scientists due to its extended and flexible modeling capacities.

The present version GaBi 4.3 is a user-friendly, powerful, and professional tool supporting users in sustainability life cycle data modeling, administration, and

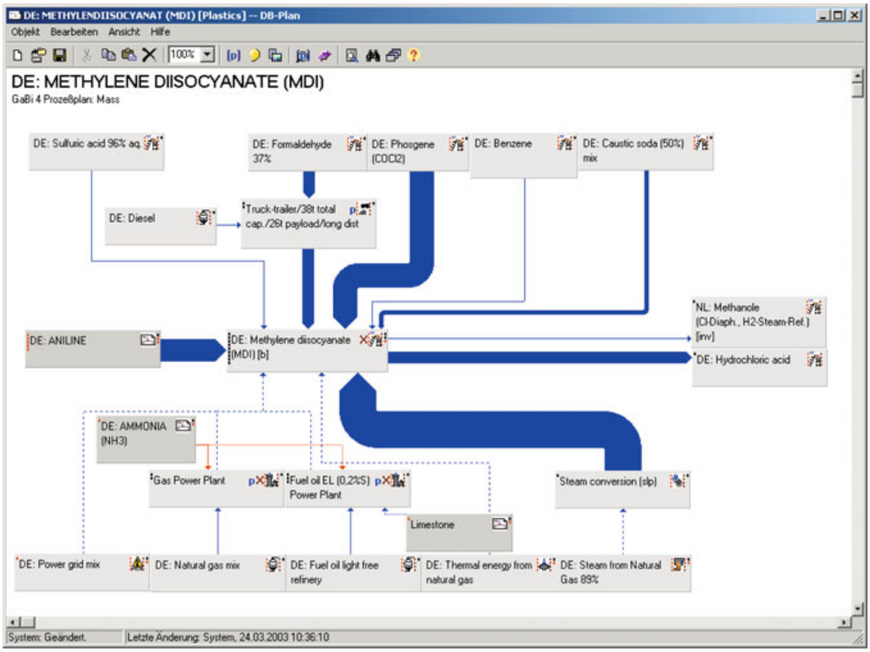

Fig. 17 Life Cycle Model in a professional software system for Life Cycle Assessment; example of production of MDI

evaluation at the process, product, or organization level. Next to support to LCA studies it offers specific functionality for life cycle cost analysis and life cycle social analysis.

Figure 17 shows a screenshot of the user interface of GaBi 4 as an example for a professional software support to life cycle modeling.

The present version GaBi 4 is available in English, German, Japanese, Spanish, Portuguese, and Chinese language versions and offers one of the world's largest, consistent LCI databases with a high level of data quality. It is organized into a main professional database and about 15 special extension databases (e.g. performance polymers, electronic components, precious metals, renewable resources etc.).

More information can be found at www.gabi-software.com.

8.3 Latest developments

At the EC's DG "Joint Research Centre," Institute for Environment and Sustainability (IES), the European Platform on LCA [41] was established by the European Commission in response to the IPP Communication to increase the availability and exchange of robust life cycle data and the use of Life Cycle Assessment (LCA) in business and public authorities. To ensure greater coherence and quality assurance across instruments, hence increased acceptance, use, and efficiency, the Platform supports the development of the International Reference Life Cycle Data System (ILCD) [42], the European Life Cycle Database (ELCD), the international resources directory, as well as a discussion forum. Particularly the ILCD is developed in a broad international effort with several other national LCA projects being involved via consultations and coordinations, as well as UNEP, the World Business Council for Sustainable Development (WBCSD) and a number of EU-level Business Associations including PlasticsEurope.

The International Reference Life Cycle Data System promotes the availability, exchange and use of coherent, robust life cycle data, methods, and studies for decision support in policy making and in businesses. The ILCD consists primarily of the ILCD Data Network and the ILCD Handbook.

The International Reference Life Cycle Data System Data Network provides a registry for consistent quality-assured life cycle inventory (ecoprofile) data sets. This network is open to all data providers from business, national LCA projects, research groups, consultants, research projects, and others. Quality and consistency is ensured through compliance with the ILCD Handbook.

The International Reference Life Cycle Data System Handbook is a series of technical guidance documents in line with the ISO 1404 and 14044 standards, along archetype goal and scope situations. This Handbook along with supporting tools provides the basis for ensuring consistency and quality across life cycle assessment data, methods, and studies for all applications.

The documentation and publication of LCI and LCIA data sets is supported by the related ILCD data set documentation and exchange format. A related data set editor allows the documentation, editing, and compliance-verification of ILCD data sets.

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Raw and Renewable Polymers

Seena Joseph, Maya Jacob John, Laly A. Pothen, and Sabu Thomas

Abstract Biopolymers from renewable resources have attracted much attention in recent years. Increasing environmental consciousness and demands of legislative authorities have given significant opportunities for improved materials from renewable resources with enhanced support for global sustainability. High-performance plastics are the outcome of continuous research over the last few decades. The real challenge of renewable polymers lies in finding applications, which will result in mass production, and price reduction. This can be attained by improving the end performance of the biodegradable polymers. The structure, properties, and applications of polymers derived from natural resources are discussed in this article.

Keywords Cellulose, Natural polymers, Natural rubber, Renewable materials

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Abbreviations

CNSL	Cashew nut shell liquid
DNA	Deoxy ribonucleic acid
DPNR	Deprotenized natural rubber
FRP	Fiber reinforced plastic
NR	Natural rubber
OENR	Oil extended natural rubber
PAN	Polyacrylo-nitrile
PMMA	Polymethyl methacrylate
PRI	Plasticity retention index
PS	Polystyrene
PVA	Polyvinyl alcohol
RNA	Ribo nucleic acid
RSS	Ribbed smoked sheet
SIR	Standard Indonesian rubber
SMR	Standard Malaysian rubber
SSR	Standard Singapore rubber
TPNR	Thermoplastic natural rubber
TSR	Technically specified rubber

1 Introduction

Nature has been using natural polymers to make life possible on this earth for a long time. We do not think of natural polymers in the same way as synthetic polymers because we cannot take credit for them as marvels of our own ingenuity, and chemical companies cannot sell them for profit. However, that does not make natural polymers less important; it turns out in fact, that they are more important in many ways. Naturally occurring polymers were used by early humans to meet their material needs. A variety of materials made from wood bark, animal skin, cotton, wool, silk, natural rubber (NR), etc., played key roles in early civilization [1].

Natural polymers include the RNA and DNA that are so important in genes and life processes. While proteins are the basic building units, enzymes help to control the chemistry inside living organisms and peptides make-up some of the more interesting structural components of skin, hair, and even the horns of rhinos. Other natural polymers include polysaccharides (sugar polymers) and polypeptides like silk, keratin, and hair. NR is another polymer, made from just carbon and hydrogen. Two important polymers, which have influenced human civilization during the last century, are rubbers and plastics. They have challenged the old materials for their well-established uses and have become part and parcel of everyday life [2]. The use of NR was well-established by the start of the twentieth century while the major growth period of the plastic industry has been since 1930. These natural polymers have found applications in various fields [3].

In ancient Egypt, mummies were wrapped in cloth dipped in a solution of bitumen in oil of lavender, which was known as Syrian Asphalt, or Bitumen of Judea. On exposure to light, the product hardened and became insoluble. This process involved the action of chemical cross-linking, which became important in the vulcanization of rubber and production of thermosetting plastics.

Depending on the nature of the heteroatom inserted in the main chain, polymers can be classified into four major types, i.e. hydrocarbon polymers, carbohydrates, carbon oxygen nitrogen polymers and carbon, oxygen, nitrogen and phosphorus containing polymers. Of these polymers, polysaccharides, proteins, and nucleic acids are polymers having pronounced physiological activity.

An in-depth review of polymers from renewable resources has been given by Gandini [4]. The author gives a critical review of polysaccharides in terms of development and an account of future biopolymers that can be used.

2 Polymers Derived from Renewable Resources

2.1 Hydrocarbon Polymers

2.1.1 Natural Rubber

NR belongs to a class of compounds known as elastomers [5]. NR was used for centuries by the Mayans in the Western hemisphere before it was introduced into Europe by Columbus. The term rubber was, however, coined by Joseph Priestly. NR is indispensable in our daily lives. The main uses of NR are concentrated in four key areas, namely: medical devices, industrial products, domestic and recreational goods, and foremost automobile products. The current elastomer consumption in the world is 18 million t per year [6]. NR supplies about one-third of the world demand for elastomers. It is also used as an industrial raw material. NR is a naturally occurring elastomeric polymer of isoprene (2-methyl-1,3-butadiene). It can be extracted from latex of only one kind of tree, *Hevea braziliensis*. Hevea rubber is produced in many tropical regions of Southeast Asia, Africa and Central and South America. There is practically only one other potential source of NR, that is the guayule shrub (*Parthenium argentatum*).

NR occurs as particles dispersed in an aqueous serum, i.e., latex, which are contained in bundles of tubular vessels in the trunk of the tree [7]. Latex is harvested from the tree by a process called tapping. The latex of the *Hevea braziliensis* tree has been described as a cytoplasmic system containing rubber and nonrubber particles dispersed in an aqueous serum phase. Freshly tapped Hevea latex has a pH of 6.5–7 and a density of 0.98 $\mathrm{g\,cm^{-3}}$. The total solids of fresh field latex vary typically from 30 to 40%, depending on weather and tapping frequency and other factors. The dry rubber content is approximately 3 wt% less than the total solids [8].

Polyisoprene exists naturally in the form of two stereo-isomers, namely *cis*-1,4-polyisoprene and *trans*-1,4-polyisoprene (Fig. 1).

Chemically NR is *cis*-1,4-polyisoprene [9]. A linear, long-chain polymer with repeating isoprenic units (C_5H_8), it has a density of 0.93 at 20°C. Natural *trans*-1,4-polyisoprene is a crystalline thermoplastic polymer, which is mainly used in golf ball covers, root canal fillings in dentistry, special adhesives and to a lesser extent in wire and cable coverings. It is obtained as gutta percha from *Palaquium oblongofolium* in South East Asia. It is much harder and less soluble than Hevea rubber. Certain trees like Chicle (*Achras sapota*) produce latex, which is a physical mixture of *cis* and *trans* polyisoprene. *Cis*-1,4-polyisoprene can be produced synthetically by stereo-specific polymerization reaction using Ziegler–Natta heterogeneous catalyst. The important components of NR are given in Table 1.

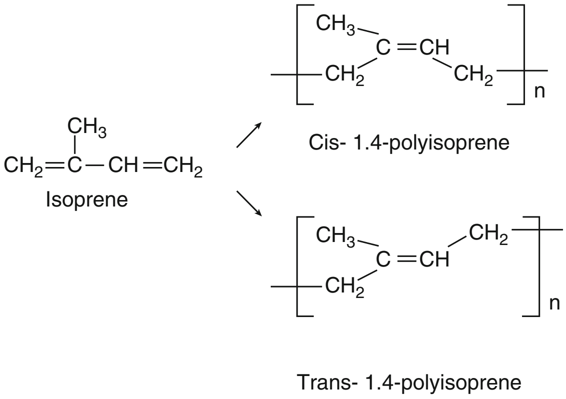


Fig. 1 Structure of *cis* and *trans* poly isoprene

Table 1 Typical analysis of NR [3]

Components	%
Rubber hydrocarbon	93.3
Acetone extract	2.9
Protein	2.8
Moisture	0.6
Ash	0.4

Table 2 Properties of NR

Property	Approximate values
Glass transition temperature (°C)	−72
Density (g/cc)	0.97
Solubility (J m^{-3})	16.2
Nitrogen content (%)	0.4
Dirt (%)	0.03
Volatile matter (%)	0.5
Ash content (%)	0.4
Plasticity (P_0)	40
Plasticity retention index (PRI)	75

The most important factor governing the properties of polyisoprene is the stereoregularity of the polymer chain. The very unique characteristic of NR is the ability to crystallize under strain, the phenomenon known as strain-induced crystallization. Stretching of vulcanizates of polyisoprene having at least 90% *cis* content leads to crystallization, which in turn leads to strengthening of rubber [10].

Another interesting aspect of isoprene rubbers is their low hysteresis, giving low heat buildup during flexing [11]. The combination of high tensile properties and low hysteresis explains the requirement of NR as the primary rubber in heavy vehicle tires. In addition to this, NR has excellent tensile and tear properties, good green strength and building tack. However, NR is not very resistant to oxidation, ozone, weathering, and a wide range of chemicals and solvents, mainly due to its unsaturated chain structure and nonpolarity. The properties of NR are given in Table 2.

!All types of NR that are not modified [such as oil-extended NR (OENR)] or technically specified rubbers (TSR's) are considered to be international grades. Grade designations usually use color or how the rubber was made; conventional grade descriptions are pale crepe, ribbed smoke sheet (RSS), air dried sheet, Michelin sheets, sole crepe, brown and blanket crepes. The main disadvantage of this system is that grading is done on visual aspects. Almost exclusively, the darker the rubber, the lower the grade. Other grading criteria such as the presence or absence of rust, bubbles, mold and cut spots are subjective in nature. Perhaps the most valid assumption is that the darker the rubber the more dirt it contains. In the 1960s, Malaysia developed a grading scheme that was more sophisticated and useful to customers. A major criticism of NR was the large and varying dirt content. The cornerstone of the new system was grading according to dirt content measured in hundreds of 1%. For example, Standard Malaysian rubber (SMR) is a rubber whose dirt content does not exceed 0.5%. Dirt is considered to be the residue on a 45 μm sieve after a rubber sample has been dissolved in an appropriate solvent, washed through the sieve and dried. The specification has other parameters including source material for the grade, ash and nitrogen content, volatile matter, plasticity retention index (PRI) and initial plasticity. Acceptance of these standards is vigorous and other rubber-producing countries followed suit. Letter abbreviations identify the rubber source; SMR denotes rubber from Malaysia, SIR indicates Indonesian product, SSR indicates Singapore product, and ISNR denotes Indian Standard Natural Rubber.

The main modifications of NR are:

Deprotenized rubber (DPNR) – this is very useful when low water absorption is wanted, vulcanizates with low creep are needed, or more than ordinary reproducibility is required. Normally NR has between 0.25 and 0.5% nitrogen as protein; DPNR has only about 0.07%. A drawback is that since protein matter in the rubber accelerates cure, DPNR requires more acceleration. DPNR is made by treating NR latex with bioenzyme, which hydrolyzes the proteins to water-soluble forms. A protease like *Bacillus subtilis* is used at about 0.3 phr. When the enzymolysis is completed the latex is diluted to 3% total solids and coagulated by adding a mixture of phosphoric and sulfuric acid. The coagulated rubber is then pressed free of most of the water, crumbed, dried, and baled.

Another modification is OENR. There are three ways to make this kind of rubber; (1) co-coagulation of latex with oil emulsion, (2) banbury mixing of oil and rubber, (3) allowing the rubber to absorb the oil in pans until almost all is absorbed, then milling to incorporate the remaining oil. Recently rubber and oil have been mixed using an extruder. A comparatively new modification of NR is epoxidized NR. The rubber molecule is partially epoxidized with the epoxy groups randomly distributed along the molecular chain. The main advantage of ENR over NR is improved oil resistance and low gas permeability. Another new modification is thermoplastic natural rubbers (TPNR) [12–14].

These are physical blends of NR and polypropylene, mixed in different proportions to give rubbers with different stiffness properties. The method of dynamic vulcanization is possible in TPNR [15]. They are suitable for injection molding into products for automotive applications such as flexible sight shields and bumper components. Grafting is another method used for the modification of NR. The properties of PMMA-g-NR, PS-gg-NR, and PAN-g-NR have been analyzed by Thomas and co-workers [16, 17].

Other modified rubbers are tire rubber, peptized rubber, powdered rubber, skim rubber, and superior performing rubber (SP) (made by blending normal latex and prevulcanized latex before coagulation and drying by conventional methods). SP rubbers confer superior extrusion properties such as better surface smoothness and lower die swell when blended with natural and synthetic rubbers.

Many other chemically modified forms of NR were available in the past. These included cyclized rubber, chlorinated rubber, hydrochlorinated rubber, and depolymerized rubber.

With such a wide range of useful properties NR can be used in a large variety of applications. These include tires, mechanical goods like hoses, conveyer belts, rubber linings, gaskets, rubber soles etc., and engineering products in dynamic applications such as springs, antivibration moldings, brushings and so forth. High fatigue resistance, good strength, and durability are other points in favor of NR. NR is now accepted as suitable for use in bridge bearings. NR-based natural fiber composites are used for the fabrication of a wide variety of products such as V-belts [18], hoses [19] and complex shaped articles. Many researchers have studied the properties of NR-based composites [20–25].

2.2 Carbon Oxygen Polymers

2.2.1 Cellulose

Cellulose is the most abundant natural polymer on the planet. The chief source of cellulose is plant fibers. Certain types of bacteria also synthesize cellulose, which can be obtained as a continuous film by cultivating the bacteria in a glucose solution. Cellulose is also secreted by such marine chordates (truncates) as the sea squirt [26].

Cellulose is found not to be uniformly crystalline. However, the ordered regions are extensively distributed throughout the material and these regions are called crystallites [27]. Cellulose exists in the plant cell wall in the form of thin threads with an indefinite length. Such threads are cellulose micro-fibrils, playing an important role in the chemical, physical, and mechanical properties of plant fibers and wood.

The plasma membrane of the plant cells has been considered the likely site for the synthesis and assembly of cellulosic micro-fibrils [28]. These micro-fibrils are found to be 10–30 nm wide, less than this in width, and indefinitely long containing 2–30,000 cellulose molecules in cross section. Their structure consists of predominantly crystalline cellulose core.

These are covered with a sheath of para-crystalline polyglucosan material surrounded by hemicellulose [29]. In most natural fibers, these micro-fibrils orient themselves at an angle to the fiber axis called the micro-fibril angle. The ultimate mechanical properties of natural fibers are found to be dependent on the micro-fibrillar angle. Gassan et al. have performed calculations on the elastic properties of natural fibers [30].

A discrepancy in the size of the crystalline regions of cellulose, obtained by X-ray diffractometry and electron microscopy, led to differing concepts on the molecular organization of micro-fibrils. Frey-Wyssling regarded the micro-fibril itself as being made up of a number of crystallites, each of which was separated by a para-crystalline region and later termed the “elementary fibril” [31]. The term “elementary fibril” is therefore applied to the smallest cellulosic strand. Electron micrograph studies of the disintegrated micro-fibrils, showing the crystalline nature of cellulose micro-fibrils (×100 nm) taken by diffraction contrast in the bright field mode.

Reports on the characterization and the make-up of the elementary fibrils and on their association while establishing the fiber structure – usually called fibrillar or fringed fibril structure – are present in the literature [32].

According to this concept, the elementary fibril is formed by the association of many cellulose molecules, which are linked together in repeating lengths along their chains. In this way, a strand of elementary crystallites is held together by parts of the long molecules reaching from one crystallite to the next, through less ordered inter-linking regions. Molecular transition from one crystallite strand to an adjacent one is possible, in principle. Apparently, in natural fibers this occurs only to a minor extent, whereas in man-made cellulosic fibers such molecular transitions occur more frequently.

The coherence of the fibrils in their secondary aggregation is given either by hydrogen bonds at close contact points or by diverging molecules. Access into this structure is given by large voids formed by the imperfect axial orientation of the fibrillar aggregates, interspaces of nanometer dimensions between the fibrils in the fibrillar aggregations, and by the less ordered inter-linking regions between the crystallites within the elementary fibrils. Dufresne [33] has reported on whiskers obtained from a variety of natural and living sources. Cellulose micro-fibrils and cellulose whisker suspension were obtained from sugar beet root and from tunicin. Typical electron micrographs obtained from dilute suspensions of sugar beet are shown in Fig. 2.

Individual micro-fibrils are almost 5 nm in width while their length is of a much higher value, leading to a practically infinite aspect ratio of this filler. They can be used as a reinforcing phase in a polymer matrix.

In terms of chemical structure, cellulose is among the simplest of natural polymers in that it contains a single repeating unit, D-glucose, linked through carbons 1 and 4 by β linkages. The ring substituents other than hydrogen, including the bonds linking the glucose rings together, are all-equatorial.

The crystallinities of cellulose are obtained from X-ray diffraction techniques, which give the most direct results, although their interpretation and evaluation is still under discussion and widely based on convenience. On the basis of the two-phase fringed-micellar structure, Hermans and Weidinger derived a theory on the proportionality of the intensity or amplitude of scattering from the amorphous and

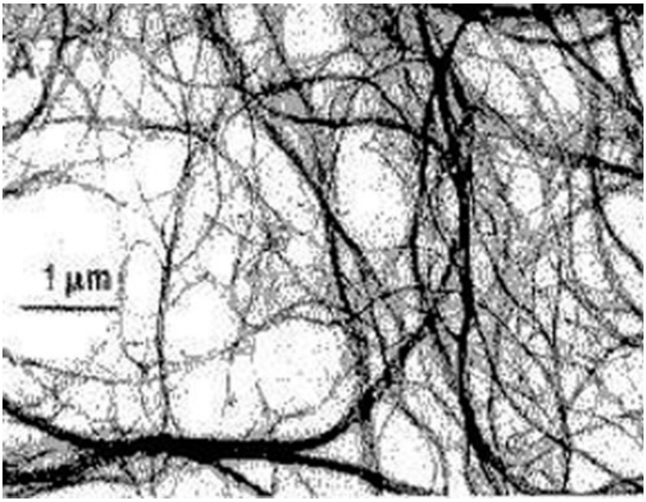


Fig. 2 Transmission electron micrograph of a dilute suspension of a sugar beet cellulose

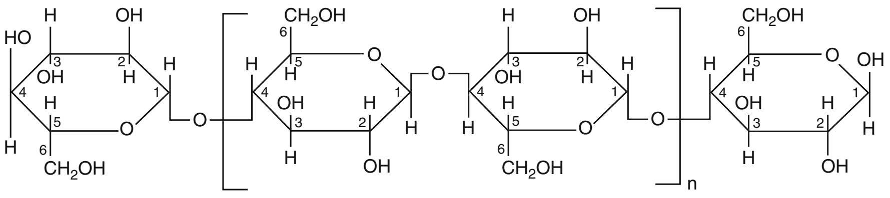


Fig. 3 Haworth projection formula for cellulose, Reproduced with permission from American Institute of Physics

crystalline phases of cellulose [34]. The respective crystallinities are based on certain expressions (Fig. 3).

Cellulose can be considered as a syndiotactic poly acetal of glucose. Terminal hydroxyl groups are present at both ends of the cellulose chain molecule. However, these groups are quite different in nature. The C (1) hydroxyl at one end of the molecule is an aldehyde hydrate group with reducing activity and originates from the formation of the pyranose ring through an intermolecular hemi acetal reaction. In contrast to this, the C (4) hydroxyl on the other end of the chain is an alcoholic hydroxyl and is nonreducing. The chemical character of the cellulose molecule is determined by the sensitivity of the β-glucosidic linkages, between the glucose repeating units, to hydrolytic attack and by the presence of three reactive hydroxyl groups, one primary and two secondary, in each of the base units. These reactive hydroxyl groups are able to undergo etherification and esterification reactions. The main cause for the relative stiffness and rigidity of the cellulose molecule is the intra molecular hydrogen bonding, which is reflected in its high viscosity in solution, its high tendency to crystallize and the ability to form fibrillar strands. The β-glucosidic linkage further favors the chain stiffness.

The molecular structure of cellulose is responsible for its supramolecular structure and this, in turn, determines many of its physical and chemical properties. In the fully extended molecule, their mean planes are at an angle of 180° to each other and orient adjacent chain units. The mechanical properties of natural fibers also depend on the cellulose type, because each type of cellulose has its own cell geometry and the geometrical conditions determine the mechanical properties. The crystal structure of natural and regenerated cellulose is known as cellulose I and II, respectively. In cellulose I the chains within the unit cell are in parallel configuration, while they have an anti-parallel configuration in cellulose II [35]. In addition to the cellulose component, natural fibers contain hemicelluloses, which consist of a group of polysaccharides that remain associated with the cellulose after lignin has been removed. The hemicelluloses differ from cellulose, in that they contain several sugar units whereas cellulose contains only glucopyranose units. Hemicellulose also exhibits considerable chain branching whereas cellulose is strictly linear. The degree of polymerization of native cellulose is also 10–100 times higher than that of hemicellulose. Unlike cellulose, the constituents of hemicellulose differ from plant to plant.

Cellulose in the form of natural fibers is finding enormous application in various fields. Plant fibers obtained from the leaf, seed, and stem of plants are used as reinforcement in various matrices and the resulting composites, which are eco friendly, are finding application in various fields like automobile, building etc. Satyanarayana et al. reviewed the potential of natural fiber as a resource for industrial materials [36, 37].

Various reports are present in the literature on the usage of cellulose fibers in the preparation of composites. Cellulose fibers like banana, sisal, oil palm, jute, pine apple leaf fiber were found to have a very good reinforcing effect on polymer matrices [38–42]. The mechanical properties and water absorption were found to be dependent on the amount of micro-fibrils.

2.2.2 Shellac

Among the natural resins used in varnishes and molding compounds, shellac is the best known. Shellac is the only commercial resin of animal origin [43]. It is the hardened secretion of a tiny insect, popularly known as the lac insect. It is a hard brittle resinous solid, heavier than water. Shellac is the refined form of lac, the secretion of the lac insect which is a parasite on certain trees in India, Burma, Thailand, and to a minor extent in south east Asian countries [44].

Lac incrustations deposited by the insects on trees are separated from the twigs by scraping. Lac, thus gathered is known as stick lac. It contains lac resin together with woody materials, sand, dust and other water-soluble impurities. This is subjected to various refining processes. The various refined forms of sticklac are seedlac, shellac, buttonlac, garnet lac, bleached lac, and decolorized lac.

Seedlac

Seedlac is obtained from sticklac. Sticklac is crushed into small grains, sieved, winnowed, washed with water and dried. This semi-refined product is known as seedlac.

Shellac

Shellac is obtained from seedlac, usually in the form of thin flakes, by stretching the heat-softened resin by solvent refining or by squeezing it out of cloth bags.

Button Lac

This is also shellac but in the form of buttons.

Garnet Lac

The impurities that remain in the cloth bag during the preparation of shellac contain a substantial amount of lac. This is reclaimed by solvent extraction as a dark colored lac called garnet lac.

Bleached Lac

The color of the lac is the result of the presence of alcohol soluble dye erythrolaccin. Bleached lac is produced by bleaching a soda solution of seedlac with sodium hypochlorite under controlled conditions [45].

The chemical nature of shellac is not completely understood. Gas chromatographic analysis of the products of chemical degradation of shellac has shown the presence of several saturated and unsaturated long-chain aliphatic acids together with other hydroxyl-substituted acids and nonaliphatic compounds [46]. Dewaxed, decolorized wax approaches most nearly lac resin in its pure form. Shellac is apparently a mixture of polyesters made up of various hydroxy aliphatic and sesquiterpenic acids. It has free carboxyl, hydroxyl, and aldehyde groups and is unsaturated. The lac resin is associated with two lac dyes, lac wax and odiferous substance, and these materials may be present to a variable extent in shellac. The resin itself appears to be a polycondensate of aldehydic and hydroxy acids either as lactides or inter-esters [47]. The resin constituents can be placed into two groups, an ether-soluble fraction (25% of the total) with an acid value of 100 and molecular weight about 550, and an insoluble fraction with an acid value of 55 and a molecular weight of about 2,000.

Hydrolysis of the resin will produce aldehydic acids at mild concentration of alkali (0.5N); using more concentrated alkalis (5N) hydroxy acids are produced, probably via the aldehydic acids. Unfortunately most of the work done in order to analyze the lac resin was carried out before the significance of the hydrolysis conditions was fully appreciated. It does, however, appear to be agreed that one of the major constituents is aleuritic acid. This is present to the extent of about 30–40% and is found in both the ether-soluble and ether-insoluble fractions. Both free hydroxyl and carboxyl groups are to be found in the resin.

The presence of free hydroxy and carboxyl groups in lac resin makes it very reactive, in particular to etherification involving either type of group. Of particular interest is the inter-etherification that occurs at elevated temperatures (>70°C) and leads to an insoluble “polymerized” product. Whereas ordinary shellac melts at about 75°C, prolonged heating at 125–150°C will cause the material to change from a viscous liquid, via a rubbery state, to a hard solid. One of the indications that the reaction involved is etherification is that water is evolved. The reaction is reversible and if heated in the presence of water the polymerized resin will revert to the soluble form. Thus shellac cannot be polymerized under pressure in a mold since it is not possible for the water to escape. Polymerization may be retarded by basic materials, some of which are useful when the shellac is subjected to repeated heating operations.

These include sodium hydroxide, sodium acetate, and diphenyl urea. Polymerization may be completely inhibited by esterifying the resin with mono basic saturated acids. A number of accelerators are also known, such as oxalic acid and urea nitrate. Unmodified lac polymerizes in about 45 min at 150°C and 15 min at 175°C. Shellac is soluble in a very wide range of solvents, of which ethyl alcohol is most commonly employed. Aqueous solution may be prepared by warming shellac in a dilute caustic solution. The resin is too brittle to give true meaning to mechanical properties. The thermal properties are interesting in that there appears to be a transition point at 46°C. Above this temperature, specific heat and temperature coefficient of expansion are much greater than below it. The specific heat of hardened shellac at 50°C is lower than that of unhardened material. From the point of view of the plastics technologist the most important properties of shellac are the electrical ones.

Stability of shellac to UV radiation is the most important optical property. The principal application of shellac was in gramophone records. The resin acts as a binder for about three times its weight of mineral filler. Today, the most important application of shellac is in surface coatings. It is also used in some French polish as adhesives and cements including valve capping and optical cements. Shellac is also used in the manufacture of sealing wax.

In an interesting study, shellac was used to coat jute fibers by Ray et al. [48]. The authors observed that low-cost natural resins such as shellac in small quantities can be utilized effectively, in their virgin form or in some suitably modified form, for the surface treatment of natural fibers.

2.2.3 Chitin

Chitin is one of the most abundant organic compounds on earth. It is present in both animals and fungi, and characteristically it is absent in plants. In nature, the most abundant crystalline form of the polymer is α-chitin, which occurs in the form of micro-fibrils. In the cell walls of fungi, chitin micro-fibrils constitute the skeleton responsible for their rigidity [49]. It makes up the shells of crawfish, shrimp, crabs, lobsters, and other crustaceans. It is hard, insoluble and yet somehow flexible. Chitin is a long unbranched polysaccharide, which may be regarded as a cellulose derivative in which the hydroxyl group on the C-2 position has been replaced by the acetyl amino group. Chitin, along with collagen is one of the major constituents of cartilage and the blood anticoagulant heparin.

Functionally, chitin is related both to cellulose and to collagen [50]. Chitin and collagen form the basis of the two principal skeletal systems of animals. It is present in the exoskeleton eye lenses, tendons and the linings of the gastrointestinal and respiratory tracts of arthropods, the largest phylum of the animal kingdom, a phylum including insects, arachnids, and crustaceans. Among plants, chitin is found in the cell walls of some fungi.

Chitin always occurs in combination with various other substances such as proteins, calcium carbonate or various pigments. Varying amounts of protein are always found in association with chitin [51]. The chitin of arthropods is α-chitin.

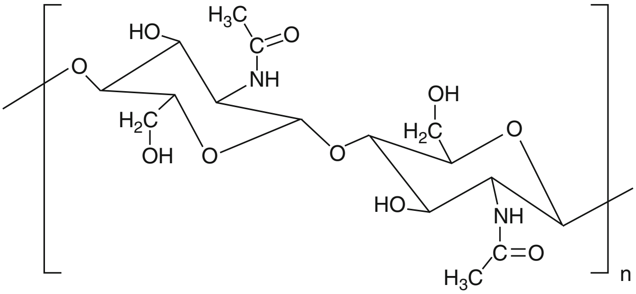


Fig. 4 Structure of Chitin

But α-chitin occurs in structures of animals from other phyla, the most notable example being the skeletal pen or internal horny shell of squids. Purified chitin is a white material resembling paper pulp. It is insoluble in water, dilute acids, dilute and concentrated alkalies and all organic solvents, but is soluble in anhydrous formic acid, in hypochlorite solution and in mineral acids.

Chemically, chitin is poly(*N*-acetylglucosamine) (Fig. 4).

The crystal structure of chitin has been studied by means of X-ray diffraction and IR spectra. The unit cell of α-chitin is similar to that of cellulose in that it contains four gluco pyranose rings linked by two pairs of (1-4)-b-glucosidic bonds.

Chitin is known to be biodegradable, biocompatible, and nontoxic. It is used in drug delivery and bio medical applications. It also used in the purification of water especially for the absorption of toxic dyes. Chitin has limited solubility in solvents but chitosan is readily soluble in acidic aqueous solutions and has more tendency to be chemically modified. Chitosan can readily be spun into fibers, cast into films, or precipitated in a variety of micromorphologies from acidic solutions. Min and Kim have reported on the adsorption of acid dyes from wastewater using composites of PAN/chitosan [52]. Shin et al. has reported on copolymers composed of PVA and poly dimethyl siloxanes cross-linked with chitosan to prepare semi IPN hydrogels for application as biomedical materials [53]. Chen and Liu have reported on the usage of regenerated chitosans as wood dressing [54].

In another interesting research work, it was shown that the deposition of chitosan films of different thicknesses on uncoated paper sheets improves the optical properties , printability and permeability properties as well [55].

The antifungal activity of chitosan is well documented by several authors. Li et al. have reported on the manufacture and properties of fibers with antibacterial properties developed from chitosan and viscose rayon [56]. However, there are only some papers describing the antifungal activity against wood decaying fungi. In general, chitosan acts by reducing the radial growth of fungi, and as a fungicide at higher concentrations. Several theories are established to explain this phenomenon. Chitosan, which is a polycationic polymer, interferes with fungal cell wall membranes causing alterations in the permeability of the membrane and promoting internal osmotic imbalances. This results in leaching of electrolytes and proteins.

2.2.4 Amber

Amber is the generic name for all fossil resins secreted in prehistoric times by certain types of evergreens, now extinct. This resin was produced in the Oligocene age by exudation from a now extinct species of pine.

The chemical nature of amber is complex. Amber consists of complex mixtures of sesquiterpenoids, diterpenoids, and triterpenoids that have undergone polymerization and molecular reorganization during fossilization. Phenolic units may also be present. Baltic coast deposits, which contain about 8% succinic acid, are often called succinite. Amber is amorphous, and its infrared spectrum closely resembles those of nonvolatile resins from extinct pine trees. It is believed not to be a high polymer, the resinous state being accounted for by the complexity of materials present. Amber also serves as a repository for a variety of extinct species of insects.

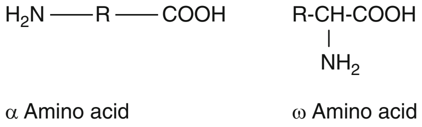
2.2.5 Asphaltenes

Asphaltenes are also called bitumens. They are resinous materials widely used in highway construction as aggregate binders and as binders for roofing and flooring composition and for water proofing buildings. They occur in natural deposits, but are obtained principally from the residue of petroleum distillation.

2.3 Carbon Oxygen Nitrogen Polymers

2.3.1 Proteins and Polypeptides

Proteins were the first examples of polyamides (a fancy word for nylon). Both share many common traits but they are very different in how they are made and in their physical properties. They are alike in that both contain amide linkages in the backbone. Amides are made from carboxylic acid groups and amine groups through the loss of water. The amide molecular segment is unique in its structure and intermolecular interactions. Because of the hybridization of the nitrogen, carbon, and oxygen of the amide group, the segment is basically flat. More importantly, the hydrogen on the nitrogen and the carbonyl oxygen are capable of a strong interaction called a hydrogen bond. Because of this, the amide groups attract each other so much that they form strong associations that give amide-containing polymers unusual properties.



$H_2N—R—COOH$

$R\text{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{-}COOH$

Fig. 5 Structure of amino acid

The differences between how nature does nylons and how we do it is striking. We mostly make nylons from molecules that have lots of CH_2 groups in them. They possess four, five, or six CH_2 groups between amide units. Nature, however, is much more economical, choosing to use only a single carbon between amide groups. What nature does differently is to substitute this carbon with lots of different functional segments and groups.

Most polypeptides and proteins are water-soluble or water swellable. Enzymes are proteins that catalyze all chemical reactions of biological origin. Enzyme functions include oxygen transport, muscle movement, nerve response, nutrient digestion and storage, hormonal regulation gene expression, and protein synthesis.

Despite the large number of functions, all proteins are similar with repeating structures along the backbone chosen from 20 amino acid monomers. These polymers, the structures of which are assembled from a template coded by messenger RNA, are monodisperse. Each protein has a unique sequence and molecular weight.

The 20 amino acids capable of appearing in various microstructural combinations of sequence lengths, and total molecular lengths, allow assembly of an infinite number of distinct proteins [57]. The side chain R may be hydrophobic, polar, acidic, or basic. The structure of the amino acid is given in Fig. 5.

Primary structure (covalent bond lengths and bond angles) is determined by microstructure of the amino acid repeating units along the chain. Numerous procedures, including sequential degradation, gel electrolysis, dye binding, and immunoassays have been used to determine sequences.

Secondary structure of proteins is determined by configuration and conformation along the backbone of the polymer. The resistance to bond rotation of the C–N bond of the peptide unit, the configuration about the chiral carbon, and conformational restrictions to rotation by short-range charge–charge interactions or intermolecular hydrogen bonding play major roles in secondary structure.

The three-dimensional structure or tertiary structure depends strongly on primary structure with the added elements of long-range intramolecular hydrogen bonding, polar and ionic effects, and chain solvation. An example of the three-dimensional structure of myoglobin is shown in Fig. 6 [58]. The compact structure illustrates the hydrophobic interior, helical features from intramolecular hydrogen bonding and the L-amino acids, and polar external groups for hydration.

Many proteins exist in subunits of a composite structure. The organization of these subunits is termed the quaternary structure and is particularly important in enzyme-mediated reactions. The tertiary and quaternary structure of native protein in water can be distributed by addition of electrolytes, alkali solutions, urea, or detergents and increasing temperature. The properties change markedly; for example enzyme activity is often lost. In most cases this denaturation is not reversible.

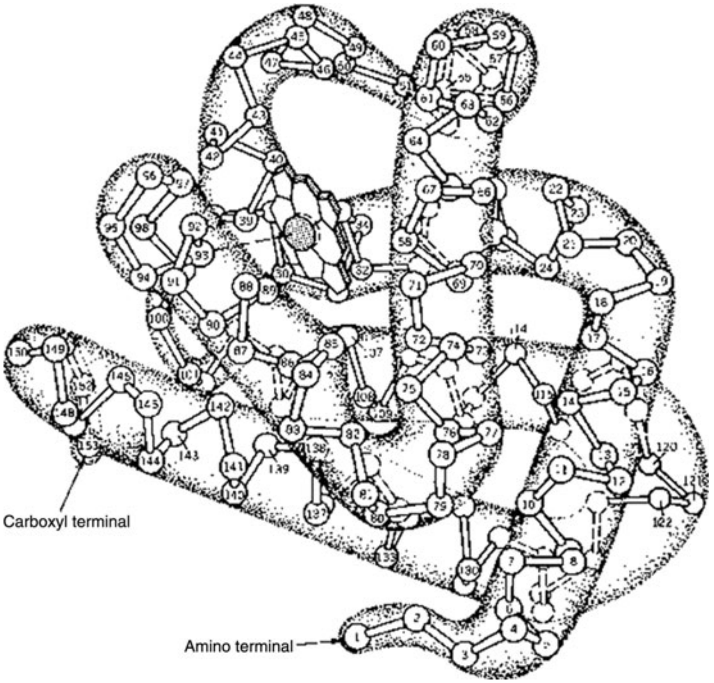


Fig. 6 Three-dimensional structure of myoglobin

The solubilities of proteins vary considerably based on compositions and conditions of ionic strength, pH, and concentrations. Those with highest density of polar groups or electrolyte character are most soluble. Therefore, solubility in water is lowest at the isoelectric point and increases with increasing basicity and acidity.

Protein biosynthesis is complex, involving 300 macromolecules. Five stages can be identified involving (1) activation of amino acid monomers and transfer to ribosomes, (2) initiation of polymerization, (3) propagation, (4) termination and release, and (5) folding and processing. Ordering of monomers is dictated by operation of the triplet code in which a sequence of these consecutive nucleotide units on messenger RNA positions specific amino acids for polymerization.

Synthetic polypeptides can be made by sequential addition of protected amino acids on to a solid support. This procedure pioneered by Merrifield, has been used to prepare hundreds of peptides of varying sizes and functions [59]. The development of recombinant DNA techniques has led to cloning of a number of genes and their expression in the form of protein products from bacterial or yeast cells [60]. Large numbers of proteins are being produced with enormous commercial potential. Among the first available genetically engineered proteins are insulin, the pituitary growth hormone and interferon [61].

In addition to the rapid growth of genetically engineered enzymes and hormones for medical and agricultural applications, other water-soluble proteins are isolated

Table 3 Typical analysis of cow's milk

Water	87%
Fat	3.5–4%
Lactose	5
Casein	3%
Globulin + albumin	0.5–1%
Other ingredients	0.5–1%

from biological sources in a more traditional manner for commercial application. Enzymes are used as detergent additives, for hydrolyzing polysaccharides and proteins, to isomerize various glucose and sucrose precursors, for wine and beer making, for leather tanning, and for mineral recovery. Support-bound enzymes are becoming commercially significant for large-scale substrate conversion.

2.3.2 Casein

Casein is a protein found in a number of animal and vegetable materials but only one source is of commercial interest, cow's skimmed milk. The amount of casein in milk will vary but a typical analysis of cow's milk is given in Table 3 [62].

Plastics materials may be produced from casein by plasticizing with water followed by extrusion and then cross-linking with formaldehyde (formalization). The resultant products have a pleasant horn-like texture and are useful for decorative purposes.

Casein is one member of the important group of natural polymers, the proteins. These materials bear a formal resemblance to the polyamides in that they contain representing –CONH groups and could be formally considered as polymers of amino acids. Unlike polymers such as nylon 6 and nylon 11 a number of different α-amino acids are found in each molecule whereas the nylons 6 and 11 have only one ω amino acid molecule (Fig. 5).

Over 30 amino acids have been identified in the hydrolysis product of casein of which glutamic acid, hydroxyglutamic acid, proline, valine, leucine, and lysine comprise about 60%. The residues of the amino acid arginine also appear to be of importance in the cross-linking of casein with formaldehyde.

The presence of both acidic and basic side chains has led to protein such as casein acting as amphoteric electrolytes and their physical behavior will depend on the pH of the environment in which the molecules exist. The isoelectric point for casein is about $\mathrm{pH} = 4.6$ and at this point colloidal stability is at a minimum. This fact is utilized in the acid coagulation techniques for separating casein from skimmed milk.

Casein plastics are today produced by the "dry process." In this process the casein is ground so that it will pass through a 30 mesh sieve but be retained by one of a 100 mesh. The powder is then loaded into a dough mixer, usually of the Artofex type. Water is fed slowly to the mixer until the moisture present forms

Table 4 Some physical properties of casein plastics

Specific gravity	1.35
Tensile strength	8,000–10,000 lbf in^{-2} (55–69 MPa)
Elongation at break	2.5–4%
Modulus of elasticity	6×10^5 lbf in^{-2} (4,000 MPa)
Izod impact strength	1.0–1.5 ft lbf in^{-}
Brinell hardness	18–24
Rockwell hardness	M 75
Breakdown voltage	200 V/0.001 in
Powder factor	0.06
Water absorption	
24 h	5–7%
28 days	30%
Heat distortion temperature	80–85°C

about 20% of the total. Water has a politicizing effect on the casein and heat is generated during the mixing operation. Mixing time for a 60 kg batch is usually about 30 min. In addition to casein and water, other ingredients like dyes, pigments, clearing agents (to enhance transparency) are added at this stage. The resultant free flowing powder should be processed soon after mixing since it will tend to putrefy. It is then extruded, so that under heat and pressure the granular powder is converted to rubbery material. The extrudate is cut up into appropriate lengths and cooled by plunging into cold water. The subsequent operations depend on the end product requirement. The rode or sheet must then be cured by a formalizing process.

Some physical properties of casein plastics are given in Table 4.

Although it is thermosetting it has a low heat distortion temperature and is not particularly useful at elevated temperatures.

In the past casein plastics were widely used for decorative purposes due to its pleasant appearance. It was also used in the button industry as well as for making buckles, slides, hairpins, knitting pin pens and pencils. These include adhesives, stabilizers for rubber latex, paper finishing agents, and miscellaneous uses in the textile industry.

3 Monomers Derived from Renewable Resources

3.1 Natural Monomers Already Polymerized

There are a variety of monomers existing in nature in the free or in the combined form that can be obtained by extraction, cleavage, or depolymerization from biomass [63–65]. There are also some naturally existing monomers/oligomers, such as the amber found in fossil resources. The monomers exhibit a variety of interesting structures that can be manipulated to obtain specialty/high-performance properties [66].

3.1.1 Chemically Modified Natural Monomers

Furans

Furans are present in xylan, one of the constituents of hemicellulose. The important products are furfural which is obtained by the steam acid digestion of corncobs, bagasse, rice husks, oat hulls, or similar materials. It acts as the precursor for the preparation of two important monomers, adipic acid and hexamethylene diamine, used in the production of nylon-66 [67]. Furfural and its derivative, furfuryl alcohol (FA), are known to polymerize to form thermosetting resins in the presence of alkaline/acid catalysts. These resins are widely used in molding compounds and in the manufacture of coated abrasives. Recently bio-based nanocomposites were produced by the in situ polymerization of FA using either montmorillonite clay (MMT) or cellulosic whiskers (CW) as the particulate phase. It was observed that FA would act as an effective surfactant for cellulose whiskers and clay particles and as the matrix precursor. Thermal stability of the nanocomposites was found to increase from the incorporation of CW and clay particles. Researchers have also used FA as a chemical treatment on bagasse and curaua fiber reinforced phenolic composites with interesting results [68].

Terpene Monomers

Terpene monomers are another class of interesting natural monomers because they give, on polymerization, plastic resins that exhibit a high degree of tackiness useful in pressure-sensitive tapes. They are also used for sizing paper and textile materials. Terpene-phenol resins are effective heat stabilizers for high-density polyethylene. But the current research has not seen much change in either the quality or a significant increase in their production.

Sorbitol

Sorbitol is an interesting natural monomer obtained from glucose (sugar waste is used for this purpose) by dehydrogenation. It easily dehydrogenates into isosorbide which is useful as a polyol for production of polymers/polyurethane [69, 70].

Lactic Acid and Levulinic Acid

Lactic acid and levulinic acid are two key intermediates prepared from carbohydrates. Lipinsky compared the properties of the lactide copolymers obtained from lactic acid with those of polystyrene and polyvinyl chloride and showed that the lactide polymer can effectively replace the synthetics if the cost of production of lactic acid is made viable [71]. Poly(lactic acid) (PLA) has found increasing application particularly in packaging and fiber technology and has reached a global capacity exceeding 250,000 t per year with a steadily declining price [72]. Poly (lactic acid) and poly(1-lactide) have been shown to be good candidates for biodegradable biomaterials. Tsuji [73] and Kaspercejk [74] recently reported studies concerning their microstructure and morphology.

In an interesting piece of research, Plackett et al. [75] used commercial L-polylactide which was first converted to film and then used in combination with jute fiber mats to generate biodegradable composites by a film-stacking technique. 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°C range were significantly higher than those of polylactide alone. Examination of composite fracture surfaces using electron microscopy showed voids occurring between the jute fiber bundles and the polylactide matrix in some cases. 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. [76]. It was found that composite films offered a great advantage in preventing the surface growth of mycotoxinogen strains because of their antifungal activity. However, the physico-chemical properties of such heterogeneous films dramatically limit their further use as packaging material. The crystallization behavior of composites based on PLA and different cellulose reinforcements, viz., microcrystalline cellulose (MCC), cellulose fibers and wood flour, has been reported by Mathew et al. [77] The effect of these reinforcements on the crystallization of PLA was studied. The MCC and WF composites were found to have a better nucleating ability than CFs. The effectiveness of natural fiber as a reinforcement for PLA was studied by Oksman et al. [78] Flax fibers were used as a reinforcement and composites were prepared using a twin-screw extruder. The extruded compound was then compression-molded. Preliminary results showed that properties of PLA and flax fiber composites are promising. Shanks et al. [79] reported on the preparation of composite materials from PLA and flax fibers. Prior to polymerization, the flax fibers were extracted with NaOH and acetone to remove lignin, pectin, and waxes from the cellulose. The surface wetting, as well as the morphology of the fibers, was studied by SEM and optical microscopy. The composites of acetone-washed fibers were found to have higher moduli than the unwashed fibers.

Lee and Wang [80] investigated the effects of lysine-based diisocyanate (LDI) as a coupling agent on the properties of biocomposites from PLA, poly (butylene succinate) (PBS) and bamboo fiber (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 [81] was hindered due to cross-linking between polymer matrix and BF. Enzymatic biodegradability of

PLA/BF and PBS/BF composites was investigated by 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.

3.1.2 Long-Chain Hydrocarbon Phenols

Long-chain hydrocarbon phenols are phenolic lipids present in plants from a number of families, notably the Anacardiacae, found in many parts of the world [82]. They are mostly monohydric or dihydric phenols or phenolic acids with a hydrocarbon side chain at the meta position. Many of these monomers are found to be mixtures of four components varying in degree of unsaturation in the side chain. Being unsaturated these phenols can undergo oxidative coupling polymerization giving rise finally to cross-linked films and have found application in surface coatings. Thus, some have found artistic use while others have found technical use [83–85].

From the point of view of chemistry, phenols are interesting because of their dual aliphatic and aromatic character. The aliphatic entity gives rise to hydrophobic behavior, whereas the phenolic moiety is hydrophilic in character. From an application point of view, the reactions are (1) that of the phenolic moiety undergoing the conventional polycondensation reaction with formaldehyde to give phenolic type resins, (2) the unsaturated side chain reaction polymerization to flexible/rubbery polymers, and (3) the auto-oxidation/oxidative coupling polymerization to give rise to cross-linked polymers. Apart from these possibilities, these lipids have numerous sites such as the hydroxyl position, the aromatic ring, and the side chain that are amenable to chemical modifications. So, compared with phenols they have more opportunities for chemical modifications and polymerization for effecting structural changes for tailor-made polymers for a specific application. Among the phenolic lipids of nonisoprinoid origin, the two most important lipids of commercial significance are those available from the trees *Anacardium occidentale* and *Rhus vernicefera*.

Rhus vernicefera

The latex is collected in the same way as the rubber plant *Hevea brasiliensis*. The product is known as urushiol, which consists of dihydric phenols of structures as shown in Fig. 7 and it is used as a lacquer.

Structure of Dihydric Phenols of Urushiol

As in the case of other phenolic lipids, urushiol is also a mixture of components varying mostly in the degree of unsaturation. Thus, the urushiol from *Rhus vernicefera* has structures as shown in Fig. 5 [86]. *Rhus toxicondron* is also known to give urushiol, but its triene component has a vinyl end group unlike that of *Rhus*

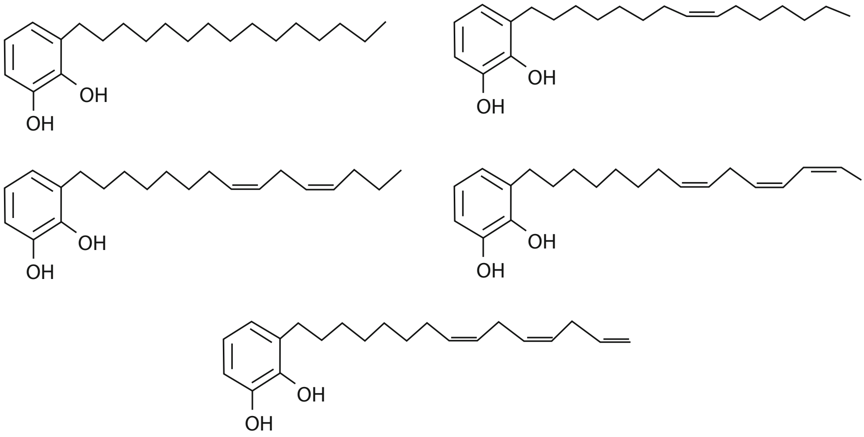


Fig. 7 Structures of dihydric phenols of urushiol

vernicefera [87]. Urushiol is used largely in Japanese lacquering. The hardening of urushiol is thought to involve oxidative polymerization and cross-linking [88]. High adhesion, thermal and alkali-resistant epoxy resin paints have been made by adding the product of reaction between urushiol and hexamethylene diamine [89]. Black ointments for printing ink, plastics, and carbon paper have been obtained from urushiol and certain iron salts [90]. Salts of thiosulfate ester of urushiol have found use as lubricants and additives.

Anacardium ocicdentale

This is one of the most widely distributed plants cultivated to obtain cashew nut. The phenolic lipid is only a by-product known as cashew nut shell liquid (CNSL). The nut, attached to the base of the cashew nut apple consists of an ivory-colored kernel covered by a thin brown membrane (testa) and enclosed by an outer porous shell, the mesocarp which is about 3 mm thick with a honey-comb structure where the reddish brown liquid (CNSL) is stored [91]. The major components of CNSL are a phenolic acid, anacardic acid, a dihydric phenol, cardol with traces of mono hydric phenol, cardanol, and 2-methyl cardol [92–95].

A number of methods exist for the extraction of CNSL, but most industries follow the CNSL bath process. Solvent extraction processes are also used at a limited scale.

The structures of anacardic acid, cardol, cardanol, and 2-methyl cardol are given in Fig. 8.

Cardanol is generally obtained by the distillation of CNSL under reduced pressure. The structure of cardanol has many interesting features when compared to phenols. The presence of a C_{15} hydrocarbon side chain at the meta position provides additional opportunities for manipulation. For example, unlike phenol,

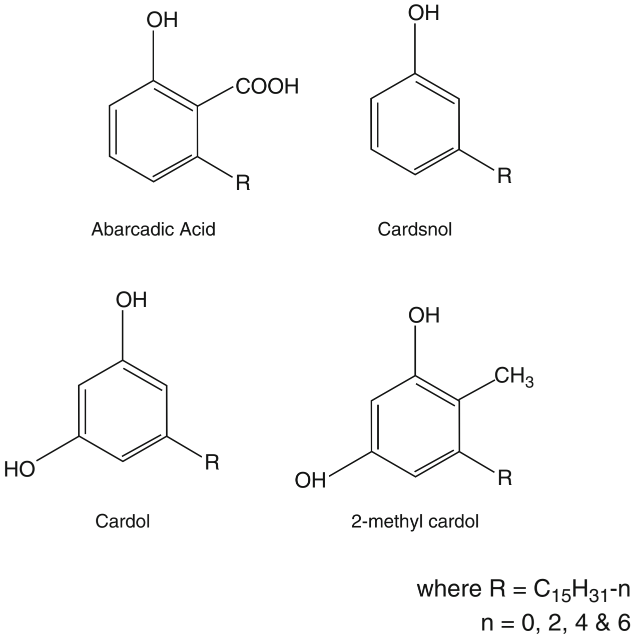


Fig. 8 Structure of CNSL components

cardanol can be polymerized by a chain reaction mechanism. This gives rise to opportunities for selection of control of polymerization for a particular product. Cardanol can also undergo chemical modifications at the hydroxyl group at the reactive sites of the aromatic ring and on the side chain. Moreover, the presence of a hydrocarbon side chain imparts additional properties such as internal plasticization, flexibility, acid and alkali resistance, moisture resistance etc.

CNSL and cardanol have found extensive uses in automotive break-lining applications [96]. Break linings and clutch facings based on CNSL polymers show very low fade characteristics and very high recovery. CNSL/cardanol-based surface coatings possess excellent gloss and surface finish with a high level of toughness and elasticity [97–100]. CNSL resins are added to laminates based on phenol formaldehyde, epoxy, etc. to reduce brittleness and to improve flexibility of product. The resins also exhibit better age hardening and improved bonding to the substrate [101].

Natural Monomers Not Yet Studied and Utilized

There exist a large number of natural monomers that need further studies for their exploitation. Pillai and Manjula [62] have reviewed the subject and have produced a comprehensive list of potential monomers and their sources.

4 Conclusions

Natural monomers and polymers have complex structure and properties, which with proper modifications could be a substitute for today's high-performance plastic materials. Existing biodegradable polymers can be blended with different materials with the aim to reduce cost and to tailor the product for specific applications. NR and almost all other natural resources are discussed and possible modifications and the applications of these natural polymers as well as polymers from natural monomers are analyzed in this review. Further studies are required to improve the performance of these materials so that synthetic polymeric materials can be replaced by polymers derived from these renewable materials.

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Sustainable Embedding of the Bioplastic Poly-(3-Hydroxybutyrate) into the Sugarcane Industry: Principles of a Future-Oriented Technology in Brazil

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Abstract To make the biodegradable polymer poly-(3-hydroxybutyrate) (PHB) economically competitive with common end-of-pipe plastic materials from petrochemistry, the production costs have to be reduced considerably. The embedding of the industrial PHB production into a sugar and ethanol factory starting from the raw material sugarcane makes it possible to achieve a production price per kilogram PHB that is 4–5 times lower than known for prior PHB production processes. This cost reduction is enabled by an extensive utilisation of by-products of the sugarcane plant, especially of bagasse. In the presented process, this typical waste product is burned for generation of the steam and electrical energy required for the process. Furthermore, the availability of the substrate sucrose in high quantities leads to the gained price advantage. Together with the application of ethanol as an alternative fuel, CO_2 emissions from the production plant return to the sugarcane fields via photosynthetic fixation, resulting in a carbon balance of nearly zero. The utilisation of medium chain length alcohols, by-products of the ethanol production integrated in this plant, substitutes the classic PHB extraction method using chlorinated agents. In this way, the major drawbacks regarding profitability and environmental

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embedding of PHB production are solved within a future-oriented, integrated process.

Keywords Autarkic energy supply, Biopolymers, Integrated production lines, Sugar cane industry, Sustainable process development

Contents

1 Poly-(3-Hydroxybutyrate): A Biodegradable Sugarcane-Based Plastic Material

1.1 Biodegradable Plastics in the Environment

A wide variety of synthetic plastics have been applied in countless products, replacing metal, wood, natural rubber, and other materials. Polymer production has been a base industry in developed countries since the early twentieth century. Today, the production of plastics amounts to about 150 million tons per year and displays an upward trend [1, 2].

The main polymeric materials are based on fossil feedstocks, and the world's growing population has led to increasing mineral oil consumption, which may result in its accelerated depletion as a natural resource [1]. Another problem is the environmental pollution resulting from the disposal of polymeric materials, which may take many years to decompose. Hence, together with the world's growing environmental awareness, the desired durability of plastic materials constitutes a disposal problem. An attempt to solve the waste problem is the use of recycling techniques. However, despite its broad acceptability, recycling alone has proved to be insufficient to solve this problem, since it is impossible to recover all discarded plastic materials by this process. The recycling of heavily soiled inhomogeneous materials is generally a more complex process. One relevant aspect is the considerable amounts of energy usually required for such processes [1–3]. Additionally, recycling has a negative impact on the mechanical properties of the materials, such as an increase in brittleness [4].

Another method for treating solid residues (discarded plastics) is incineration. However, its use generates environmental problems, such as air and water pollution, because it releases aggressive chemical agents like dioxins and causes global warming through the release of carbon dioxide. These effects are not restricted to the places where such techniques are employed, but spread around the globe [1, 2, 4].

Within this context, the search for a material that is durable while in use and degradable after its disposal has led to the emergence of biodegradable plastic—materials that decompose into carbon dioxide and water as the final result of the action of microorganisms such as bacteria and fungi [5]. Polyhydroxyalkanoates (PHAs) constitute examples of such materials.

Biodegradable materials were initially used in medical applications such as sutures, prostheses, controlled drug-release systems, and vascular grafts. These applications are enabled by their biocompatibility, their ability to be absorbed by the body, and because of their mechanical properties appropriate for such applications [6].

More recently, biodegradable plastics have been applied in other areas, including packaging and agriculture (plant containers, mulch films, controlled release of chemical substances, etc.). After hydrolysis of PHAs, the follow-up products can be used as enantiomerically pure starting materials for chiral high price compounds [7–9].

It is worth noting that biodegradable plastics cannot yet compete with traditional plastics because of their higher production cost [10]. Therefore, the reduction of PHA production costs is presently one of the major topics in biopolymer research [11].

2 General Aspects of Biodegradability

It is important to clearly define the concepts of degradation and biodegradation. The definitions according to ASTM D-833 are the following [12]:

- Degradable plastic: which, under specific environmental conditions, will present significant changes in its chemical structure, resulting in the loss of some of its properties, and
- Biodegradable plastic: whose degradation also results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae.

Biodegradable plastic must initially be broken down into fragments of low molecular mass through chemical or enzymatic reactions, after which they can be absorbed by microorganisms [2]. These reactions can be induced by oxidative or hydrolytic enzymes, which generate superficial erosion, or by abiotic mechanisms (without the presence of living organisms) through hydrolytic or oxidative reactions [13, 14].

In the former case, a bacterial or fungal colony on the surface of the material releases an extracellular degrading enzyme which breaks down the polymer chains into smaller units (dimers and oligomers), which then are absorbed through the microorganisms' cell membrane and metabolised as a source of nutrient (carbon). It has been proposed that this mechanism first hydrolyses the chains of the amorphous phase of poly-(3-hydroxybutyrate) (PHB) and then proceeds to attack the chains in the crystalline state. The enzymatic degradation rate decreases as the crystallinity increases [15, 16].

In the latter situation, hydrolytic and oxidative mechanisms take place in the absence of living microorganisms and are restricted to the amorphous phase and the borders of the crystals, since the crystalline regions are practically impermeable to water and oxygen. Although the phenomenon of biodegradation appears rather simple, it is actually quite complex, for it is affected by several factors which are often interrelated. The biodegradation rate of these materials may vary over time and depends on material and environmental factors, such as the type of repeating monomer unit (nature of the functional group and its degree of complexity), morphology (degree of crystallinity, size of the spherulites), hydrophilicity, accessible surface area, presence of additives, level of humidity, temperature, pH, etc. [5, 16]. The products resulting from the biodegradation process are carbon dioxide and water in aerobic environments, and carbon dioxide and methane in anaerobic environments [17].

A deeper understanding of the degradation process will enable the optimisation of the entire life cycle of the materials produced [18].

3 Polyhydroxyalkanoates: Characteristics and Processing

*3.1 General Aspects of Poly-(3-Hydroxybutyrate) and the Copolymer Poly-(3-Hydroxybutyrate-*co*-3-Hydroxyvalerate)*

PHB is an environmentally degradable material belonging to the family of the PHAs, polyoxoesters of hydroxyalkanoic acids. PHB was first identified in 1926 by Lemoigne as a reserve material of *Bacillus megaterium* [19]. Figure 1 shows the general chemical structure of PHAs (a) and the biodegradable PHB homopolyester (b).

PHB is a material that features outstanding properties among thermoplastics by being embedded into nature's closed cycles. The polyester can be produced from renewable raw materials such as sucrose from sugarcane via microbial cultivations in bioreactors. For their biosynthesis, several microbial strains are of interest. These organisms accumulate PHA as intracellular storage compounds. After extraction and purification of the polymer, it can be processed into desired products and

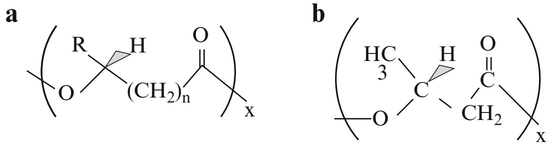

Fig. 1 Chemical structure of the repeating unit (monomer) in PHA macromolecules (**a**) and structure of the biodegradable bioplastic PHB (**b**). *R:* side chain (PHB: R=CH_3; P(3HV): R=C_2H_5; P(4HB): R=H); n: number of methylene groups (indicating the length of the backbone of the building block; PHB and P(3HV): n = 1; P(4HB): n = 2); x: number of repeating units in the polyester chain

Table 1 Comparison of selected properties of PHB and polypropylene [24]

Property	PHB	Polypropylene
Molecular weight (10^5g mol^{-1})	1–8	2.2–7
Density (kg m^{-3})	1.25	0.905
Melting point (°C)	171–182	176
Crystallinity (%)	80	70
Glass transition temperature (°C)	5–10	−10
O_2-permeability [cm^3/(m^2atmd)]	45	1,700
UV-resistance	Good	Bad
Resistance to solvents	Bad	Good
Tensile strength (Mpa)	40	38
Elongation to break (%)	6	400
Biodegradability	Yes	No

further, after a certain period of use, discarded and transformed into compost, thus completing the natural cycle of mineralisation. In the absence of microorganisms capable of degradation of PHB, hydrolysis of this material in aqueous environments is slow because of its hydrophobic nature. Thus, in principle, the lifetime of a not composted PHB product is unlimited but, after its disposal, the material will be degraded e.g., in compost piles [20, 21].

PHB is a biocompatible, biodegradable, thermoplastic, and hydrophobic material consisting of *R-(-)*-configured building blocks of 3-hydroxybutyrate. Because of the high degree of polymerisation, it has a high molecular mass and a high degree of crystallinity (55–75%), exhibits good chemical resistance, and its barrier properties are of interest for practical packaging applications (see Table 1) [22, 23]. Many of the physical and mechanical characteristics of PHB are similar to those of polypropylene (PP) [22]. Table 2 compares significant characteristics of PHB and PP.

The characteristics of processibility, high crystallinity, and high melting point (T_m value) of PHB can be modified by the microbial fermentation strategy, which can be adjusted for the production of co- and terpolymers, or by the generation of polymeric blends.

The most familiar examples of copolyesters are poly-(3HB-*co*-3HV) and P(3HB-*co*-4HB). Poly-(3HB-*co*-3HV) consists of *(R)*-3-hydroxybutyrate (3HB) and *(R)*-3-hydroxyvalerate (3HV), forming an ethyl group as a side chain. Poly-(3HB-*co*-4HB)

Table 2 Selected properties of poly-(3HB-*co*-3HV) in dependence on the molar ratio of 3HV [24]

% 3HV (mol mol^{-1})	Melting point (°C)	Glass transition temperature (°C)	Tensile strength (MPa)	Elongation to break (%)
0	179	10	40	5–8
9	162	6	37	20
20	145	1	32	45
34	97	−8	18	970
71	83	−13	11	5

is composed of *(R)*-3-hydroxybutyrate and 4-hydroxybutyrate (4HB), which is the most common achiral PHA building block.

Copolyesters are characterised by their lower crystalline melting point, hardness, tensile strength, and crystallisation rate (hence, greater ductility and elasticity) than pure PHB. Their physical and thermal properties can be adjusted by varying the molar concentrations of 3HV in poly-(3HB-*co*-3HV) or of 4HB in poly-(3HB-*co*-4HB), respectively. Simply varying the co-monomer content opens the way from a rigid and highly crystalline plastic to a high-tech material with features of elastomers [21, 23, 24]. In the case of poly-(3HB-*co*-3HV), the degree of crystallisation usually decreases with increasing 3HV content. The crystalline melting point T_m (normally approximately 175°C) drops to 71°C for poly-(3HB-*co*-40%-3HV). The glass transition temperature T_g corresponding to poly-(3HV) varies from 10 to 12°C and the T_m ranges from 107 to 112°C [15]. Table 2 shows the properties of PHB and poly-(3HB-*co*-3HV) with differing 3HV contents.

Copolymers such as poly-(3HB-*co*-3HV) are less sensitive to thermal degradation during thermal processing because they show a lower crystalline melting point compared to the homopolyester PHB. Additionally the co-monomers must be inserted homogeneously into the polymeric chains (random distribution). The formation of blocks of one of the monomers must be avoided. For example, for a co-monomer content of 16% molar of 3HV inserted homogeneously into the polymeric chains, the thermal curves produced by a differential scanning calorimeter (DSC) will show a single melting endotherm peak. However, if the co-monomer is not inserted uniformly into the PHB chains, multiple melting peaks will appear, and the highest melting peak among these multiple peaks will be located at a temperature exceeding the material's thermal stability (below 160°C). Therefore, both the 3HV content and the homogeneity of the co-monomer distribution in the copolyester are important for lowering the polyesters T_m [25].

4 Processing of Poly-(3-Hydroxybutyrate)

PHB can be processed like a conventional thermoplastic in most industrial transformation processes, including extrusion, injection molding, and thermo-pressing [26, 27].

By the extrusion process, PHB can be transformed into rigid shapes (such as pipes) and films for packaging. PHB can also be modified by extrusion through the incorporation of additives (stabilisers, plasticisers, and pigments), fillers (wood and starch powder) or by blending with other plastics. Since it undergoes thermal degradation at temperatures above 190°C [28], the extruder's temperature profile and the screw speed must be as low as possible. Because of the need for strict control, the processing window of PHB is narrow in comparison to other conventional plastics. It should be pointed out that after the isolation step, raw PHB is processed starting from powder form, requiring an appropriate screw profile to allow it to be processed efficaciously [29].

PHB is highly versatile when used in the injection molding process, and pieces of varying shapes and sizes can easily be manufactured, which may range from a few grams to several kilograms. The main applications of this material include packaging for cosmetics and food, agro-toxic packaging and seedling recipient, medical and veterinary implants. As in the extrusion process, injection molding of PHB must be performed following a nonaggressive temperature profile and a low injection pressure to prevent the appearance of burrs [29].

PHB can also be thermo-pressed in the shape of sheets or other flat shapes [26]. It has to be emphasised that by applying the above processes certain characteristics (such as crystallinity, physical shape, molar mass distribution, and compaction of the material) can be affected during processing. PHB samples that have undergone different forms of processing therefore may not present the same rate of biodegradation [30].

Several operational procedures must be observed in order to obtain products with satisfactory end quality using most types of conventional equipment, without the inclusion of special modifications such as screws or matrixes with specific designs. Extrusion or injection processes can use typical polymer processing screws (L/D of 20:1) designed to minimise the exposure time of the melted biopolymer. After use, the equipment can be purged using low-density polyethylene (PE) resin as a vehicle [29].

PHB should not be exposed to temperatures exceeding 160–170°C for a period of more than 5 min in order to prevent thermal degradation. The polymer's "window of processibility" is relatively narrow compared to that of fossil-based polymers, requiring precise control of the processing temperature to prevent temperature peaks in the heating resistances, which would lead to the rapid degradation of the material. The window of processibility can be monitored by observation of the surface characteristics of the moulded component, such as rugosity and shine, which are very particular in this polymer [31].

When using multistage injection equipment, it is advisable to fill the mould cavity rapidly, using high injection velocities combined with high pressures, and ensuring that the injection pressure applied does not lead to the appearance of defects such as burrs and rugosity, since the fluidity index of PHB drops rapidly when the mass is subjected to high shearing rates [29].

PHB does usually not require longer cooling times in the mould compared to fossil-based polymers.

To minimise the PHB molding "cycle times", it is advisable to use injection moulds heated in the range of 20–40°C rather than injection moulds with cold water systems in the order of 10°C, which allows for a higher crystallisation rate with direct consequences on the thermo-mechanical properties of the moulded component. This mould temperature is appropriate, since it is about 50°C higher than the polymer's vitreous transition temperature. The use of this procedure improves the characteristics of ejectability of the moulded component, resulting in a gain in "cycle times" [29]. For a more effective improvement in the crystallisation rate, it is desirable to use a nucleating agent. For this purpose, several products are used as nucleating agent in PHB, including bore nitride, saccharine, and talc.

5 Economic Drawbacks in PHA Production and Possibilities to Overcome Them

Conventional plastics from fossil feedstocks like PE and PP are produced at a price of less than US$ 1 kg^{-1}. In 1995, the Monsanto Company sold PHA-products at about seventeen times the price of synthetic plastics [32]. Several stages in biotechnological PHA production can be pointed out as decisive for cost-effectiveness:

- Costs for the carbon source
- Costs for the nitrogen source
- Precursor costs
- Isolation costs including separation yields

It is clear that for achieving a real cost-effective process, all production steps have to be taken into account [33]. In 1995, Hänggi pointed out that the raw materials constitute the major part of the production cost for biopolymers [3]. Recent studies emphasise that PHA production from purified substrates such as glucose or sucrose can more or less be regarded as optimised and therefore it is of importance to further improve the fermentation technologies by using cheaper carbon sources as basic feedstocks [34]. Here sucrose from sugarcane agriculture is a raw material of major interest [27, 35].

It has been accounted that, on a production scale of PHB of 100,000 tons per year, the production costs will decrease from US$ 4.91 to US$ 3.72 kg^{-1}, if hydrolysed corn starch (US$ 0.22 kg^{-1}) is chosen as the carbon source instead of glucose (US$ 0.5 kg^{-1}) [33]. But this is still far beyond the cost for conventional polymers, which in 1995 was less than US$1 [32]. Lee et al. estimated that PHB and *mcl*-PHA can be produced at a cost of approximately US$ 2 kg^{-1} [36]. The precondition therefore would be attaining high productivity and the use of inexpensive carbon sources. Among such substrates, molasses [37], starch [38], whey from the dairy industry [37–42], surplus glycerol from biodiesel production [39, 43], xylose [44, 45], and plant oils [46] are available.

An additional cost factor in normally phosphate-limited PHA production processes is the expenses for complex nitrogen sources. It was found that supplementation of a defined production medium with small amounts of a complex nitrogen source such as tryptone could enhance PHB production by recombinant *E. coli* [47]. Examples of complex nitrogen sources are fish peptone [48], meat extract, casamino acids, corn steep liquor, soybean hydrolysate, and cotton seed hydrolysate [44]. Instead of expensive complex nitrogen sources cheaper products like silage juice [49] or meat and bone meal hydrolysate can successfully be applied in PHA production processes [39].

Product quality of PHAs is very much dependent on the polyester composition (see 3.2.2.1). In 1987, Byrom found that poly-(3HB-*co*-3HV) can be produced in large-scale fed-batch culture by supplementing the nutritional medium of a glucose-utilising mutant of *Alcaligenes eutrophus* (today known as *Cupriavidus necator*) with propionic acid (precursor for 3HV formation) [50]. Later it was shown that the utilisation of valeric acid instead of propionic acid results in a higher proportion of 3HV units [51]. The improvements in product quality of co- and terpolyesters, however, results in an increase of the production costs of the polymer because of the high price of the precursors.

Additionally to the expenses for raw materials, the improvement of the biotechnological production in bioreactors (optimisation of process parameters such as dissolved oxygen concentration that can strongly influence product yields) is decisive for cost-effectiveness [52].

After biosynthesis of the polyester and separation of the bacterial biomass from the supernatant, the required recovery process (typically a solid–liquid extraction procedure) can constitute another not negligible cost factor, especially in large-scale production. Here extraction solvents that can easily be recycled will be of interest [53]. In order not to leave the patterns of sustainability in biopolymer production, it will be indispensable to concentrate the development of new extraction processes on such recyclable solvents that are also of environmentally sound nature [54]. Typical harmful chlorinated solvents like chloroform must be avoided. A PHB production process embedded in an ethanol production plant has the advantage to utilise the medium chain length alcohol fraction (fusel alcohols) from the distillery step, consisting mainly of iso-pentanol. The application of the fusel alcohols as extracting solvents unites two important points: On the one hand, this liquid normally constitutes a surplus product that has little market value. When used as an extraction solvent the costs for alternative solvents are saved. Furthermore, this extraction solvent is less harmful to handle than the classical extraction solvent chloroform [27].

6 PHB and Ethanol from Sugarcane

6.1 Background Information of Ethanol Production from Sugarcane

Globally, the major ethanol producers are Brazil and the USA, which account for 62% of the annual world-wide ethanol production. In the USA the feedstock used is corn whereas in Brazil sugarcane is the basis for ethanol production. Brazil is the largest single producer of sugarcane, from which both fresh sugarcane juice and the by-product molasses are used for ethanol fermentation [55]. Since 1903, ethanol produced from sugarcane has been used as an engine fuel in Brazil. The wide use of ethanol as fuel and the production of ethanol from sugarcane are partly due to the Brazilian government's desire to be less dependent on mineral oil fuels that have to be imported. The oil crisis in the 1970s led to a severe setback in the economy of the country, as it imported 80% of the oil used. Therefore, the Brazilian fuel-ethanol program (PROÁLCOOL) was founded. Within this program the production of ethanol and the use of ethanol as fuel were strongly promoted. This led to an increased production of both sugarcane and ethanol. The ethanol distilleries were combined with the sugar mills for a very effective production of ethanol from sucrose [56]. The ethanol produced in Brazil is widely used as engine fuel both pure and as a mixture with gasoline, resulting in a daily consumption of 200,000 barrels of gasoline equivalent, which represents 40% of the total fuel consumption of Otto-cycle engines in Brazil [56, 57].

In many Brazilian sugar mills the molasses, a sucrose-containing by-product of sugar production, is used as the raw material for ethanol fermentation. Another waste product in sucrose production is bagasse, a lignocellulosic residue obtained after the juice extraction from the sugarcane. The bagasse is used for energy production for the sugar mill as well as for the ethanol fermentation and the distillation process [27]. Comparison of sugarcane and corn for ethanol production has shown that the sugarcane-derived ethanol production is much more favourable considering the energy and fossil fuel demand of the process [56].

The yeast *Saccharomyces cerevisiae* and the bacterium *Zymomonas mobilis* are the most frequently used microorganisms in ethanol fermentation [58]. The most-common ethanol production process in Brazil is the discontinuous Melle–Boinot process. A drawback of this process is the need for continuous centrifugation and recycling of the yeast used for the fermentation. Further high fermentation capacities are needed, unproductive steps occur in the process and the medium composition has to be varied during the production process. However, the process has been improved and optimised within the PROÁLCOOL program. The fermentation time has been decreased to 5–8 h and the process efficiency increased up to 92%. Another alternative is the use of a continuous process with free, flocculent or immobilised cells [59]. Yields up to nearly 0.5 g ethanol per gram of sugar have been achieved with a continuous fermentation process [60]. According to the literature the continuous fermentation method is very efficient and is also being used on industrial scale in several ethanol-producing regions in Brazil (cited in [59]).

7 From Sugarcane Harvest to Disposal of Residues

Sugarcane is cultivated in enormous quantities in tropical areas, such as the central-southern region of Brazil. Here, 265 million tons of this valuable plant is harvested per year [27].

Sugarcane is typically crushed in a series of large roller mills, after disintegration with rotating hammers or “shredders”. The extraction of sucrose from the shredded material is conducted as a counter-current process using fresh hot water at one end pumped in the opposite direction to that of the cane. Here the optimised amounts of water and sugarcane are of importance, because the subsequent water evaporation is energy demanding.

The sweet juice is separated, and the remaining fibres are further used for energy recovery in boilers. Typically, cane contains 12–14% of fibres (bagasse). Beside sucrose, the sweet juice still contains contaminants such as soil, fibre residues and green extract from the original plant [27].

The juice is further clarified by a liming step. Here the juice is preheated and mixed with $Ca(OH)_2$ (lime milk) in the required ratio. This mixture is transferred into a settling tank (clarifier), where solid compounds are separated. By this procedure, clear juice is obtained. The mud from the clarifier still contains considerable amounts of valuable sugar. Therefore, the mud is filtered on rotary vacuum filters. This way, the residual sugar is extracted; the mud is washed again, releasing sweet water that is united with the clear juice [61–63].

Sugar liquor suitable for crystallisation contains about 80% (w/w) of sucrose. Because of the fact that the juice coming from the clarifier only contains about 15% (w/w) of sugar, evaporation of water is an indispensable subsequent process step. This is normally accomplished in steam-heated multiple effect evaporators [61–63].

The final step is the transfer of the syrup into a vacuum pan, a large container with steam-heated pipes for boiling off water until a sugar concentration is reached that enables the formation of sugar crystals. These pans can operate in discontinuous or in continuous mode. The mixture of crystals and mother liquor, called the “massecuite”, is dropped into a crystalliser, where the crystals continue to grow by being cooled down. From the crystalliser, the massecuite is separated from the sugar crystals by centrifugation. Finally, the sugar crystals are dried by hot air before being dispatched. The part of sugar that has not crystallised from the juice, a sweet by-product called “molasses”, can be used as cattle feed additive, or as a substrate both in ethanol- and PHA production [31, 62, 63].

8 CO_2 and Energy Balances of Sugar and Ethanol Production

The remaining by-product of sugar production, bagasse, is burned in large boilers to produce high-pressure steam exhibiting 60 bar. By being expanded in turbines, this steam is employed to generate electricity, thermal and mechanical power. The amounts of energy produced from bagasse are not only sufficient for sugar- and ethanol processing, but provides even a surplus that can be used for domestic and industrial demands and for supplying a PHB production process integrated in the sugar mill. Here two major advantages of the entire process can be pointed out [56]:

Firstly, high amounts of energy are generated from renewable resources instead of energy recovery from fossil feedstocks. The energy recovery by burning bagasse

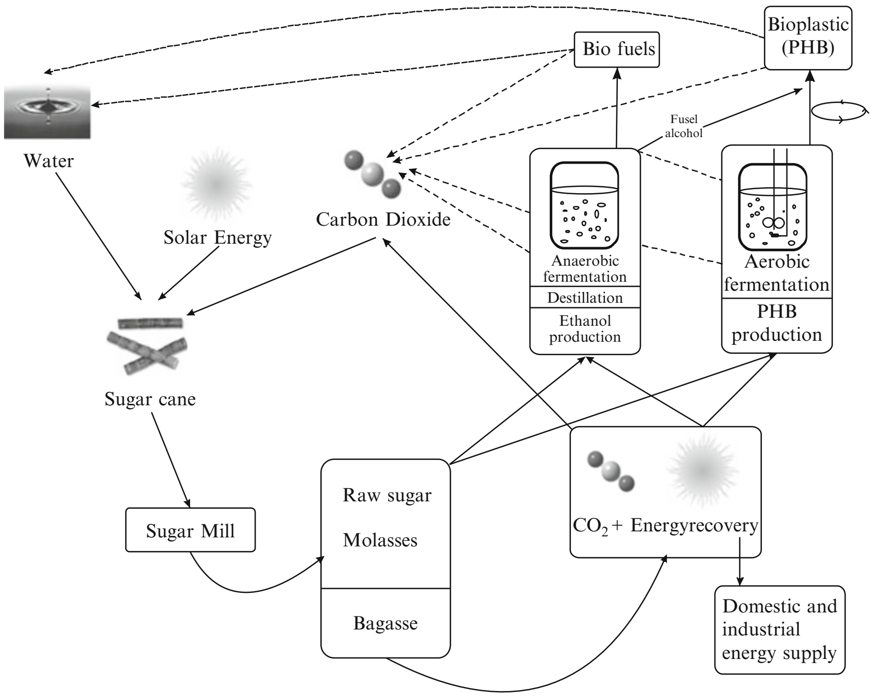

Fig. 2 Closed carbon cycle in PHB production integrated in a sugar mill with ethanol

only releases the amounts of carbon dioxide that has originally been fixed via photosynthesis by the sugar cane to build-up the fibres. In contrast to this the burning of fossil fuels releases huge amounts of carbon dioxide that have been fixed in the earth's interior, thus contributing to prevailing contemporary problems like the greenhouse effect and global warming [27, 56].

Secondly, this alternative energy source makes the energy supply of the ethanol- and PHA production independent of the availability of limited feedstocks such as fossil fuels. This energetic self-sufficiency makes the process economically more profitable [27, 56]. Figure 2 shows a scheme of the entire process.

9 Integration of PHB Production Process into the Sugarcane Mill and Cost-Effectiveness

Until today, biotechnological production of PHB requires more energy than the production of petrochemical plastics [64]. The integration of PHB production into the sugarcane mill unites several advantages:

- The sugar and ethanol mill supplies enough energy to run the production process.

- Raw materials are available directly from the mill.
- Extraction solvents for PHB are available from an ethanol production side stream.

Approximately 12,000 tons of sugar cane is milled per day in an average sugar mill in the south-central region of Brazil, demanding about 25 km^2 of cultivation land. This daily amount of harvested sugarcane yields 1,000 tons per day of sugar, 293 m^3 ethanol and approximately 31 tons of PHB. Making up the balance, this corresponds to 10, 000 tons of PHB produced per season (calculated via 180 days per milling season).

Starting from cane sugar, 3 kg sucrose is needed to produce 1 kg PHB, together with 39.5 kg steam and an electricity demand of electrical energy of 3.24 kWh. The electricity demand is supplied by generation of electrical power via high pressure steam from bagasse burning. Low-pressure steam that is additionally needed for heating is also provided from bagasse burning [27].

In direct comparison with calculations for other PHA production processes, the integration of the sugar and ethanol mill is definitely of economic advantage. Monsanto sold its product at 10–20 US$ per kilogram [32]. Bertrand calculated the production costs for PHB from glucose at US$ 5.85 kg^{-1} [65]. A study for an annual production of 100 ,000 tons PHB from sucrose as the carbon source with energy supply from fossil fuels estimates the price at US$ 2.65 kg^{-1} PHB [66]. Calculations done by Nonato and colleagues demonstrate that this lowest estimated limit could be approached depending on the changing prices for sucrose. Without considering taxes, sucrose accounts for nearly 29% of the total process costs [27]. Normally, the costs for the carbon substrate used during PHB production accounts for approximately 50% of the total process costs [3, 33, 66–68].

In order not to leave the patterns of sustainability, PHB production has to be environmentally sound in every single process step. This requires the abdication of chlorinated solvents which, on the one hand, provide high-purity products at high extraction yields, but, on the other hand, are inconsistent to the claims of sustainability. The integration of the bioplastic production into the sugar and ethanol factory opens the door for a new extraction process using alternative "green solvents". These compounds, consisting mainly of medium chain length fusel alcohols such as iso-pentanol are a by-product of the ethanol production process from sugarcane. This PHB isolation process saves the costs for extraction solvents and provides a rather pure product (purity $>98\%$) at high yields (95%) [27].

Figure 3 shows a mass and energy scheme for the intended annual production of 10,000 tons of PHB. Because of the fact that the sugar season in Brazil is limited to 180 annual production days, but the PHB production plant itself will run for 330 days per year, stocks of bagasse (energy supply) and sugar (substrate supply) have to be created. Starting from 2.16 Mt of milled sugarcane, the annual production of sucrose will account for 180,000 tons, together with an output of 52,575 m ethanol. The required demand of 32.4 GW h^{-1} of energy for PHB production is entirely provided by the self-sufficient energy generation from burning of bagasse [27].

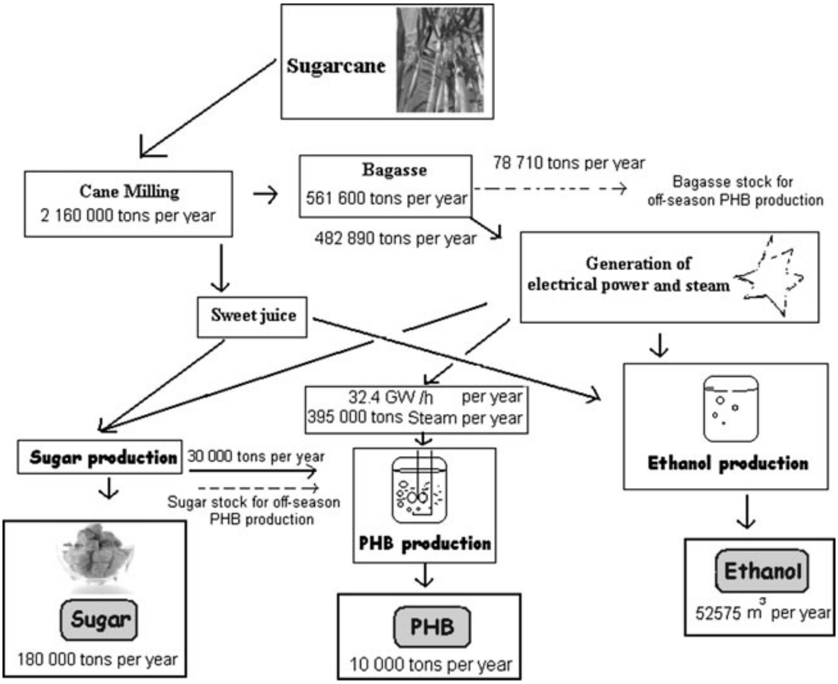

Fig. 3 Mass and energy balance for the production of 10,000 tons poly-(3-hydroxybutyrate) per year in an integrated sugar and ethanol production process [27]

10 Conclusion

According to the data presented, the biotechnological production of PHB on a large scale (10,000 tons per year) can become economically profitable, when integrated into a combined sugar and ethanol factory. The convenient substrate availability together with the self-supply of energy needed for generation of steam and electricity enables a reduction of the costs per kilogram PHB to only about 20–25% of the price that was paid for PHB in the past.

The discussed process is not only of economic interest, but constitutes a prime example for an environmentally sound and future-oriented technology. This is due to the fact that, since all carbon involved as substrate or as fuel is originated directly from sugarcane, CO_2 emissions from the entire process are fixed again by sugarcane and thus are kept within nature's closed cycles. Beside the sustainable CO_2 balance, numerous by-products from the sugar production itself or from the integrated ethanol distillery are extensively used instead of being disposed of or sold at crash prices.

Because only about 17% of the total sugar produced is diverted to PHB biosynthesis, the polymer production will not affect sugar stocks and will not cause a significant increase of the sugar price. Biopolymer production should even upgrade the sugarcane industry in Brazil and, together with an expected increasing market for alternative bio-based and biodegradable materials in future, lead to an expansion of the PHB production capacity. This will require additional areas for sugarcane cultivation. However, this fact will not be a drawback, as there are high quantities of arable areas available that are suitable for agriculture in Brazil.

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Additives for the Manufacture and Processing of Polymers

Rainer Höfer and Klaus Hinrichs

Abstract Plastic additives are a diverse group of specialty chemicals that are used to manufacture polymers (polymerization aids like initiators, surfactants and protective colloids) or are incorporated into the plastic product prior to or during processing. They may become part of the polymer network (like initiators do) or remain without a chemical linkage to the polymer. Additives aid in the processing of the polymer and in the manufacture of the plastic end product (lubricants, plasticizers) or improve characteristics and performance of the final product (flame retardants, antistatic agents, impact modifiers, and heat/light stabilizers). Additive manufacturers are faced with the imperative to develop products that not only enhance the overall processability and functionality of the plastic end products, but to satisfy environmental and health demands as well. Additives are regulated by national or international authorities in order to protect consumers, when leaching or extraction from elastomeric or plastic components or from a coating film occurs or when volatilization into the environment may happen.

Keywords Antioxidants, Emulsifiers, Initiators, Integrated product policy, Lubricants, Plasticizers, Polymerization, Protective colloids, Renewable resources, Stabilizers, Surfactants, Sustainability

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Contents

1 Sustainability

Sustainable development of products is a key demand in a world of limited resources and endangered ecosystems. Potential eco-toxicological and health risks of anthropogenic chemicals, as well as the processes involved have to be evaluated in order to find an adequate balance of risk and benefit and to provide guidance for an appropriate risk management.

1.1 Integrated Product Policy (IPP) of the EU

It is inevitable that products have an impact on the environment and consumer at all stages of the products' life cycle, e.g., raw material production, manufacturing of products, use, recycling and disposal. The Integrated Product Policy (IPP) seeks to minimize this impact.

In order to achieve that objective a variety of tools – both voluntary and mandatory – can be used such as economic instruments (e.g., funding, fees), substance bans, voluntary agreements, environmental labelling and product design guidelines. The application of principles of life-cycle analysis for additives clearly indicates that raw materials, energy and pollution from renewable resources are preferred when compared to petrochemically based processes and products.

Examples of life cycle analysis which have been performed under EU contracts can be found for various PVC products [2].

1.2 Principles of Sustainability

Reduction of pollutants like sulphur dioxide, nitroxides, ammonia, VOC (volatile organic compounds), greenhouse gases like carbon dioxide has to be managed globally as laid down in Agenda 21 (Rio Earth Summit 1992 [3]) which is followed up by the Kyoto protocol 1997 [4]. National commitments fix National Emission Ceilings (NEC). The German government is committed to achieve a reduction of 21% compared to the 1990 level of the greenhouse gases by 2012 [5]. In support of the global sustainability policy many more specific regulations have been set up, e.g., the European VOC directive (1999/13/EC [6]) limits the maximum emissions for a number of productions, which use VOC-containing products, e.g., automotive lacquer, printing machines, wet coating, and others (2004/42/EC) [7].

1.3 Chemical Regulation

Manufacture and use of chemicals is nowadays tightly regulated around the globe and not limited to the industrialized countries. Prior to marketing every producer or importer has to comply with a general chemical regulation that asks either for a notification of new substances and/or products or compliance with existing chemicals inventories, e.g., in EU [8], the USA [9], Japan [10], Canada [11], Australia [12], Korea [13], China [14], Philippines [15] and others.

Safe handling and storage of substances is subject to several multinational and national laws and regulations, e.g., European safety data sheet directives (91/155/EEC; 93/112/EEC, 2001/58/EC [16]); the European dangerous substances directive as amended (67/548/EEC [17]); the restrictions on the marketing and use directive (76/769/EEC as amended [18]) and dangerous preparations directive (1999/45/EC as amended [19]). The various international rules for transportation of dangerous goods have to be observed on roads (ADR [20]), rail (RID [21]), water (ADNR [22], IMDG [23]) and by air transport (IATA [24], ICAO [25]).

In order to conclude on appropriate measures such as risk management and risk reduction the key information about hazard and exposure at the workplace, at the use of the final product, in the environment have to be made available.

In a tiered approach depending predominantly on the volume manufactured, marketed or imported (e.g., 1, 10, 100, 1,000 tonnes/year/company) a certain range of data have to be provided.

The physico-chemical properties of a substance determine the distribution in the environmental compartments: air, soil, water. Technical guidance documents of the EU Authorities list the suitable endpoints to characterize the hazard of a substance with regards to environmental and consumer safety [26].

Looking into the details of the requirements prior to REACH for existing and new chemicals it is obvious that two different standards have been applied, asking for a thorough risk assessment for new substances while chemicals existing on the market are accepted with much less knowledge about their toxicological profile.

In the past as with REACH, the regulation of the EU requires a risk assessment, risk management and risk communication only for *new substances* where all stages of a product/substance lifecycle are taken into account:

- Raw material availability
  (limited like crude oil , renewable like starch, vegetable oils, etc)
- Workplace hygiene at the chemical production sites
- Storage, handling, transportation
- Processing to final articles
- Use (standards for consumer safety)
- Disposal, recycling

Compliance with these regulations ensures society that all areas of chemical handling are well under control.

Existing chemicals were basically accepted without extensive testing. During the last two decades some initiatives at national, (e.g., German existing chemicals programme [27]), European [28], OECD [29], US [30] and global level [31] have been started to improve the knowledge of existing substances.

Historically, several international instruments, including the Stockholm Persistent Organic Pollutants Convention (POPs) [32], the Rotterdam Primary Informed Consent Convention [33] and the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes [34], OSPARCOM [35], HELCOM [36] and their disposal address specific chemical issues.

1.4 REACH = Chemical Regulation in the EU since 01.06.2007

In order to fill the data gaps for existing chemicals the corresponding regulation has been revised in the European Union aiming at a nearly equal treatment of new and existing chemicals under the acronym REACH = Registration, Evaluation and Authorization of Chemicals [37].

REACH cuts across the spectrum of voluntary regulatory initiatives that currently exist helping to ensure that substances are used safely at all stages of their life cycle by requiring all those manufacturing, importing, or using substances to fulfil certain obligations which are specified as test requirements and documentation. In a tiered approach tests are requested for all chemicals according to manufactured/imported quantities per year (Table 1, Fig. 1).

Polymers are exempted from REACH as it is thought that the registration and evaluation of starting materials like monomers will cover the risks of polymers as well. Priority is set on potentially dangerous substances but it is not excluded that at a later time polymers will be reviewed in more detail.

The REACH process will last in total until 2018. Until 1 December 2008 the "pre-registration" of all chemicals produced had to be finalized with ECHA (European Chemical Agency) [38]. Only registered and pre-registered substances may be produced beyond 1 June 2008, nevertheless underlying a step-wise phase-in depending on production volumes.

The pre-registration has two major targets: generate an inventory of all substances on the market and provide a forum where importer/manufacturer of the same substance can meet in a SIEF (Substance Information Exchange Forum). A SIEF shall ensure that joint submissions of a registration dossier are done using data and cost-sharing procedures. The obligation to generate joint submissions shall avoid unnecessary animal tests.

The very large number of pre-registrations (ca. 2,750,000 on ca. 146,000 substances by more than 65,000 companies in 27 EU member states; Table 2) has

Table 1 Tiered approach for test requirements under REACH

1–10 t	Physico-chemical, toxicological and eco-toxicological data
10–100 t	Base set according to Annex VII a
100–1,000 t	"Level 1" set (adopted to application and exposure)
>1,000 t	"Level 2" set (adopted to application and exposure)

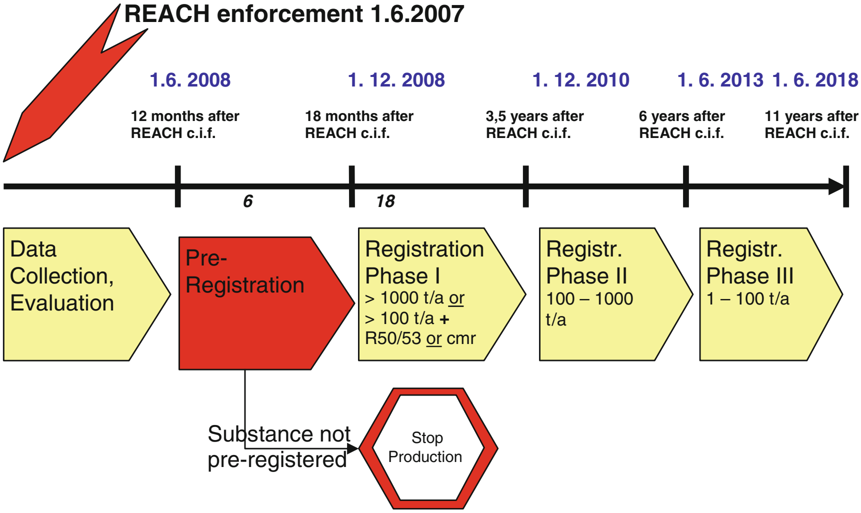


Fig. 1 Schedule of REACH registrations

Table 2 REACH pre-registrations per country

EU Member State	Companies	Pre-registrations
Germany	8,669	8,19,648
United Kingdom	22,247	4,41,945
France	4,426	3,37,964
Poland	2,438	1,88,217
Netherlands	5,529	1,34,243
Italy	4,651	1,18,530
Spain	2,633	88,227
Ireland	3,264	78,598
Belgium	1,926	71,469
Estonia	153	53,988
Finland	1,388	42,851
Slovakia	506	36,526
Sweden	1,277	36,098
Austria	857	35,380
Czech Republic	946	28,967
Denmark	469	23,561
Portugal	407	14,767
Hungary	641	14,310
Greece	537	10,076
Romania	577	10,020
Bulgaria	716	9,312
Norway	394	7,458
Slovenia	234	5,137
Lithuania	176	4,063
Luxembourg	139	3,769
Liechtenstein	48	3,375
Latvia	191	3,224
Cyprus	241	2,373
Malta	39	276
Iceland	39	157
Sum:	65,758	2,624,529

in turn led to some very large SIEFs; 140 have over 1,000 members, 3,500 over 100 members. Most of these are expected to submit their registrations in 2010.

The list of pre-registered substances (19 Dec 2008) can be accessed via a dedicated page in the ECHA CHEM section of the Agency website [39].

2 Surfactants for Polymerization

2.1 *Technological Functions*

Natural Rubber (NR) is a well-known example of a polymer emulsion made by nature. A relatively broad number of different plants produce a rubber-containing latex, but only *Hevea Brasiliensis* and, to a much lower extent, the Guayule plant, *Parthenium Argentatum*, the roots of Kok-Saghys, *Taraxacum Bicorne*, and the

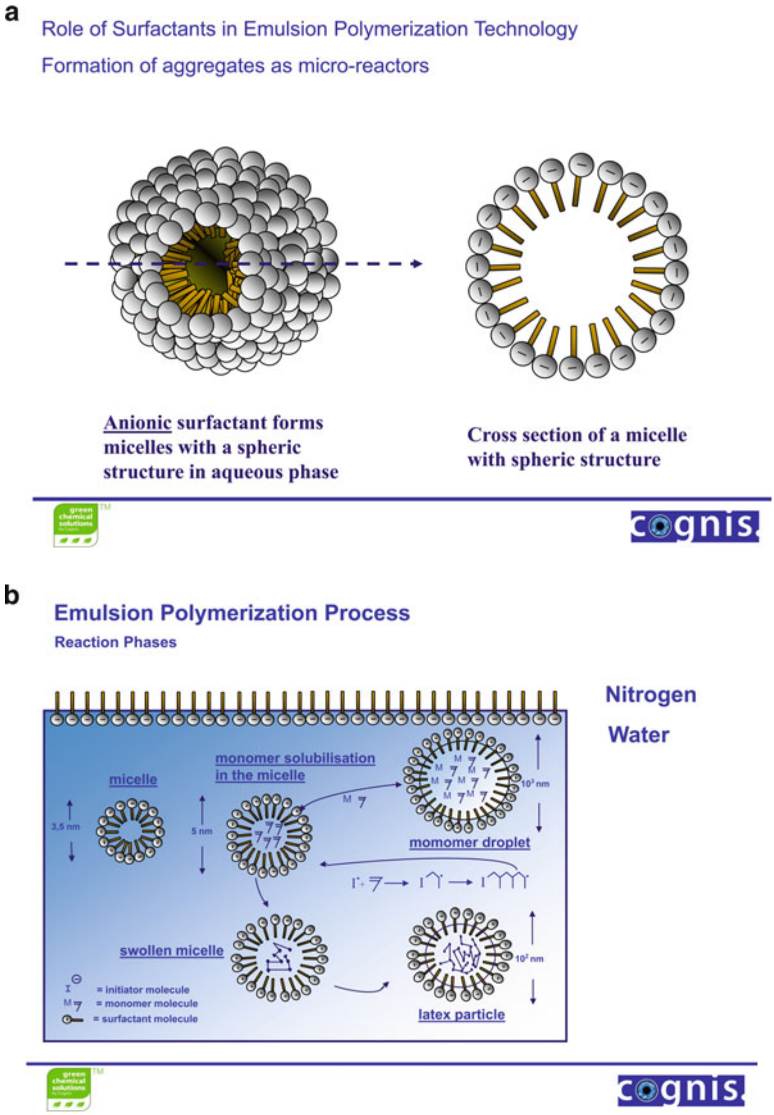
Balata tree, *Mimusops Balata*, have achieved economic importance or are considered as resources for natural rubber as a renewable polymer. Chemically, natural rubbers are polyterpenes consisting of 1,4-*cis*-(rubber) or 1,4-*trans*-(gutta-percha, balata) polyisoprene, generated by enzymatically catalyzed biosynthetic polymerization of isoprene, and stabilized by phospholipids.

Material properties, limited availability and growing demand initiated, at the beginning of the twentieth century, scientific and commercial efforts for the manufacturing of synthetic rubber [40]. Regarding economy, safety, and technical flexibility emulsion polymerization, besides mass and solution polymerization, turned out to be the most appropriate technology. In addition to synthetic rubber and other elastomer syntheses, emulsion polymerization technologies are employed for E-PVC and paste PVC and are of paramount importance for the manufacture of dispersion polymers.

Emulsion polymerization is one of the most sustainable technologies for the manufacturing of binder materials for paints, coatings, adhesives, leather finishes, textile and paper coating and even for construction materials. Technologically, emulsion polymerization allows achieving very high molecular weight polymers with good film formation properties and without the viscosity problems occurring with solution polymerization. Emulsion polymerization avoids safety problems due to solvent handling. Fires caused by accident or by inappropriate handling of solvents have, indeed, been one of the major problems faced in former times by coating, adhesives and ink resin manufacturers.

Surfactants are the key ingredient for emulsion polymerization [41–45]. It is a two-phase process based on water as the continuous phase; monomers with low water solubility, water-soluble emulsifiers, and a water-soluble initiator that decomposes to produce radicals in the aqueous phase (see Fig. 2)

The emulsifier concentration in the continuous aqueous phase at the beginning of emulsion polymerization is above the critical micelle concentration (CMC) and thus micelles form. The hydrophobic interior of the micelles contains solubilized monomers, which migrate by diffusion out of the emulsified monomer droplets and through the aqueous phase. The water-soluble initiator decomposes in the water phase to generate primary radicals, which react with monomer dissolved in water to form oligomeric radicals with surface active properties. When such a surface active oligomeric radical enters a micelle it propagates rapidly with solubilized monomer to form a polymer particle. In a typical emulsion polymerization there are about 10^{13} monomer droplets per litre of emulsion, with an average droplet size of about 10^4 Å. This compares with ca. 10^{18} micelles with a diameter of about 50 Å. The total interfacial area of the micelles is about three orders of magnitude larger than that of the monomer droplets. Consequently, oligomeric radicals in the aqueous phase are much more likely to diffuse into a micelle swollen with monomer than into a monomer droplet. Polymerization thus occurs almost exclusively in the micelles and in the polymer particles which are later formed, consuming monomer that arrives by diffusion through the aqueous phase from the monomer droplets. Micelles are thus gradually transformed into polymer particles with a diameter of about 10^3 Å.



Role of Surfactants in Emulsion Polymerization Technology

Formation of aggregates as micro-reactors

Anionic surfactant forms micelles with a spheric structure in aqueous phase

Cross section of a micelle with spheric structure

Emulsion Polymerization Process

Reaction Phases

Fig. 2 Schematic representation of emulsion polymerization. (**a**) Role of surfactants in emulsion polymerization technology. (**b**) Emulsion polymerization process

The emulsifier in emulsion polymerization has three key functions, namely: stabilizing the monomer droplets during the first stage of the emulsion polymerization, supplying surfactant micelles as the site of the polymerization reaction (literally the micelles can be regarded as some kind of micro-reactors) and stabilizing the latex particles at the end of the emulsion polymerization process pending transportation, storage and handling until the latex is intentionally destabilized by coagulation or spray drying to isolate the polymer or by evaporation of water and film formation.

Surfactants like ammonium salts of fatty acids or hydroxy fatty acids, fatty alcohol sulphates and alkylbenzenesulphonates are also used in micro-suspension polymerization mainly employed for manufacturing of paste or plastisol PVC. Certain surfactants like fatty acid polyglycolesters and glycerylmono- or glycerylmono/distearate are also used as co-stabilizers in suspension PVC manufacturing.

Except for the case of copolymerizable surfactants the emulsifier molecules are not chemically bound to the polymer but physically adsorbed at the latex–water interfaces. Because of this the emulsifier can interfere in the later handling of plastics, for example, as a lubricant in PVC processing or as an antistatic agent or can be washed out by rain as in the case of exterior decorative architectural paints and coatings. Surfactants and latex stabilizers used in special emulsion polymerization processes like manufacturing of polyacrylic binders for water-based news inks or inverse emulsion polymerization can come into contact with the environment through waste paper deinking or through flocculation processes in waste water treatment.

2.2 Chemical Composition (Fig. 3)

- Surfactants based on coal and crude
- Surfactants based on renewable resources

Petrochemical surfactants are mainly derived from ethylene, propylene, butylenes, benzene, and also naphthalene as building blocks [46]. The most important emulsifiers for emulsion polymerization are anionic and non-ionic surfactants. Cationic and amphoteric surfactants are only used in special cases and are of minor importance as emulsifiers for polymerization.

Alkyl naphthalene sulphonates have been used by IG Farben for BUNA polymerization. 2-Isopropylnaphthalene is yielded by alkylation of naphthalene with propene and used to make sodium isopropylnaphthalenesulphonate (Nekal® A). Sodium dibutylnaphthalenesulphonate (Betan®, Nekal® BX) is made by butylation of naphthalene with butanol/sulphuric acid and subsequent sulphonation with oleum. Naphthalenesulphonate formaldehyde condensation polymers (Tamol®, Lomar®) are largely used as latex stabilizers during synthetic rubber manufacturing. Manufacturers of naphthalene intermediates have made considerable efforts in order to develop ecologically safe production processes [47].

Secondary alkane sulphonates, also called paraffinsulphonates, are generated by sulphochlorination or by sulphoxidation of linear paraffins. Sulphochlorination (*Reed reaction*) means introduction of the SO_2–Cl moiety in a paraffin molecule by action of Cl_2 and SO_2 under UV-irradiation followed by hydrolysis and neutralization with NaOH. Reaction of SO_2 and O_2 with n-paraffins under UV light is called sulphoxidation.

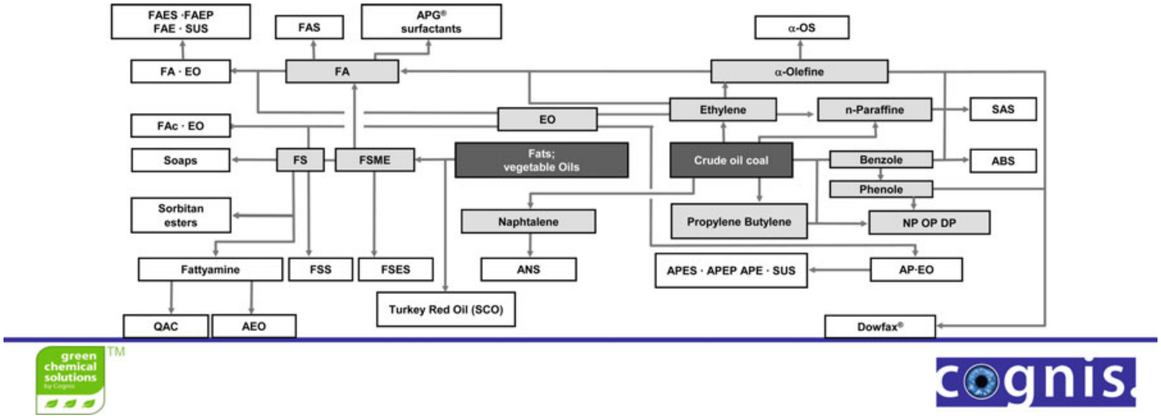


Fig. 3 Oleochemical vs. Petrochemical surfactants. *αOS* alpha olefin sulphonates; *SAS* secondary alkane sulphonates; *ABS* alkyl benzene sulphonates; *NP* nonylphenol; *OP* octyl phenol; *DP* dodecyl phenol; *AP.EO* alkylphenol polyglycolethers; *APES* alkylphenol ethersulphates; *APEP* alkylphenol etherphosphates; *APE.SUS* alkylphenolpolyglycolether sulphosucinic acid monoesters; *ANS* alkyl naphthalene sulphonates; *SCO* sulphated castor oil; *FSME* fatty acid methylester; *FS* fatty acid; *FSS* fatty acid sulphonates; *FSES* fatty acid methyl ester sulphonates; *QAC* quaternary ammonium compounds; *AEO* fatty amine ethoxylates; *FS.EO* fatty acid polyglycol esters; *FA* fatty alcohols; *FA.EO* fatty alcohol polyglycolethers; *FAS* fatty alcohol sulphates (for example, sodium lauryl sulphates); *APG* surfactants alkyl polyglycosides; *FAES* fatty alcohol ethersulphates; *FAEP* fatty alcohol etherphosphates; *FAE.SUS* fatty alcohol polyglycolether sulphosuccinic acid monoesters

α-Olefin sulphonates, AOS, are anionic surfactants, which are made by sulphonation of α-olefins with gaseous SO_3 followed by neutralization with aqueous NaOH.

Alkyl benzene sulphonates are one of the most important groups of surfactants and detergents. More particularly, lin. dodecylbenzenesulphonate is used as an anionic emulsifier for manufacturing of E-PVC as well as for polymer dispersions, whereas the usage of the branched tetrapropylenebenzene sulphonate, TPS, has been reduced to a very limited number of applications.

Another alkylarylsulphonate of particular importance as an emulsifier for emulsion polymerization is alkyldiphenyloxide disulphonate, Dowfax® 2A1. The surfactant is manufactured by addition of α-olefin to diphenylether followed by sulphonation with SO_3 in liquid SO_2.

Alkyl phenol ethoxylates have been over many years the workhorses as non-ionic emulsifiers for emulsion polymerization. Depending on availability and price of buten and propen, nonyl (tripropylene)phenol ethoxylates or octyl (dibutylene) phenol ethoxylates have been very broadly used, whereas dodecyl (tetrapropylene or tributylene)phenol and tri tert-butylphenol ethoxylates were merely regarded as specialties. These alkyl phenol ethoxylates can also be used as intermediates for the synthesis of anionic alkyl phenol ether sulphates. Sulphation by chlorosulphonic acid or sulphur trioxide besides formation of the ether sulphate end group inevitably leads to certain amounts of ring sulphonation in the phenyl group, whereas amidosulphonic acid gives sulphonate-free alkyl phenol ether sulphate ammonium salts.

Alkyl phenol ethoxylates can also react with P_4O_{10} yielding alkyl phenol etherphosphates as a mixture of mono-/diesters or with maleic anhydride to yield maleic acid monoesters, which then react with $NaHSO_3$ to yield sulphosuccinate monoesters. Alkylphenolpolyglycolether sulphates, phosphates or sulphosuccinates are mainly used as primary anionic emulsifiers for the manufacturing of acrylic, styrene/acrylic or vinyl acetate co-polymer dispersions. Another type of non-ionic emulsifier is block copolymers of ethylene oxide with propylene oxide.

Sulphosuccinic acid diesters play a role above all in American polymerization formulations. They are rarely used as principal emulsifiers, but rather to control secondary properties, for example, for the production of highly concentrated low viscosity acrylate dispersions. The branched sodium di-2-ethyl hexyl sulphosuccinate is widely used, combining favourable emulsifier properties with excellent wetting power. Dicyclohexyl sulphosuccinate has a particularly high CMC and a particularly high surface tension [48].

Fats and vegetable oils, including tall oil are renewable resources for surfactants. The soaps of natural fatty acids and disproportionated rosin soaps are the most important emulsifier types for the production of synthetic rubber, and sodium or ammonium salts of fatty acids and hydroxy fatty acids are also largely used in PVC manufacturing.

Sulphonated natural oils, sulphonated oleic acid esters and α-ester sulphonates were investigated as polymerization emulsifiers and have been successfully used as special emulsifiers for establishing certain product properties [49]. Fatty alcohol sulphates have been used as emulsifiers since the very beginning of emulsion polymerization, and are distinguished by particularly good polymerization behaviour and by formation of fine-particle polymer dispersions. Partly unsaturated oleyl/cetyl sulphate is described as an emulsifier for the production of low-foaming polymer dispersions.

Since the problematic biodegradability of alkyl phenol-based surfactants has been the subject of discussion, fatty alcohol ethoxylates, and more particularly specially designed species (Disponil® A, Disponil® AFX) have changed the scenario in surfactants for emulsion polymerization and are largely used as non-ionic emulsifiers by most of the major multinational manufacturers of polymer dispersions [50–53]. Alkyl polyglycosides and sorbitol fatty acid esters are green surfactants completely derived from the renewable resources starch or sorbitol, respectively, and vegetable oils, and have also been described as non-ionic emulsifiers for polymerization. Hand in hand with the move towards green non-ionic emulsifiers the polymerization industry is exchanging anionic alkyl phenol ether sulphates, phosphates and sulphosuccinic acid semiesters with the corresponding fatty alcohol ether sulphate, phosphates and sulphosuccinates. This move was significantly fostered since the FDA (Food and Drug Administration) approved Disponil® FES-type surfactants according to FDA § 178.3400.

2.3 Environmental Assessment of Surfactants for Polymerization

Environmental risk assessment has to address all compartments of the environment like air, water, sediment and soil. The partition of a substance between the various compartments is controlled by the physico-chemical parameters of a substance. Water-soluble or dispersible surfactants and emulsifiers will predominantly affect the water and sediments. As surfactants are widely used not only in manifold industrial applications but also in consumer products the pollution is widely dispersed. The contribution of surfactants used in polymer production is comparably rather small but has nevertheless to be controlled and monitored.

Important parameters to characterize the impact of the chemical on the environment, here the compartment “water” are

- Biodegradability (Table 3)
- Aquatic toxicity (fish, daphnia, algae, bacteria) (Tables 4, 5)
- Fat solubility which might lead to bioaccumulation and bioconcentration along the “food chains”.

Results illustrate that these surfactants are all biodegradable and thus the organic load is considerably reduced by sewage water treatment plants which leads to less pollutant effluents reaching surface water (Table 6).

In order to arrive at a risk assessment the environmental concentrations (measured and/or estimated) are put together and a resulting PEC (Predicted Environmental Concentration) is determined.

From the hazard characteristics of the surfactants, like NOEC the PNEC (Predicted No Effect Concentration) can be deduced.

The risk of a substance for the environment is considered basically acceptable if the ratio follows the equation: $\mathrm{PEC/PNEC} < 1$

Table 3 Biodegradability of some surfactants in the environment [54]

Chemical	Aerobic condition	Anaerobic condition
Linear Alkylbenzene Sulphonate (LAS)	Degradable [55], [56]	Persistent [32]
Secondary Alkane Sulphonates (SAS)	Readily degradable [57]	Persistent [32]
Soap (Fatty Acid Salts)	Readily degradable [58]	Readily degradable [32]
Fatty acid esters (FES)	Readily degradable [59], [60]	Persistent [61]
Alcohol Sulphates (AS)	Readily degradable [62]	Degradable [63], [64]
Alcohol Ether Sulphates (AES)	Readily degradable [32]	Persistent [32]
Alkyl Phenol Ethoxylates (APE)	Degradable [65], [66], [67]	Partially degradable [68]
Alcohol Ethoxylates (AE)	Readily degradable [69], [70], [71]	Degradable [72], [73], [74]

The degree of biodegradation is basically characterized by the levels:
Readily biodegradable: more than 60% within a 10-day window
Biodegradable: more than 60%
Persistent: less than 20%

Table 4 Aquatic toxicity of some anionic surfactants

Chemical	Species	Endpoint	Ref
C10 LAS (Linear Alkylbenzene Sulphonate)	*Daphnia magna*	LC50 48 h 13,9 mg L^{-1}	[75]
C12 LAS	*Daphnia magna*	LC50 48 h 8.1 mg L^{-1}	[57]
C14 LAS	*Daphnia magna*	LC50 48 h 1.22 mg L^{-1}	[57]
C12 LAS	*Dunaliella* sp.(green algae)	EC50 24 h 3.5 mg L^{-1}	[76]
C12 LAS	*Salmo gairdneri*(rainbow trout)	NOEC 54 days 0.2 mg L^{-1}	[77]
Decyl sulphate (C12 AS)	*Salmo gairdneri*(rainbow trout)	EC50 48 h 3.63 mg L^{-1}	[78]
Sodium Dodecyl Ethoxy Sulphate (SDES)	*Salmo gairdneri*(rainbow trout)	EC50 48 h 10.84 mg L^{-1}	[60]

Table 5 Aquatic toxicity of some non-ionic surfactants

Chemical	Species	Endpoint	Ref
Decyl ethoxylate	*Salmo gairdneri*(rainbow trout)	EC50 48 h 22.38 mg L^{-1}	[60]
Octyl phenol ethoxylated	*Salmo gairdneri*(rainbow trout)	EC50 48 h 6.44 mg L^{-1}	[60]
Nonyl phenol (NP)	Fathead minnow	LC50 96 h 0.3 mg L^{-1}	[79]
Nonyl phenol (NP)	*Daphnia magna*	LC50 48 h 0.19 mg L^{-1}	[61]
Nonyl phenol ethoxylated (NPE)	Fathead minnow	LC50 96 h 4.6 mg L^{-1}	[61]
Nonyl phenol ethoxylated (NPE)	*Daphnia magna*	LC50 48 h 14 mg L^{-1}	[61]

LC50: Lethal dose 50%
EC50: Effective concentration 50%
NOEC: No-observed-effect concentration

Table 6 Use pattern and environmental concentrations

Lifecycle stage	Environment compartment	Data
Production site:Emulsion polymerization	Effluent to the waste water treatment	Biodegradation
	Release to fresh water (river)	Concentration
Use in carpet manufacture	Waste waterrelease to river	Concentration
Use in paper coating	Waste waterrelease to river	Concentration
Paper recycling	Waste waterrelease to river	Concentration

For more details the EU Technical Guidance Document has to be consulted [80].

Uncertainties and data gaps are reflected by additional "safety" or "uncertainty factors".

Several factors have a direct influence on the PEC which – in the absence of precise data – normally has to be estimated on a worst-case scenario [81].

- Market share
- Direct discharge of raw sewage into rivers or the sea
- Dilution and mixing in the receiving waters
- Bioconcentration factors

Factors that influence PNEC include

- Application factor on a conservative scenario which means dividing the lowest toxicity values by a large safety factor so that the results will protect all species
- Physico-chemical properties
- Results of biodegradation and absorption properties including metabolites

The assessment of a risk for humans has to consider the intrinsic hazard of a substance which is characterized by a set of adequate in vitro and in vivo test results. It is assumed that animals like rats, mice react similarly to the test substances like human beings.

Important parameters to characterize the toxicological hazard of a substance for humans are (typical results in Table 7)

- Acute toxicity
- Mutagenicity
- Subchronic toxicity, e.g., 90-day feeding study
- Long-term toxicity (carcinogenicity), e.g., 2-year feeding study
- Reproduction toxicity
- Teratogenicity

As important as the hazard identification for a substance is the characterization of exposure to human beings. All known conditions of use have to be compiled to estimate the most realistic exposure of a substance to the environment including an estimate of the intake of a substance via inhalation, dermal contact, oral intake (Table 8). A major result of a risk assessment is the comparison of exposure levels to NOELs.

The HERA project [94] resulted in complete and systematic risk assessments reviewing extensive data sets for all major surfactants where – beyond others - the NOEL and the total exposure is determined.

Table 7 Simplified toxicological profile of some surfactants

Surfactants	Mutagenicity	90-day study (rat, oral) NOEL mg kg^{-1} BW	Carcinogenicity (rat, oral) NOEL mg kg^{-1} BW	Reproductive toxicity (rat, oral) NOEL mg kg^{-1} BW
Fatty Acid Salts (Soaps [82])	Negative, in vitro	Considered safe as is part of the human diet	Not carcinogenic	Not reprotoxic
LAS [83]	Negative, in vitro, in vivo	>85	Not carcinogenic	>350
AES [84]	Negative, in vitro, in vivo	>200	Not carcinogenic	>300
Fatty alcohol ethoxylated FAEO	Negative, in vitro, in vivo [85]	>25 [86]	(C12-13 EO) Not carcinogenic [87]	(C14-15 EO) >300 [88]
Di i-octyl sulpho succinate	Negative, in vitro [89, 90]	>500 [91]	Not carcinogenic [92]	>500 [93]

The results of toxicological tests are often summarized as "effect levels", "no-effect-levels" (NOEL) and "no adverse effect levels" (NOAEL), which indicate the dose tested that showed no adverse changes in the test organism

Table 8 Total consumer exposure (All routes)

Route	Exposure to soap (mg $kg^{-1}day^{-1}$)
1. Dermal	
Hand laundry	1.4×10^{-4}
Fabric pre-treatment	2.0×10^{-3}
Wearing laundered fabric	7.9×10^{-4}
Total dermal	2.9×10^{-3}
2. Oral	
Accidental Ingestion	–
Indirect exposure via drinking water	Negligible
Total oral	Negligible
3. Inhalation	
Pouring product	1.4×10^{-6}
Spray cleaner	6.0×10^{-7}
Total inhalation	2.0×10^{-6}
Total (all routes)	2.9×10^{-3}

Example: soaps in household cleaning products.

As no NOELs have been determined because soaps are part of the natural human diet a "hypothetically high" NOEL of 500 mg kg^{-1} BW is assumed

The ratio NOEL/100 divided by the total exposure should be greater than one and the size of this value characterizes the margin of safety (MOS)

MOS = NOEL/(100*exposure level) = 500/(100*0.0029) = 1724

2.3.1 Risk Management and Precautionary Principle

The performance of systematic risk assessments is a task often taken by federal agencies like US EPA, US FDA, EU EFSA or national institutions. The result of a risk assessment is a starting point for the risk manager, e.g., the ministries, to develop adequate measures, like controls, limits or use restrictions. In the structured approach to the risk analysis the precautionary principle can be particularly relevant to the risk management. It shall be applied in those circumstances where scientific evidence is insufficient or uncertain and when there are indications for concern [95]. In order to prevent a disproportionately intensive use measures based on the precautionary principle should be

- transparent
- proportional to the level of protection
- non-discriminatory in their application
- consistent with similar measures already taken
- subject to review in the light of new scientific data

Examples of risk-management decisions applying the precautionary principle are the use restrictions of APE (Alkyl phenol ethoxylates) and phthalates. Although a reliable test battery to establish endocrine effects of a substance for human beings is still missing APE is restricted due to evidence of interference with hormone systems of aquatic species. Although complete risk assessments for various phthalates have been generated their use is restricted due to very high production volumes, manifold uses, and global distribution.

2.3.2 Restricted use of Alkyl Phenol Ethoxylates (APE)

APEs are well performing and cost-effective non-ionic surfactants which can be used in manifold ways in industrial processes as well as in consumer products.

In the environment under aerobic conditions APE is degraded stepwise with NP (nonyl phenol) as the resulting metabolite. NP is biodegradable although at a slower pace. In the aquatic environment the metabolites like short-chain NPE with 1–3 ethyleneglycol units are found to be toxic to aquatic organisms. The technical substitute FAEO (fatty alcohol ethoxylated) is completely biodegradable (Fig. 4). The toxicological profile of APE is well investigated and does not raise special concerns (Table 9).

Studies investigating hormonal activity revealed the oestrogenic activity of short-chain NPE in a number of test systems using either recombinant yeast, oestrogen-sensitive MCF-7 cells [98] or a rodent uterotrophic assay response. None of these assays have yet been validated as an internationally accepted toxicity test method, although the MCF-7 and uterotrophic assays have been established for a number of years as standard assays for oestrogenic activity.

Overall, these in vitro and in vivo studies show that nonylphenol has an oestrogenic activity to aquatic organisms of a potency that is between 3 and 6 orders of

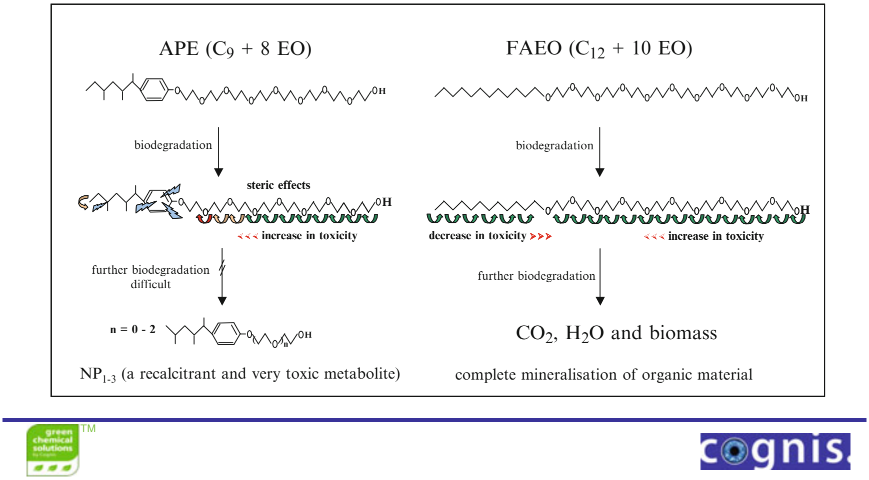


Fig. 4 Ecological properties of APE compared to FAEO

Table 9 The hazard for humans according the standard toxicological endpoints is well characterized and does not cause a major concern

Surfactants	Mutagenicity	90-day feeding study (rat, oral) NOEL mg kg^{-1} BW	Carcinogenicity (rat, oral) NOEL mg kg^{-1} BW	Reproductive toxicity (rat, oral) NOEL mg kg^{-1} BW
4-Nonyl phenol (NP) [96], [97]	Negative, in vitro, in vivo	50	Low concern	LOAEL = 15

magnitude less than that of oestradiol, a natural oestrogen. It should be noted that the significance to human health of oestrogenic activity detected in these assays has yet to be established.

As a consequence, the EU Commission has recommended implementation of a risk reduction strategy, which – among other measures – foresees strict emission controls for various industrial and consumer applications of NPE as a surfactant [99].

Since January 2005 nonylphenol and nonylphenol ethoxylates may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0.1% by mass for the following purposes (except for the use in closed systems):

(1) Industrial and institutional cleaning
(2) Household detergents and cleansers
(3) Textiles and leather processing
(4) Emulsifier in agricultural teat dips

(5) Metal working
(6) Manufacturing of pulp and paper
(7) Cosmetic products
(8) Other personal care products
(9) Co-formulants in pesticides and biocides

Some industry associations have already pro-actively taken measures to phase out NPE, e.g., the European detergent industry (AISE [100]) by a voluntary commitment.

In addition and recognizing development of new EU Community procedures [101], additional pollution control measures for NP and NPEO should be considered for the following sectors:

- production of NP and NPE
- use of NPE in the synthesis of other chemicals (e.g., NPE phosphates)
- use of NPE in emulsion polymerization, in particular use in vinyl or acrylic polymer dispersions for coatings, adhesives and fibre bonding
- production of phenol/formaldehyde resins using NP
- production of plastic stabilizers using NP

Alternatively, NPE can be substituted by surfactants like fatty alcohol ethoxylates (FAEO), or specially designed trademark products like Disponil® A and Disponil® AFX which have a more favourable ecological profile.

3 Protective Colloids

Instead of low *Mw* surfactants or in combination with those natural or semi-synthetic colloids are used in suspension polymerization of PVC and in emulsion polymerization of vinyl acetate homo- and co-polymers as protective colloids also called suspension stabilizers or suspending agents.

Manufacturing procedures for PVC suspension polymerization [102, 103] contain water, vinyl chloride monomer, an oil-soluble initiator system, and a suspension stabilizer system consisting of one or two water-soluble primary suspending agents, which determine particle size and particle size distribution, and a secondary suspension aid, which controls porosity and plasticizer absorption of the PVC particles. The protective colloids form a stabilizing layer around the monomer droplets formed by agitation. The monomer soluble initiator upon heating starts the polymerization in these monomer droplets. Suspension polymerization can thus be regarded as some kind of mass or bulk polymerization taking place in the monomer droplets, while the heat of polymerization is controlled by the surrounding water phase. Primary suspension stabilizers are cellulose ethers or polyvinyl alcohols of 75–90% hydrolysis. Secondary suspending agents are typically surfactants in the HLB range 4–10, for example, sorbitan monolaurate or polyvinyl alcohols of 25–40 % hydrolysis.

3.1 Cellulose Ethers

Cellulose, the feedstock for cellulose ethers, is a polysaccharide like xanthane, guar and starch. It is a biopolymer made by photosynthesis and thus a renewable raw material. Cellulose is water insoluble, and only becomes water-soluble after hydrolysis and etherification [104, 105] (Fig. 5).

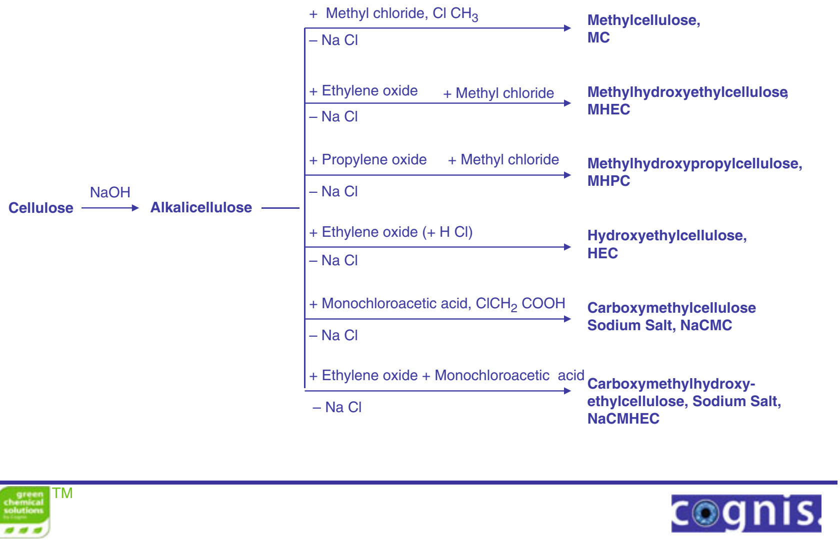


Fig. 5 Manufacturing of cellulose ethers

Cellulose ethers, more particularly methyl cellulose (MC), methylhydroxypropyl cellulose (MHPC) and hydroxypropyl cellulose (HPC) are used as protective colloids also called primary suspending agents in suspension polymerization for the manufacturing of S-PVC. Their role is maintaining the particle size of the resin. Hydroxyethyl cellulose (HEC) is preferred for manufacturing of vinyl acetate emulsion polymers and as a thickening agent in dispersion paints.

3.2 Starch and Dextrin

Starch, often in its degraded form dextrin, and starch esters have long found application in general emulsion and dispersion technology, mainly in adhesives, construction materials or in pharmaceuticals for example, as aqueous coating material for controlled-release products [106].

3.3 Polyvinyl Alcohols

Polyvinyl alcohols (PVAl) are manufactured by saponification of vinyl acetate polymers (PVAc). Properties of PVC using PVAl as a protective colloid are influenced by the solution viscosity of the PVAl, i.e. the degree of polymerization of the PVAc and the degree of saponification. Polyvinyl alcohols of 75–90% hydrolysis are primary suspension agents for S-PVC, whereas polyvinyl alcohols of 25–40% hydrolysis are secondary suspension agents, which control the agglomeration of the primary particles. Partially hydrolyzed PVAc can be block or random polymers.

3.4 Environmental Assessment of Protective Colloids

It is estimated that more than 50 billion tonnes of cellulose are synthesized naturally every year by photosynthesis, which makes cellulose the biggest renewable raw material. It is environmentally friendly, because the combustion or decomposition releases only as much CO_2 as was bound beforehand by the photosynthesis of the plants. Cellulose derivatives in general are not harmful to the environment, they are biodegradable, and have a low toxicity to water organisms [107].

The favourable technical and consumer friendly properties encouraged the use of cellulose and modified cellulose in many consumer products like in plasterwork and filling compounds, adhesives and surface coatings, toothpaste and fruit juices.

The safety standards for consumer products like food [108], [109], [110] or food-contact materials [111], [112] uses are very strict. A JECFA (Joint FAO/WHO Expert Committee on Food Additives) report on microcrystalline cellulose concludes that there are no risks to be seen from the use of micro cellulose particles [113].

At EU level the Scientific Panel on Food Additives, Flavourings, Processing Aids and Materials in Contact with Food (now EFSA = European Food Safety Agency) evaluated the safety of ethyl cellulose and placed no limits for a food (contact)use. Other cellulose derivatives are qualified as direct food additives [114]:

- methyl cellulose (E461)
- hydroxypropyl cellulose (E463)
- hydroxypropyl methyl cellulose (E464)
- ethyl methyl cellulose (E465)
- carboxymethyl cellulose (E466)

JECFA has also evaluated modified celluloses. In 1990 JECFA allocated a group ADI (Accepted Daily Intake) “not specified” to seven modified cellulose derivatives including ethyl cellulose indicating the low risk potential of these substances.

At national level protective colloids like cellulose ether and polyvinyl alcohol are widely approved for various applications in food-contact materials (Tables 10, 11).

Table 10 Food-contact material approvals for cellulose derivatives and polyvinyl alcohol according to BfR (Federal Institute for Risk Assessment in Berlin, Germany)

BfR recommendation number	BfR recommendation title[a]	Polyvinyl alcohol	Cellulose derivates
II	Plasticizer-free polyvinyl chloride, plasticizer-free copolymers of vinyl chloride and mixtures of these polymers with other copolymers and chlorinated polyolefins containing mainly vinyl chloride in the total mixture	X	
III	Polyethylene	X	
V	Polystyrene produced exclusively from the polymerization of styrene	X	
VI	Styrene copolymers and graft polymers, and mixtures of polystyrene with other polymers	X	
VII	Polypropylene	X	
XII	Unsaturated polyester resins	X	
XIV	Plastics dispersions	X	X (MC,CMC, HEC, HEMC)
XV	Silicones	X	
XXI	Commodities based on natural and synthetic rubber	X	X (MC,CMC, HEC)
XXII	Polymers based on esters of acrylic and methacrylic acids, their copolymers, and mixtures of these with other polymers	X	X (MC,CMC, HEC)
XXXVI	Paper and board for food contact		X (MC,CMC, HEC)
XLIV	Artificial sausage casings		X (MC,CMC, HEC)
LI	Temperature-resistant polymer coating systems for frying, cooking and baking utensils		X (MC,CMC)

[a] The specific limits for the corresponding application can be found on the BfR website [115]

MC = Methyl cellulose

CMC = Carboxy methyl cellulose

HEC = Hydroxy ethyl cellulose

HEMC = Hydroxy ethyl methyl cellulose

Table 11 Food-contact material approvals for cellulose derivatives and polyvinyl alcohol according to the FDA (Food and Drug Administration, Washington, DC, USA)

FDA CFR number	FDA title[a]	Polyvinyl alcohol	Cellulose derivates
172.868	Ethyl cellulose		X
172.870	Hydroxypropyl cellulose		X
172.872	Hydroxypropyl cellulose		X
172.874	Hydroxypropyl methylcellulose		X
			X
173.310	Boiler water additives		X
175.105	Adhesives	X	X (MC, HEC, CMC)
175.210	Acrylate ester copolymer coating		X (MC)

(*continued*)

Table 11 (continued)

FDA CFR number	FDA title[a]	Polyvinyl alcohol	Cellulose derivates
175.300	Resinous and polymeric coatings		X (MC, HEC, CMC)
175.350	Vinyl acetate/crotonic acid copolymer	X	
176.170	Components of paper and paperboard in contact with aqueous and fatty foods		
176.200	Defoaming agents used in coatings		X (MC)
177.1200	Cellophane	X	X
177.1400	Hydroxyethyl cellulose film, water insoluble		X
177.1670	Polyvinyl alcohol film	X	
177.2260	Filters, resin-bonded	X	X (MC)
181.32	Acrylonitrile copolymers and resins	X	
182.70			X (CMC)
182.1480			X (MC)
182.1745	Sodium carboxymethylcellulose		X

[a] The specific limits for the corresponding application can be found on the FDA website [116]

4 Initiators for Radical Polymerization

Free-radical polymerizations can be initiated thermally by thermal initiators, by redox initiators, by photo initiators, or electrolytically. The polymerization process starts with the generation of radicals, high-energy species, which are capable of interacting with the double bond of vinyl, acrylic or olefin monomers. The source of these species is a molecule called the initiator. Thermal initiators dissociate homolytically into two radicals at elevated temperature, usually 60–80°C, whereas redox initiators form radicals by a redox mechanism, normally at lower temperatures than thermal initiators. Photoinitiators form radicals by action of UV light.

For the bulk polymerization of styrene, high-temperature initiators such as 1,2-dimethyl-1,2-diethyl-1,1-diphenyl-ethane or vinylsilane triacetate are preferred. Many other bulk polymerizations employ diisopropyl peroxydicarbonate (IPP). For styrene polymerization in suspension, dibenzoyl peroxide (BPO) (C_6H_5CO–O–O–OCC_6H_5) and *tert*-butyl perbenzoate [C_6H_5CO–O–O–$C(CH_3)_3$] are used.

For S- and M-PVC manufacturing a range of initiators has been used, but currently relatively few are widely employed. At one time benzoyl peroxide and azo initiators (AIBN) were typically used, but diacetyl peroxides, peroxydicarbonates (PDC) and alkyl peroxyesters are now preferred. AIBN is also employed as a blowing agent for PVC foam. Typical organosoluble initiators are

Diacyl peroxides

1. acetylcyclohexane sulphonyl peroxide
2. dioctanoyl peroxide
3. didecanoyl peroxide
4. dilauroyl peroxide

Peroxydicarbonates

5. bis(2-ethylhexyl) peroxydicarbonate
6. dicyclohexyl peroxydicarbonate
7. dicetyl peroxydicarbonate
8. bis(4-tert-butyl cyclohexyl) peroxydicarbonate
9. dimyristyl peroxydicarbonate

Alkyl peroxyesters

10. tert-butyl peroxyneodecanoate
11. tert-amyl peroxyneodecanoate
12. cumyl peroxyneodecanoate
13. tert-butyl peroxypivalate

Azo initiator

14. Azobisisobutyronitrile (AIBN)

Water-soluble initiators used in emulsion polymerization are preferentially sodium, potassium or ammonium persulphate operating at 50–80°C. Redox systems use hydrogen peroxide or a persulphate as the oxidizing moiety and sodium metabisulphite, sodium hydrosulphate (also known as hyposulphite or dithionite), sodium thiosulphate and sodium formaldehyde sulphoxylate as the reductant.

Photochemical initiators are utilized for the production of lithographic plates and for radiation curing coatings and inks but not in the manufacture of plastics. Electrolytic polymerizations find applications in the coating of metal sheets by plastics.

Organic peroxides are also used as curing agents for unsaturated polyesters (UPE), as cross-linkers for polyethylene and as rheology modifiers in polypropylene.

4.1 *Environmental Assessment for Initiators*

Synthesis, handling and storage are somewhat critical with regard to workplace hygiene because these substances are highly reactive and even can cause explosions.

In the polymerization process initiators are used in small quantities and by definition they decompose on purpose to highly reactive radicals which start chain reactions and consequently become part of the final polymer. Other side reactions of the radical occur, for example with solvents, and then lead to non-reactive products of low concern. The use of the final polymer products by the consumer will generate a negligible exposure to initiators due to the fact that the amount is very small and the mobility of these substances in the polymeric matrix is greatly reduced. Nevertheless, when initiators are used in applications like materials intended to come into contact with food some EU countries like e.g., Germany [115] request that initiators and their reaction products have to pass an approval process. Producers are asked to assess the migrants from the final polymer product and the amounts in terms of exposure.

5 Plasticizers

A plasticizer is a substance, which is incorporated into a plastic or a coating to increase flexibility, workability or distensibility. This is achieved by loosening the strength of intermolecular forces resulting in a higher flexibility of macromolecules or segments of macromolecules (Brownian motion). A plasticizer thus may reduce the melt viscosity and lower the temperature of the second-order transition or glass transition temperature, T_g, of the product. Plasticizers are inert, organic substances with low vapour pressures, predominantly esters [117–120].

The most widely plasticized polymer is polyvinyl chloride (PVC) due to its excellent plasticizer compatibility characteristics. Only by incorporation of a plasticizer a degree of flexibility is achieved, which makes PVC suitable for applications such as cable insulation or sheathing, calendered sheets, floor covering, flexible profile or synthetic leather. However, plasticizers have also been used and remain in use with other polymer types.

Plasticizers can be divided into two principal groups: primary and secondary. Primary plasticizers lower the glass transition temperature T_g and increase the elongation and softness of the polymer. Secondary plasticizers, when added to the polymer alone, do not bring about such changes and may also have limited compatibility with the polymer. However, when added to the polymer in the presence of a primary plasticizer, secondary plasticizers enhance the plasticizing performance of the primary plasticizer.

5.1 Phthalates

Phthalic acid esters are by far the largest and most widely used family of plasticizers (Fig. 6). More than 90% of phthalates produced in Europe are used to plasticize PVC. They are usually produced by reaction of phthalic anhydride with an excess of alcohol using p-toluenesulphonic acid as catalyst. The excess alcohol is recycled. Commercial phthalate esters are usually colourless and mostly odourless liquids.

Dioctyl phthalate (DOP or DHEP, di-2-ethylhexyl phthalate) is the most broadly used phthalate plasticizer counting for more than 50% of world plasticizer consumption. Other broadly used phthalate plasticizers are diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP), whereas butylbenzyl phthalate (BBP) and diisotridecyl phthalate are regarded as specialty phthalates. Dibutylphthalate (DBP) is mainly used as a plasticizer in coating applications to flexibilize nitrocellulose resins.

Dimethyl isophthalate is used as a plasticizer and modifier for polyethylene terephthalate, PET, and as a reactive intermediate for optical plastics.

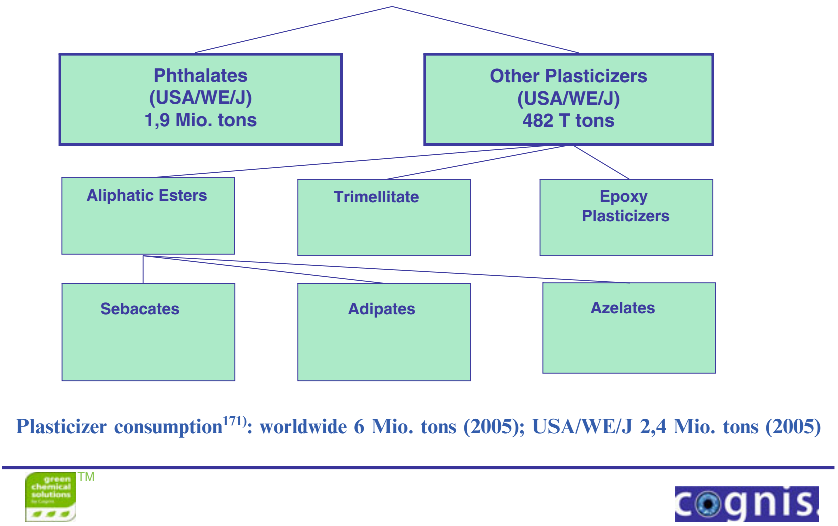


Fig. 6 Plasticizer classification [171]

5.2 *Other Plasticizers*

The huge interest in flexibilizing rigid polymer resin has lead to a broad spectrum of chemical substances, which have been employed as plasticizers.

5.2.1 Aliphatic esters

The bulk of aliphatic ester plasticizers are derived from adipic, sebacic and azelaic acid esterified with linear or branched monofunctional alcohols of short to medium-chain length, for example, dioctyl adipate (DOA, di[2-ethylhexyl]adipate), diisononyl adipate (DINA), di[n-butyl]sebacate (DBS). Adipate, azelate and sebacate plasticizers are distinguished by their low viscosity, thus making them particularly attractive to the plastisol sector, and giving excellent low-temperature flexibility properties.

Esterification with difunctional alcohols like propylene glycol or butylene glycol leads to polymeric plasticizers with molecular weights ranging between 1,000 and 6,000. Most polymeric plasticizers are adipates, azelates and sebacates, some glutarates and phthales are also used. Because of their high *Mw* polymeric plasticizers exhibit low volatility and resistance to migration and extraction by oils, fats or water which makes them particularly suitable for food-contact applications.

Fatty acid esters of short-chain monofunctional alcohols act as secondary plasticizers in PVC.

5.2.2 Trimellitates

These materials are produced by the esterification of a range of alcohols with trimellitic anhydride (TMA), which is similar in structure to phthalic anhydride with the exception of a third functionality on the aromatic ring. Consequently, esters are produced in the ratio of three moles of alcohol to one mole of anhydride. A common ester in this family is tris-2-ethyhexyl trimellitate (tri-octyl trimellitate – TOTM).

Esters of trimellitic (1,2,4-benzenetricarboxylic acid) anhydride provide excellent resistance to volatile loss and oxidation under heat ageing conditions making them the material of choice in applications for which high-temperature thermal stability is required. Insulation for automotive and aircraft cables are typical areas of application. The low volatility of trimellitates is also exploited in car interior components.

5.2.3 Epoxy plasticizers

Epoxidized vegetable oils and epoxy fatty acid esters play a particular role as non-gelatinizing secondary plasticizers for polyvinyl chloride, nitrocellulose and other polymers. Their high *Mw* makes them comparable to polymer plasticizers and partially explains the excellent resistance to extraction and migration. The most commonly used epoxy plasticizers are epoxidized soja bean oil (ESO) and epoxidized linseed oil (ELO). In PVC and other chlorine-containing polymers as well as in chloroparaffines epoxidized vegetable oils exercise the action of scavenger for HCl and co-stabilizer especially in synergism with mixed-metal stabilizers [121] (see 6.1.3). Epoxidized oils are manufactured by reaction of performic or peracetic acid on soja bean or linseed oil. The peracids are formed in situ by reaction of formic or acetic acid with hydrogen peroxide. Epoxidation of linseed oil is generally done in a solvent. Epoxidized fatty acid esters like epoxy stearic acid ester are manufactured from refined grades of unsaturated fatty acids through esterification with monofunctional alcohols, particularly 2-ethylhexanol. The unsaturated esters are then epoxidized with a peracid similar to the epoxidized oils. Because of their high polarity epoxy plasticizers have wetting and emulsifying properties, which makes them suitable for pigment pastes and compounds. The reactivity of the epoxy moiety makes them also suitable as renewable building blocks for polymers [172].

5.2.4 Phosphates

Alkyl diaryl and triaryl phosphates have a synergistic action as plasticizers and as flame retardants. Phosphate plasticizers are prepared from $POCl_3$ and monofunctional alcohols or alkylated phenols. Industrial manufacturing necessitates the manipulation of HCl by-product, which is very corrosive and can cause undesirable side reactions. Because of their flame-retardant properties phosphate plasticizers are employed in fire-retardant applications such as cables and spread contract flooring.

5.2.5 Chloroparaffines

Chloroparaffines are yielded by chlorination of petrochemical paraffines with chain length between C_{10} and C_{30}. Chlorine content is about 70–73%. Chloroparaffines are liquids and are used as secondary plasticizers for PVC and VC-Copolymers.

Chloroparaffines are hydrocarbons with a straight carbon chain which consist of 10–30 carbon atoms and where 40–70% of the hydrogen atoms are exchanged for chlorine atoms. They are divided into short-, medium- and long-chain, depending on the length of the carbon chain, the short chain having 10–13 carbon atoms, medium-chain 14–17 carbon atoms and long chain more than 17 carbon atoms.

Chloroparaffines are used, for instance, in coolants and lubricants in the metal-working industry and as additives in paints, plastics and rubber. They fulfil the function of plasticizer and flame retardant.

5.3 Environmental Assessment of Plasticizers

Phthalates are widely spread chemicals used in clothes, PVC building materials, medical products, cosmetics, toys, child care articles, food packaging, etc.

Three phthalates underwent a complete risk assessment in the frame of the existing chemicals programme.

DBP [122] and DINP [123] came out to present no further concerns while for DIDP [124] further testing and risk reduction measures are requested.

A result of the risk assessments was that DEHP, DBP and BBP are toxic for reproduction. Accordingly, they were classified as CMR (carcinogen, mutagen, reprotoxic) substances, category 2 which is reflected in the classification and labelling with R-phrases 60–62 (Tables 12, 13).

Table 12 Classification and labelling according to the EU Dangerous substances directive

Phthalate	Carcinogenicity	Reproduction	Teratogenicity	Environment	ECB report
DBP	No R-phrase	R62	R61	R50	+
DEHP	No R-phrase	R60	R61	No R-phrase	
DINP	No R-phrase	No R-phrase	No R-phrase	No R-phrase	+
DIDP	No R-phrase	No R-phrase	No R-phrase	No R-phrase	+
BBP	No R-phrase	R62	R61	R50/53	

Table 13 Risk phrases used in the above table:

R50 Very toxic to aquatic organisms.
R51 Toxic to aquatic organisms.
R52 Harmful to aquatic organisms.
R53 May cause long-term adverse effects in the aquatic environment.
R60 May impair fertility.
R61 May cause harm to the unborn child.
R62 Risk of impaired fertility.

Category 1 [125] Substances known to impair fertility in humans

Category 2 Substances which should be regarded as if they impair fertility in humans

Category 3 Substances which cause concern for human fertility

The environmental fate of phthalates used in PVC products has been extensively examined [126]. A major concern with phthalates is the fact that they have low-level but worldwide environmental distribution. Phthalates have been found in human and animal tissues. Numerous in vitro and some in vivo laboratory studies have shown that in large doses they have potential for causing pronounced biological effects.

From the many toxicity studies available it can be concluded that phthalates are not mutagenic, and not carcinogenic even though tumours are induced in rodents via the peroxisome proliferation of liver cells. It has been confirmed that this mechanism is specific for rodents only and thus not relevant for humans.

The perceived potential regarding the possibility that the toxicity of some phthalates like DEHP and DINP may be the result of endocrine disruption is the principal cause for concern over phthalates, however there is a general lack of relevant information concerning possible adverse effects of endocrine-disrupting chemicals on humans at environmental exposure levels.

5.3.1 Ban of Phthalates in Soft PVC Toys, an Example to Apply the Precautionary Principle

At EU level the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) has established standard protocols for the extraction of phthalates from plasticized PVC toys. In 1999 the European Commission banned the use of DEHP in PVC toys and other easily mouthed items intended for children under 3 years of age as a precaution against the uncertain impact of phthalates on young children [127].

A permanent ban for phthalates in toys has been set on 5 July 2005. Three phthalates, namely DEHP, DBP and BBP, which have been identified as reprotoxic, will be banned in all toys and childcare articles. DINP, DIDP and DNOP (Di-n-octyl phthalate), will be banned from use in toys and childcare articles if those articles can be put in the mouth by children [128].

5.3.2 Aliphatic Esters

The polyesters made from polyols like glycol, glycerol, pentaerythritol and dicarboxylic acids like adipic, sebacetic, azelaic acids as starting materials easily reach a molecular weight above 1,000 Daltons. It is well established that molecules with molecular weights above 1,000 normally show a very reduced bioavailability. Data show that esters are in principle hydrolyzed, however those at higher molecular

Table 14 Adipic acid, Dialkyl (C7–C9) ester are used as an illustrative example [131] for an environmentally friendly class of products (CAS No. 68515-75-3

Chemical name	Biodegradation rate (24 h)	Stability in water	Fugacity	Photodegradation rate
Adipic acid, Dialkyl(C7–C9) ester	67–88%	3.21 years	Air-0.3, Water-3.6, Soil-27.3 Sed.-68.8	0% (14 days)

Table 15 Aquatic toxicity parameters for Adipic acid, Dialkyl (C7–C9) ester

Chemical name	Fish LC 50 (mg L^{-1})	Invertebrate LC50 (mg L^{-1})	Algae EC50 (mg L^{-1})
Adipic acid, Dialkyl (C7–C9) ester	>1,000 (96-h trout)	1.9 (48-h daphnia)	2.5 (96-h)

weight at a very low rate. Thus, mainly the fractions below 1,000 are considered in risk assessments [129]. The available toxicological data indicate that the current uses do not lead to concerns. Further evaluation can be found in the frame of the US HPV programme [130] (Tables 14, 15).

5.3.3 Trimellitate Esters

TOTM is undergoing a risk assessment in the existing chemicals programmes run by the OECD. Available data are compiled on the corresponding ECB (European Chemical Bureau) website [132].

Hydrolysis is an important environmental fate process. Hydrolysis rate is characterized by a half-life of 17.5 and 11.9 days at pH 7 and 9, respectively. TOTM is not readily biodegradable. Bioconcentration factors are measured up to 2.7 which is considered low if released into surface water. TOTM is expected to absorb to suspended solids and the sediment. Because of the major use in electric wire and cable TOTM is fixed in the matrix and no substantial exposure is expected.

The available toxicity studies show that there is no mutagenicity potential. Repeated dose studies and reprotox studies resulted in NOAEL above 100 mg L^{-1}.

The EFSA working group "food-contact materials" evaluated trimellitic acid and approved the use for food-contact materials up to migration limits of 5 mg kg^{-1} food [133].

5.3.4 Chloroparaffines

Chloroparaffines are stable, persistent compounds that bioaccumulate in the environment with BCF about 1,000. Short- and medium-chain paraffines are very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment [134].

Because of the risks for the aquatic environment in the PARCOM Decision 95/1 11 countries (Belgium, Denmark, Finland, France, Germany, the Netherlands, Norway, Spain, Sweden, Switzerland and the United Kingdom) [135] joined to phase out short-chain chlorinated paraffines on a voluntary basis.

Short-chain chloroparaffines have been restricted in the EU through Directive 2002/45/EC which contains prohibitions on use in metalworking and leather oils.

Risk assessment of medium-chain chloroparaffines is in progress under the EU's Existing Chemicals programme, and a decision has been taken to draw up a risk-management strategy.

The long-chain chloroparaffines are also being assessed for risk, but outside the Existing Substances Programme [136].

Short-chain chlorinated paraffines show fairly high NOAELs in repeated dose, reprotox and teratogenicity studies. The main concern results from the findings in carcinogenicity studies. It was concluded that short-chain chlorinated paraffines are carcinogenic. For chlorinated paraffines of average carbon chain length C_{12} and average degree of chlorination approximately 60% are *possibly carcinogenic to humans* (Group 2B) [137].

6 Stabilizers

In order for a plastic to increase virgin resin's resistance to degradation and maintain the physical and chemical properties of the compounded materials at suitable values throughout the processing and service life of the material and/or the parts made therefrom different kind of stabilizers are employed as plastic additives. *Heat stabilizers* are added to plastics to protect them from thermal degradation, even in the absence of oxygen, during processing but also during the useful life of the finished products. *Light stabilizers* are used in a variety of resins to limit the effects of sunlight or other sources of ultra violet radiation. *Antioxidants* can be used as sacrificial additives to protect plastics from oxidizing environments.

6.1 Heat Stabilizers

PVC is inherently the most heat-sensitive of the major commercial thermoplastic resins. Stabilization consists primarily of a stabilizing action on labile chlorine atoms in the PVC resin in order to prevent dehydrohalogenation and secondly in the neutralization of HCl by incorporation of bases [138]. Worldwide consumption of heat stabilizers is slightly above 300 thousands of metric tonnes per annum [139] (Table 16).

There are many different stabilizer systems for plastics (Fig. 7), depending on the type and products of oxidation. Metallic salts were originally used to stabilize PVC, the most common being based on barium, cadmium, lead or zinc, often mixed together to obtain a synergistic effect. Organometallic compounds are also used, mainly based on tin. A third group is non-metallic organic stabilizers, in which

Table 16 World consumption of stabilizers

	World 000t	USA 000t	W Europe 000t	Japan/Asia 000t
Heat stabilizers	280	66	150	64
UV stabilizers	16	7	5.5	3.5
Heat and UV stabilizers	296	73	155.5	67.5

Source: based on estimates by Business Communications Co., Rapra and Townsend

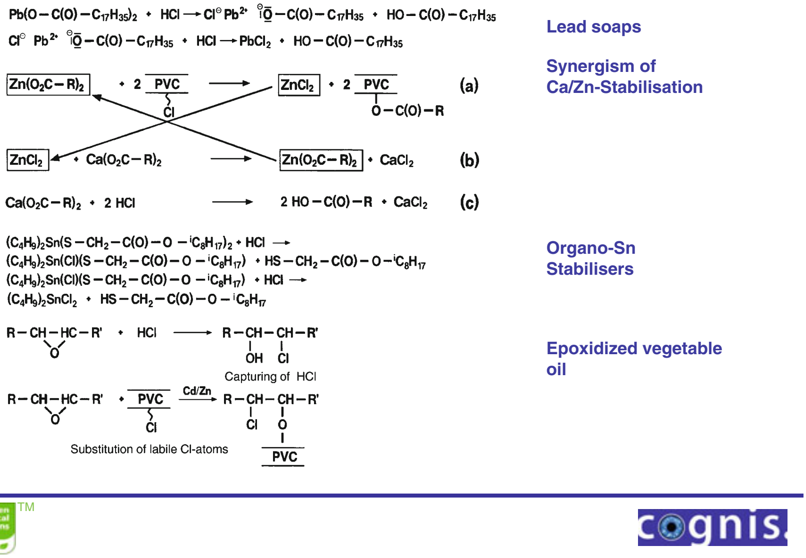


Fig. 7 Stabilizing mechanisms for PVC

phosphites play an important role, improving transparency, initial colour and lightfastness. Epoxies (particularly derivatives of soya bean oil) are also used, acting also as plasticizers, for non-toxic products.

For many years the trend in construction worldwide was to use lead-based materials, most specifically for piping. In early European and US construction, lead was used in decorative fixtures, roofs, pipes, paints, colourants, wire and cable, water lines, and windows. In more recent years, use of cadmium, tin and lead-based stabilizers in conventional PVC piping became the standard. Although cadmium and lead carboxylates provided high performance and cost-effectiveness, their environmental implications remain severe. In the mid-1980s, PVC became a high performance, cost-effective choice for many decorative and functional interior and exterior applications that are utilized to an even greater degree today.

Liquid calcium-zinc stabilizer blends present a green alternative without sacrificing performance.

Instead of using cadmium, tin and lead, these stabilizer products present a non-toxic, haze-free, phenol free, heavy-metal-free alternative (Table 17).

Table 17 Stabilizer systems used in different PVC applications

Applications	Pb	Ba/Cd/Pb	Ba/Zn	Ca/Zn	Zn
Unplasticized PVC (PVC-U)					
Pipe	+++			+	+
Injection moulding	++				+
Profile extrusion	+++	+		+	++
Sheet	++			+	++
Film					+++
Bottles				++	+
Plasticized PVC (PVC-P)					
Cable	+++			+	
Coatings			++	+	+
Imitation leather			++	+	
Profiles			++	+	
Film			++	+	+

Source: Cognis/Sidobre Sinnova/Plastiques Modernes et Elastomères

As with UV light, heat tends to oxidize polymers. The symptoms are embrittlement, melt flow instability, loss of tensile properties and discolouration. The mechanism of stabilization is therefore to prevent oxidation or to mitigate its effects. Plastics, particularly thermoplastics, also require stabilization protection against degradation from heat during processing or in use.

Another important growth area for heat stabilizers is recycled materials, where they will be used increasingly in inhibiting degradation and secondly in re-stabilizing post-use plastics waste.

6.1.1 Lead Stabilizers

Bivalent lead oxide, litharge (PbO), is among the oldest PVC stabilizers and its properties include its basicity, its complexing properties and its extremely fine particle size, which facilitates incorporation. The improvements in lead stabilizers over the years can be viewed as improvements on the basic characteristics of litharge, with the yellow colour, of course, being one of the apparent disadvantages, but the greatest deterrent to the use of lead stabilizers is their acute and cumulative toxicity.

The most important lead stabilizer compounds, all produced by reacting litharge with the corresponding acids, are:

- tribasic lead sulphate $3\ PbO{\cdot}PbSO_4{\cdot}H_2O$
- tetrabasic lead sulphate $4\ PbO{\cdot}PbSO_4{\cdot}1/4H_2O$
- dibasic lead phosphite $2\ PbO{\cdot}PbHPO_3{\cdot}1/2H_2O$
- dibasic lead phthalate $2\ PbO{\cdot}Pb(OOC)_2C_6H_4$
- dibasic lead stearate $2\ PbO{\cdot}Pb(OOCC_{17}H_{35})_2$
- neutral lead stearate $Pb(OOCC_{17}H_{35})_2$
- dibasic lead carbonate $2\ PbO{\cdot}PbCO_3$

Lead stabilizers are primarily used in wire and cable and in rigid pipe applications.

6.1.2 Organotin Stabilizers

Organotin stabilizers are primarily used for rigid PVC. Synthesis of tin stabilizers starts from tetralkyltins via Grignard or alkylaluminium synthesis. The tetraalkyltin is then reacted with stannic chloride yielding dialkyltin and/or monoalkyltin chloride, which reacts with an alkylmercaptan, a thiocarboxylate, a thioglycolic acid or a β-mercaptopropionic acid ester to yield the stabilizer compound. Alternatively the organotin chloride may be converted into an organotin oxide and then react with organic acids or mercaptans.

Another class of organotin heat stabilizers is the sulphur-free estertins or organotin carboxylates like dibutyltin maleate. Estertins work especially well in out-door applications like transparent and translucent double-walled panels for greenhouses, sidings, and window profiles.

6.1.3 Mixed Metal Salts

To better distinguish from lead stabilizers combinations of Ba/Cd, Ba/Zn and Ca/Zn salts are called mixed-metal stabilizers. They are primarily used in combination with organophosphites for flexible or semi-rigid PVC. Their efficacy is also greatly enhanced in combination with ESO. Only the combination of alkaline earth metal carboxylates and zinc or cadmium carboxylates provides desirable properties like good early colour, colour retention, and long-term stability. Apart from simple mixtures like calcium stearate and zinc stearate mixed-metal stabilizers are multi-component systems. This is particularly true for Ca/Zn stabilizers, which have more recently been finding many applications because of the two non-toxic components calcium and zinc stearate. They are always used in combination with co-stabilizers, epoxy plasticizers, and antioxidants [121, 140].

6.1.4 Other Stabilizers and Co-Stabilizers

When used in PVC organophosphites act as secondary heat stabilizers. In other resins such as PP, PS, HDPE and ABS plastics they function as antioxidants.

β-Diketones are well-known co-stabilizers more particularly for zinc carboxylates.

The synergistic action of epoxidized fatty acid esters like ESO or butylepoxy stearate as plasticizer, HCl scavenger and stabilizer for labile chlorine atoms in the catalytic presence of Zn and Cd salts is shown in Fig. 7 (see also 5.2.3)

Hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, a synthetic clay mineral with a layered structure of hexagonal platelets, acts as HCl scavengers in PVC stabilization [141]. Together with mixed-metal Ca/Zn systems hydrotalcite constitutes an environmentally friendly, non-toxic, heavy-metal free method of PVC stabilization in flexible, rigid and transparent PVC applications [142].

6.2 Antioxidants

Antioxidants interrupt the degradation process in two ways, depending on structure by chain-terminating primary antioxidants and by hydroperoxide decomposing secondary antioxidants.

Organics can react with molecular oxygen in a process called autoxidation, initiated by heat, light (high-energy radiation), mechanical stress, catalyst residues or reaction with impurities, to form alkyl radicals. The free radicals can, in turn, react to cause the polymer to degrade. Oxidation-in-chain scission, producing a change in molecular weight, discolouration and loss of properties – is the main chemical process causing plastics to degrade. Hydroperoxides break down into free radicals, which cause the damage. Under heat, some polymers may undergo chain scission with cross-linking and formation of hydroperoxides and free radicals. Oxidation can be slowed by chain-breaking antioxidants, to reduce the rate of propagation, or preventative antioxidants, which prevent initial formation of free radicals. Antioxidants deactivate the sites by decomposing the hydroperoxide or by terminating the free radical.

6.2.1 Primary Antioxidants

Primary antioxidants react rapidly and are termed "radical scavengers". The most important are sterically hindered phenolics and secondary aromatic amines. Hindered phenolic is a high molecular weight antioxidant. It protects against degradation at high processing temperatures and is highly efficient, low in volatility and non-staining, with wide toxicological clearance. The efficiency can be enhanced by using hindered phenolic with other antioxidants such as phosphites and thioesters, producing synergistic effects for effective and economical formulations. The antioxidant is effective at very low dosages (0.01–0.1%) in low- and high-density polyethylene (especially carbon black-filled grades for pipe and copper cable insulation), polypropylene (especially hot water applications), high-impact polystyrene, ABS and MBS. It can also be added to PVC plasticizers (in which it can be dissolved) to inhibit oxidative degradation and embrittlement of PVC wire and cable insulation. The material can be used in polyamides and hot melt adhesive formulations.

6.2.2 Secondary Antioxidants

Secondary antioxidants react with hydroperoxides to produce non-radical products and are therefore often termed "hydroperoxide decomposers". They differ from primary phenols and amines in that they are decomposed by reaction with hydroperoxide, rather than containing it. They are particularly useful in synergistic combinations with primary antioxidants.Systems that do not contain a phenolic can provide good colour stability and gas fade resistance, which are important properties in PP fibres and other applications. A breakthrough was claimed by Ciba with IRGASTAB® FS systems, the first of which was based on a new hydroxylamine – a high molecular weight compound offering outstanding compatibility with polypropylene, which functions through several different stabilization mechanisms to give both processing and long-term thermal ageing stability. It also appears to improve the activity of the hindered amine stabilizer that is also a component of the system, as both a thermal and light stabilizer.

Phosphite/phosphonites are generally regarded as the most effective stabilizers during processing, protecting both the polymer and the primary antioxidant. Hydrolytically stable phosphites are the most frequently used processing stabilizer in high-performance additive systems. A solid phosphite antioxidant has been developed by GE Specialty Chemicals in its Ultranox® range (now with Chemtura Corp.). Designed to meet the demand for a high activity stabilizer with superior hydrocarbon stability and improved handling characteristics, it is based on butyl ethyl propane diol chemistry, rather than the usual pentaerythritol. It has been granted FDA approval for food contact in certain applications and is expected to find applications in polyolefins, styrenics, PVC, engineering thermoplastics, elastomers and adhesives.

Thioethers increase long-term stability in conjunction with phenolic antioxidants. Their use is limited to applications where possible effect on odour or taste and negative interaction with HALS (hindered amine light stabilizers) is not important.

6.3 Environmental Assessment of Stabilizers

6.3.1 Lead Stabilizer [143]

The use of lead in consumer end products is increasingly restricted due to findings which resulted in a listing/classification/labelling with a risk phrase R62 (R62=Risk of impaired fertility) according to EU dangerous substances directive.

Restrictions for lead are included in the EU Directive on Waste Electronic and Electrical Equipment [144] and EU Directive on Restriction of Hazardous Substances Directive [145], the EU End-of-Life-Vehicle [146] Directive.

In the USA the use of lead in NSF Certified products for drinking water appliances including pipes is restricted by NSF General Policy *GP–60* that indicates:

“There shall be no lead as an intentional ingredient in any material contacting food or drinking water, except brass meeting the definition of “lead free” under the specific provisions of the Safe Drinking Water Act of the United States, as amended in 1986. In the absence of further regulatory guidance, the EPA Action Level of 15 ppb shall be used for purposes of establishing the maximum extraction levels for products [147]”.

Currently, EU member states handle the approval of organic polymers for drinking water supply systems on a national level where the use of lead stabilizers is still allowed under strictly controlled conditions. Harmonization of a European system called EAS (European Acceptance System) is about to be developed. One element of the EAS will be a list of authorized substances where lead stabilizer will be excluded.

The European Union PVC Industry has therefore agreed and committed to gradually replace Lead (Pb) in stabilizers. Although there is a clear trend to phase out lead stabilizers in consumer products and despite the classification of lead compounds as dangerous these stabilizers are still used because of their very good performance in cable and wire application and construction parts.

Once the lead stabilizer is incorporated into the PVC matrix, it is immobilized and is no longer bioavailable. The typical lead metal content in major applications is: Pipe 0.75%; Window Profile 2.7%; Wire and Cable 2.0%.

The inertness of lead-stabilized PVC can be demonstrated by extraction studies. For instance, several studies have shown that the amount of lead extracted from lead-stabilized water pipes is negligible when tested according to the requirements of the EU "plastics" Directive (2002/72/EC) which specify the maximum amount of lead that can be extracted from plastics in contact with food which includes drinking water [148].

6.3.2 Organotin Stabilizers

Products used as stabilizers in PVC are distinguished by their respective alkyl groups: octyl, butyl and methyl. The group comprises only mono- and di-organotin stabilizers which are to be differentiated from tri-organotin stabilizers like the very effective biocide (anti-fouling agent) tri-butyl tin.

Mono- and di-organotin stabilizers are part of various risk-assessment programmes.

Although some ambiguous data have been generated with mutagenicity screening tests, the results from long-term feeding studies did not indicate a potential for cancerogenicity. On the basis of the currently available data it is concluded that organotin stabilizers are safe, both for processors and consumers [149].

Methyl-, octyl- and dodecyltin stabilizers have widespread national approvals for food-contact applications. The Scientific Committee for Food (SCF) and now EFSA of the EU has defined specific migration limits for organotin stabilizers based on the tolerable daily intake value (TDI). Although the TDI-value for dioctyltin stabilizers is most restrictive, recent evaluation of migration data reconfirmed that this requirement can well be fulfilled. Therefore, the use of these organotin stabilizers in PVC for food packaging is not a risk for the consumer.

Exposure limit values in the workplace have been defined based on the available toxicological data.

The MAK (Maximale Arbeitsplatz-Konzentration) Commission setting OEL (Occupational Exposure Limits) in Germany as well as the ACGIH (American Conference of Governmental Industrial Hygienists, Inc.) in the U.S., established

$0.1\ \mathrm{mg\ m^{-3}}$ for tin as the 8-hour TLV (threshold limit value) while the TLV-STEL (short-term exposure level) is $0.2\ \mathrm{mg\ m^{-3}}$ for tin.

Because they improve thermal stability, tin stabilizers make it easier to recycle vinyl products by helping to reduce degradation during the process steps required for recycling. Vinyl siding, for example, is being recycled both by manufacturers (e.g., manufacturing off-cuttings and construction site waste) and after consumer use, by removal and recycling at the end of the product's useful life. Vinyl products also can be safely disposed of in landfills. Studies have shown that levels of tin stabilizer leaching from vinyl products in landfill conditions are very low, usually attributable to wash-off from the product's surface and pose no undue risk to human health or the environment.

6.3.3 Mixed Metal Salts, Ca/Zn

A full risk assessment has been performed under the existing chemicals programme for Ca/Zn stabilizers [150].

As only limited data are available for zinc distearate the assessment was based on toxicological data of other zinc compounds like zinc gluconate, zinc sulphate or zinc oxide assuming that the availability of zinc ions is controlling the toxicological behaviour. It is further assumed that calcium does not contribute to adverse effects at the expected concentration levels.

From the available data it was concluded that zinc stearate is not mutagenic or carcinogenic. No indications were found for reproduction toxicity.

Zinc and calcium stearate are approved substances up to a limit of $60\ \mathrm{mg\ kg^{-1}}$ food for materials intended to come into contact with food.

7 Lubricants

The term lubricant is not used in a standard way. Synthetic lubricants in automotion and in machinery in general – mainly liquids – are designed to reduce the friction and wear of/or between (mainly) metallic parts in the widest sense. In a similar way, lubricants are understood in textile and fibre processing, where they are externally applied to reduce friction between textile fibres and metallic machinery parts. The same applies for example, to processing of PVC films on a calendar, where lubricants may be fed externally by a roller device.

Internal lubricants are added as part of the formulation during plastics processing. Depending on their compatibility with the resin they can have a more pronounced internal lubrication effect mainly interacting with the molecules of the polymer melt or they can have a more pronounced external effect, i.e. additionally reduce friction at the interface between processed plastic melt and metallic machinery parts [121, 151–153]. Lubricants in resin systems improve flow characteristics and reduce adhesion in the polymer melt. Added in very small quantities

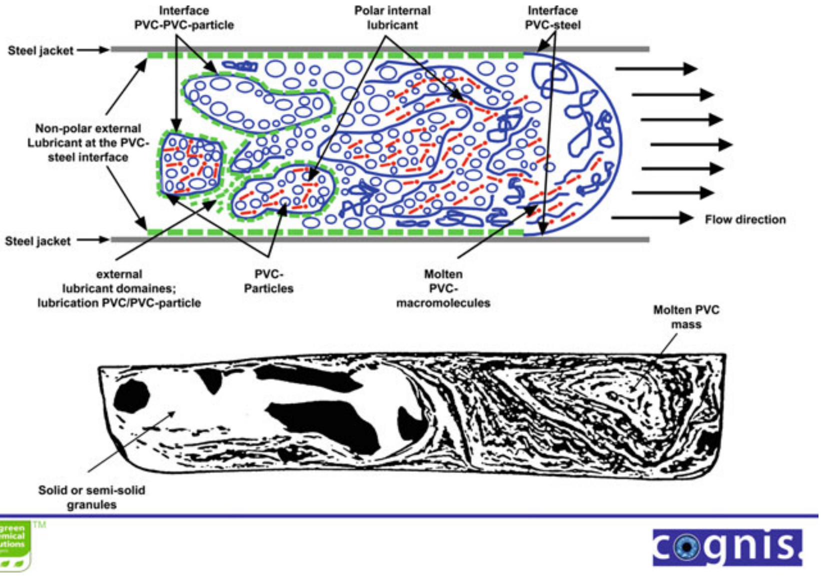


Fig. 8 Lubricants in PVC processing

they decrease the internal and external friction in the molten polymer, which reduces shear and equipment wear, increases production rates, and reduces energy consumption (Fig. 8).

Lubricants for plastics processing are to a large extent synthetic waxes derived from coal or petrochemical syntheses or natural waxes derived from renewable resources.

Important lubricant groups [154] are synthetic and natural hydrocarbon waxes and natural waxes derived from renewable resources, more particularly natural fats and oils.

7.1 Lubricants Based on Renewable Resources

Long-chain fatty acid lubricants are manufactured by hydrolysis of vegetable oils or animal fats and subsequent hardening. The waxy stearic acid for example, is a widely used lubricant with excellent internal lubricating properties but relatively high volatility limits application.

Similarly, fatty alcohols with chain length from C_{12} to C_{22}, which are industrially produced by hydrogenation of fatty acid methyl esters are efficient internal lubricants and exhibit good compatibility with PVC. However, they also have the disadvantage of high volatility under plastics processing conditions.

By esterification of fatty alcohols with dicarboxylic acids, highly polar lubricants such as adipic acid distearylate or distearyl phthalate with excellent compatibility are obtained.

Fatty acid esters, because of the great variety of molecular structures that are possible, offer great versatility to the plastics compounder. Liquid fatty acid esters of short-chain monofunctional alcohols have a distinct secondary plasticizer action, whereas fatty acid esters of long-chain fatty alcohols like stearyl stearate or cetyl palmitate are well known as wax esters and because of their thermal stability, good flow properties and resistance to plate out are broadly used as lubricants for PVC and other polar plastics.

Fatty acid esters of polyfunctional alcohols are known as partial esters. Partial esters of glycerol are the liquid glycerol mono- or dioleate and the waxy glycerol mono stearate (GMS). Both, esterification and transesterification yield glycerol monostearates of about 50% monoester, which are largely used as relatively low cost lubricants for PVC, PE, PP, polycarbonate (PC), PS, and styrene co- and graft polymers with α-methyl styrene, vinyl toluene, divinylbenzene, acrylonitrile, butadiene as well as for polyamides. Manufactured adequately, GMS is perfectly neutral in odour and taste and can be used for plastic packaging, gaskets and sealants in direct food contact or as an anticaking agent in gelatine-free Swiss caps for the oral dosage of vitamins, minerals, essential lipids and liquid pharmaceuticals. High mono GMS with monoester content of 90% besides being a lubricant offers distinct antistatic properties. Among the glycerol triesters hydrogenated castor oil (HCO) the triglyceride of 12-hydroxystearic acid has the strongest polarity and is one of the most important internal lubricants for transparent PVC applications.

Pentarerythritol tetrastearate besides PVC is particularly suitable as a lubricant for PC because of its low volatility and good thermostability.

Polycondensation of dicarboxylic acids, polyols, and long-chain fatty acids yields so-called fatty acid complex esters, which are highly compatible PVC lubricants offering a good combination of release effect and transparency. Typical examples are glycerol adipate stearate or pentaerythritol adipate oleate.

Whereas bis(stearoyl)ethylenediamine (EBS), generally known as amide wax, shows an unusually high melting point of 140°C and has a good balance of internal and external lubricating properties for PVC, the fatty acid monoamides, more particularly oleamide, stearylamide, and erucamide show a pronounced external effect. They are more particularly used as lubricants, mould release and antiblocking agents in polyolefins.

Metal soaps, especially fatty acid soaps of alkaline earth metals have an external lubricating effect in PVC, contribute to good release and are co-stabilizing. In fact, some are true stabilizers.

Traditionally metal soaps have been manufactured by reaction of alkali- or alkaline earth oxides or carbonates with natural fats or oils. Both components are mixed and at higher temperatures the triglyceride is decomposed yielding metal soap and glycerol. Under such conditions the soap is dispersed in an excess of oil or molten fat, and lubricating greases are yielded that way.

Metal soaps are mainly manufactured nowadays by the so-called "melt process", i.e. heating of a fatty acid together with a metal oxide, -hydroxide or -carbonate and evaporating the water formed by the neutralization reaction.

Another method to manufacture metal soaps is the so-called "precipitation process". Saponification of fatty acid in water yielding an aqueous sodium, potassium or ammonium soap solution is followed by reaction with an alkaline earth metal chloride, and results in formation of a precipitated calcium stearate, which needs to be thoroughly washed and dried. Solid calcium stearate is a voluminous powder, which can be used as

- internal and external lubricant and/or in combination with zinc stearate as a stabilizer for PVC
- internal and external lubricant for rubber
- lubricant for polyethylene and polypropylene
- mould release agent for PVC, polystyrene or other plastics

Aqueous calcium stearate dispersions can be used in all the above applications as long as water can be accepted as a carrier.

7.2 Synthetic Waxes

Synthetic waxes are produced by polymerization of low molecular weight hydrocarbons containing a reactive double bond like ethylene and propylene. Thermal degradation of high *Mw* resins is another option though leading to thermally not stable and organoleptically inferior waxes. Polymerization of polyethylene can lead to LDPE- or HDPE-waxes with *Mw* ranging from 1,000 to 10,000. PE waxes are highly incompatible with polar plastics like PVC. Applied as internal lubricants they have a pronounced external lubrication effect. The same is true for natural and synthetic paraffin waxes, and more particularly for the Fischer–Tropsch paraffin waxes.

Polar polyethylene waxes distinguish via oxygen-containing polar groups, which are introduced by oxidation of PE waxes or paraffin waxes in air. Because ketone, alcohol and ester groups are formed along with the acid groups the increase in polarity is much greater than might be expected by a simple molecular model.

Polar polypropylene waxes are produced by grafting of PP with maleic anhydride.

7.3 Montan Waxes

Crude montan wax (a mixture of esters of straight-chain saturated C_{26}–C_{34} carboxylic acids) is a by-product of lignite and separated from lignite by an extraction process. Oxidative bleaching of black crude montan wax with hot chromosulphuric acid produces off-white, industrial montan wax acids. Esters of mono- and polyfunctional short-chain alcohols, esters of long-chain natural or synthetic fatty alcohols as well as complex esters are synthesized starting from montan wax acid [155].

7.4 Environmental Assessment of Lubricants

7.4.1 Lubricants Based on Renewable Resources

Vegetable oils and tallow are the main sources for fatty acids, their glycerides and partial glycerides. All derivatives from renewable natural fats and oils have a favourable profile in toxicity and ecotoxicity because they are an essential part of the human diet. In this context the fatty acids, the derived fatty alcohols and the (partial) glycerides are preferred whenever technically feasible. Consequently, many of these components are regulated as direct food additives which implies that no concern is assumed with regards to consumption. This is reflected in the corresponding EU regulation generic entries like “E 471 mono- and di-glycerides of fatty acids” [156].

Fatty acids and their salts (soaps) are widely investigated under the existing chemicals programme [157]. Because of a very rapid biodegradation no adverse effects to the environment have been identified from the current uses.

Complex esters like glycerol adipate stearate or pentaerythritol adipate oleate (Loxiol® G 70 series) have been fully assessed by EFSA for the use in food-contact materials. These esters still function as lubricants but due to higher molecular weight migration from food-contact material to food is considerably reduced.

Wax esters can be found in plants, bacteria, and animals including human beings indicating that these compounds can be metabolized and catabolized which is considered as low concern at the concentrations found. Wax esters protect plants against water loss, for example, as surface lipids in cabbage [158], grapes, apples and wheat [159]. Wax esters also appear in many different fish species, especially in fish eggs and liver. Sperm whales contain high amounts of ambergris (cetyl palmitate) and sperm oil (oleyloleate) [160]. Human skin fat contains about 20–25% of wax esters [161]. Long-chain alcohols, which together with fatty acids form wax esters, are to be found in extracts of the guts. These esters are not produced by bacteria but are a natural secretion of the guts [162]. These fatty alcohols serve as precursors to forming etherglycerides and plasmologen. They can also be esterified to yield wax esters [163], [164]. Fatty alcohols and their derivatives like ether lipids and wax esters are also detected in tissues of other mammals [165].

In addition to the broad knowledge of naturally occurring wax esters some oral feeding studies with rats exist confirming that there are no adverse effects observed with the highest tested dosages (Table 18).

Amide waxes like stearamide, oleamide, erucamide are subject to extensive risk assessments under the existing chemicals HPV programme in the USA [169]. The available data indicate that there is no mutagenic or reprotoxic potential identified. Repeated dose feeding studies up to 2 years did not reveal a carcinogenic effect. The NOEL was determined to be >7,500 mg kg^{-1} body weight/day.

Stearamide, oleamide, erucamide, N,N′-ethylenebis(stearamide) are allowed as an additive in plastics for food-contact use in various countries. Within the EEC, all

Table 18 Subchronic data on typical wax ester

Substance	Duration oral feeding study with rats	Highest dosage	Result	Reference
Cetyl palmitate (CAS No: 540-10-3)	90 days	20% in feed	No effects	[166]
Decyl oleate (CAS No: 3687-46-5)	28 days	20% in feed	No effects	[167]
Butyl stearate (CAS No: 123-95-5)	2 years	6.25% in feed	No effects	[168]

Table 19 Lubricant components evaluated for food-contact materials [112]

REF_N	CAS_N	NAME
32840	1119-74-0	Adipic acid, di-n-Octadecyl ester
43120	8001-78-3	Castor oil, Hydrogenated
58240	555-43-1	Glycerol tristearate
70400	57-10-3	Palmitic acid
70720	540-10-3	Palmitic acid, Hexadecyl ester
75760	14117-96-5	Phthalic acid, di-n-Octadecyl ester
89040	57-11-4	Stearic acid
52720	112-84-5	Erucamide
88960	124-26-5	Stearamide
68960	301-02-0	Oleamide
53520	110-30-5	N,N′-ethylenebis(stearamide)
67850	08002-53-7	Montan wax
95859		Waxes, refined, derived from petroleum-based or synthetic hydrocarbon feedstocks The product should have the following specifications: – Content of mineral hydrocarbons with Carbon number less than 25, not more than 5% (w/w) – Viscosity not less than $11 \times 10^{-6} m^2 s^{-1}$ (11 centistokes) at 100°C – Average molecular weight not less than 500.
95883		White mineral oils, paraffinic derived from petroleum-based hydrocarbon feedstocks The product should have the following specifications: – Content of mineral hydrocarbons with Carbon number less than 25, not more than 5% (w/w) – Viscosity not less than $8.5 \times 10^{-6} m^2 s^{-1}$ (8.5 centistokes) at 100°C – Average molecular weight not less than 480

amides are on a draft positive list of processing materials and additives for plastic materials intended to come into contact with food (Table 19).

In the USA, the amides are allowed as an indirect food additive by the Food and Drug Administration (FDA) for various applications including resinous and polymeric coatings, components of paper and paperboard in contact with aqueous and fatty foods and components of paper and paperboard in contact with dry food (21 CFR 175.300; 21 CFR 176.170 and CFR 176.180).

All amides show a biodegradation above 60% or higher. As the amides act as surfactants toxicity towards aquatic organisms is rather high with values of LC50 (EC50) below 10 mg L^{-1}. This behaviour is comparable to other surfactant types like polyglycolethers etc.

7.4.2 Synthetic Waxes

Mineral hydrocarbon waxes are a heterogeneous group of substances consisting of mixtures of different-sized hydrocarbon molecules, which may include saturated and/or unsaturated hydrocarbons; these may be linear, branched or cyclic. The relative proportions of these different hydrocarbon molecules varies widely and is best defined on the basis of their physical characteristics, such as viscosity and density, rather than on the basis of their precise chemical identity.

They are used in human medicines, pesticides, food-contact materials, food-processing aids, chewing gum bases and in human foods as food additives. Evaluations for the various application fields have to take into account that only paraffins with more than 30 carbon atoms are not significantly absorbed while lower molecular weight material is finally distributed to the adipose tissue where it accumulates. Consequently, the higher molecular weight microcrystalline waxes are selected.

While no potential for mutagenic or teratogenic effects have been identified subchronic feeding studies revealed a more differentiated picture. High molecular weight waxes above 500 Daltons show no adverse effects in subchronic 90-day-studies at the highest dose tested, e.g., up to 2,000 mg kg^{-1} body weight/day. Other materials provoked haematological effects and inflammatory lesions.

The microcrystalline waxes and high-viscosity mineral hydrocarbons are unlikely to pose a consumer risk as these are of low toxicity and are poorly absorbed from the gastrointestinal tract. Similarly, the very light mineral hydrocarbons are unlikely to pose a consumer risk as these are rapidly metabolized to simple products such as carbon dioxide and water. ADIs had been set by JECFA for several groups of compounds including the microcrystalline waxes, the high viscosity oils, the low viscosity oils and the medium/low viscosity oils; the ADIs for the waxes and high viscosity oils were permanent but the others were temporary. SCF had established a tADI for the waxes. Many of these ADIs or tADIs were of a similar order (0–20 mg kg^{-1} bw) except for the medium viscosity oils (0–1 mg kg^{-1} bw) and the low to medium viscosity oils (0–0.01 mg kg^{-1} bw) [170].

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Environmental Aspects of Initiators for Plastic Manufacture and Processing

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Abstract Organic peroxides, persulfates, carbon–carbon initiators, and azo initiators generate radicals mainly by thermal or redox decomposition. Decomposition products mostly remain in the polymer or become incorporated in the polymer chain. Solvents, temperature, concentration, and reaction partners vary the type of decomposition products generated. Uncontrolled decomposition could cause fire and explosions. Storage and transport therefore need temperature control, which is also necessary to maintain quality. A small number of initiators cause toxicity problems and have been mostly eliminated. The FDA and BfR produce a positive list for food package polymers. Most polymers being manufactured require low-odor initiators. Benzene, PCBs, aromatic amines, or heavy metals cause changes in initiator type used as well as in processing conditions.

Keywords Environmental aspect, Initiator, Plastic manufacture, Polymerization, X-linking – curing

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Abbreviations

ACSP	Acetylcyclohexylsulfonylperoxide
AIBN	Azoisobutyronitrile
APS	Ammoniumpersulfate
BCHPC	Di-4-t-Butylcyclohexyl-peroxidicarbonate
BP	Di-benzoyl-peroxide
BfR	Bundesinstitut für Risikobewertung
CEPC	Di-cyclohexylperoxidicarbonate
CUPND	Cumyl-perneodecanoate
DClBP	Di-2,4-chloro-benzoyl-peroxide
DCUP	Dicumylperoxide
DIPP	1,3-Di(2-*tert*.butylperoxyisopropyl)benzene
EHPC	Di-2-ethyl-hexyl-peroxidicarbonate
EINECS	European inventory of chemical substances
ELINCS	European list of notified chemical substances
EPDM	Ethylen-propylen-dien-rubber
EPM	Ethylen-propylen-rubber
EVA	Ethylen-vinylacetate copolymer
FDA	Food and drug administration
HDPE	High density polyethylen
IBC	Intermediate bulk container
INP	Di-isononanoyl-peroxide
LP	Di-lauroyl-peroxide
MEKP	Methyl-ethyl-ketone-peroxide
MSDS	Material safety data sheet
MYPC	Di-myrystyl-peroxidicarbonate
PAA	Peracetic acid
PCB	Polychlorinated biphenyls
PMBP	Di-4-methyl-benzoyl-peroxide
PVC	Polyvinylchloride
QM	Silicone rubber
TBPB	*Tert*.butyl-perbenzoate
TBPEHC	*Tert*.butyl-2-ethyl-hexyl-monocarbonate
TBPND	*Tert*.butyl-perneodecanoate
TOPND	*Tert*.octyl-perneodecanoate
VC	Vinylchloride
XLPE	Crosslinked polyethylen

1 Introduction

2 Decomposition Products of Organic Peroxides

Organic peroxides and peroxodisulfates as well as some azo compounds and carbon–carbon compounds are mainly used as initiators in radical polymerization. The production volume of these initiators exceeds 250,000 metric tons. More than 50% of all polymers are made industrially by radical polymerization. Considering that the annual worldwide production of polymers is in the range of 200 Mio metric tons, it indicates that initiators have fundamental importance. The quantity of initiator used varies in a range from 0.01—~5% depending on the process and polymer applied (Fig. 1). Their decomposition products become incorporated or remain as a residue in this large volume of polymers (Fig. 2).

Polymertype	World production Year 2004 Miotons	application	Peroxide dosage % w/w
PE-LD	18	Polymerization	0,05 – 0,2
PVC	30	Polymerization	0,03 – 0,1
PS	15	Polymerization	0,01 – 0,3
PP	32	Degradation*	0,01 – 0,1
UP-resins	2.0	Curing	1 – 5
PE-X	0.5	crosslinking	0,3 – 3

Fig. 1 Application field and dosage of organic peroxides for the production and processing of polymers (* Controlled rheology)

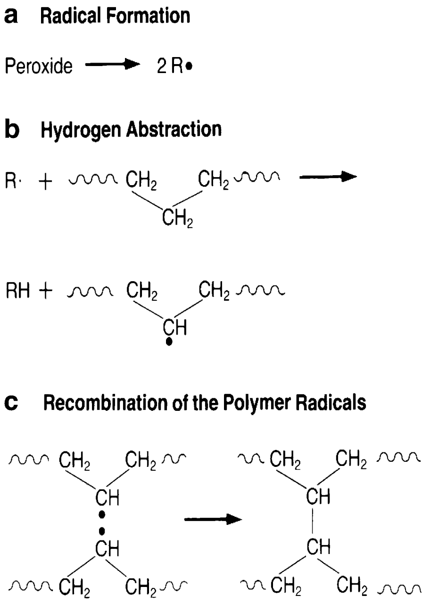


Fig. 2 Crosslinking of polyethylen

Table 1 Organic peroxides consist mainly of eight different basic substance classes. Peroxodisulfates are also important radical generators; on a smaller scale azo-initiators and carbon–carbon initiators are used

Dialkylperoxides
Hydroperoxides
Perester
Perketales
Ketonperoxides
Diacylperoxides
Peroxidicarbonates
Peracids
Peroxodisulfates
Azo-initiators
CC-initiators

a) thermal	R-OO-R	→	2 RO*	~ T, halflife
b) catalytic	R-OOH + Cat	→	RO*+OH^{-}	~ T, Catalyst type

A typical side reaction could be heterolytic cleavage forming no radicals e.g. in strong alkaline or acidic conditions. This reaction gets used in organic synthesis e.g. Phenol production from Cumene hydroperoxide.

Fig. 3 Organic peroxide decomposition mechanism

The decomposition reaction generates a product spread not according to a simple scheme; it is ruled by concentration, temperature, reaction media, and reaction partners. In polymerization reactions the radical part is added; in stochiometric reactions like crosslinking, grafting, or degradation, decomposition products result from the radical, which has made a hydrogen abstraction (Fig. 3).

Peracids are not used as initiators; they are applied in chemical synthesis as epoxidation reagents or in disinfection (Table 1). For decomposition schemes of various classes see Figs. 4–9.

More than 100 different initiator types industrially used as a radical source exist. Therefore, the products shown in Figs. 4–9 only represent the most important products in their substance class and the most typical decomposition products. The quantities generated depend on reaction conditions such as concentration, temperature, solvents, and reaction partners (Fig. 10). The polarity of solvents and concentration of initiators influences half-life.

3 Safety Aspects

3.1 Safe Handling—Accidents

Being thermally sensitive, thermally degradable, flammable, and combustible, these initiators need special care to avoid decomposition. Accidents could occur

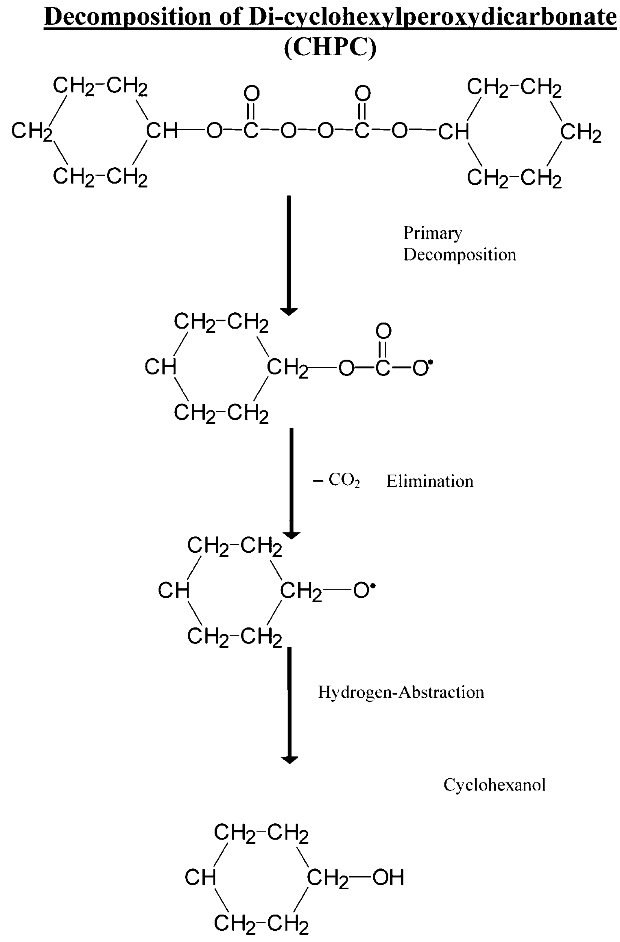


Fig. 4 Peroxodicarbonates

starting with deflagration and even potentially causing an explosion. As most of the initiators and their decomposition products are easily ignitable a violent fire is often the result of such an accident. These events incur severe negative effects for the user and his neighborhood. The extent of environmental damage depends greatly on fire fighting and draining systems.

Fortunately most of these initiators with the exception of some azo-initiators and some aromatic diacylperoxides are not and do not form toxic products.

AIBN (2,2′-azoisobutyronitrile) upon being decomposed generates the toxic succinic acid dinitrile, especially as a pure substance!

DClBP(2,4-dichlorobenzoyl-peroxide) can form PCBs (polychlorinated biphenyls) upon being decomposed.

BP(Di-benzoylperoxide) and TBPB(*tert.*Butylperbenzoate) can generate benzene!

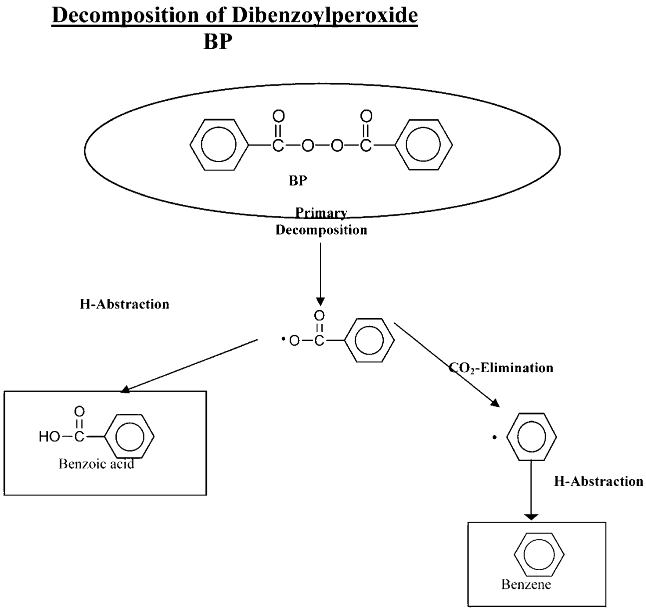


Fig. 5 Diacylperoxides

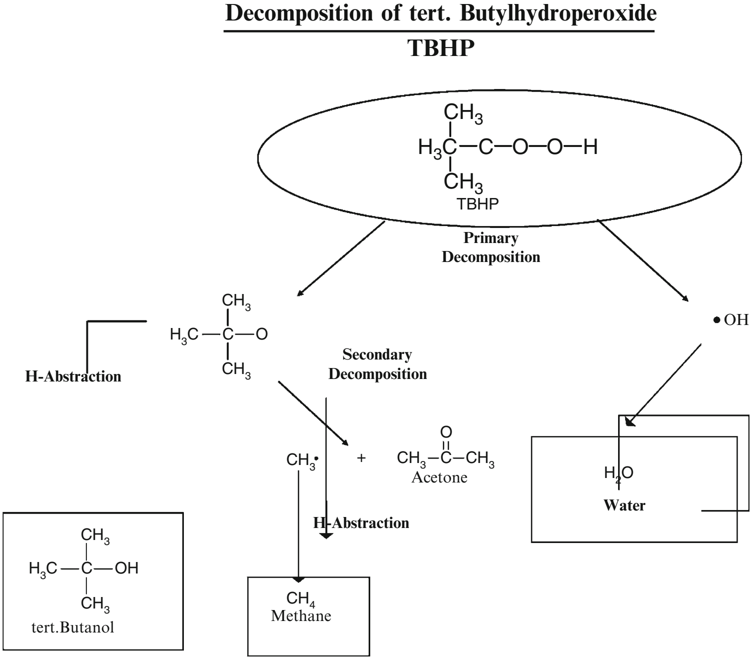


Fig. 6 Hydroperoxides

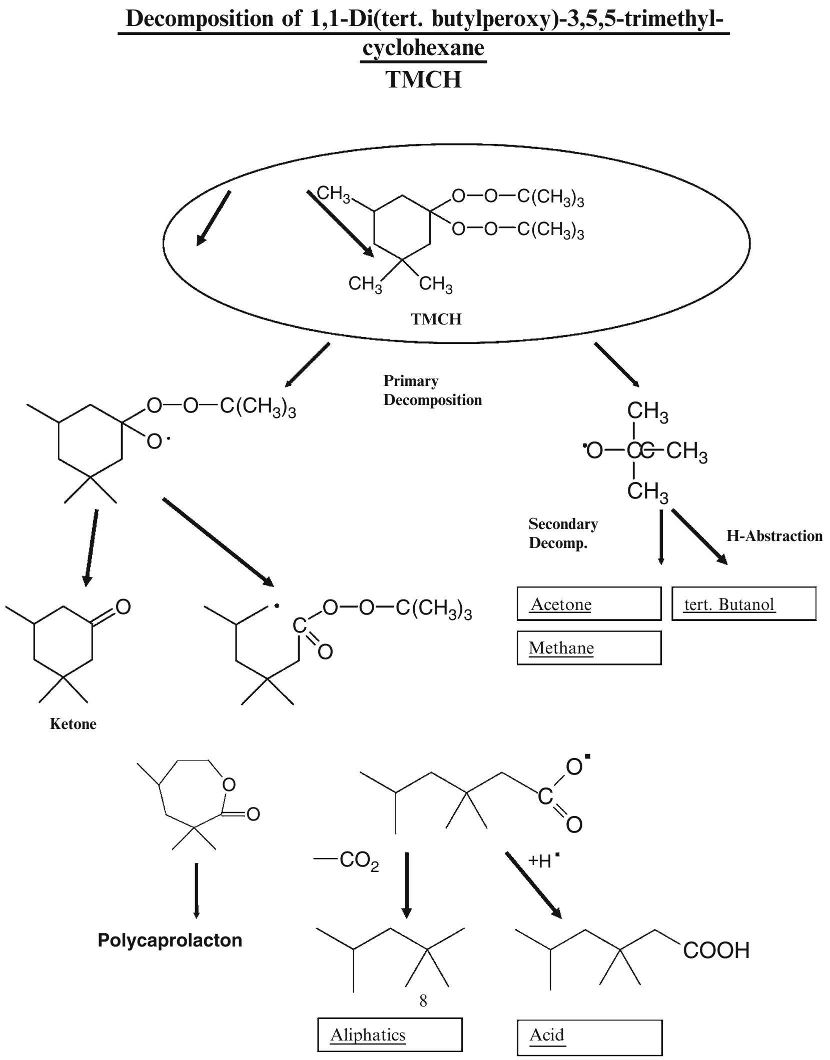


Fig. 7 Perketales

3.2 *Food Packaging*

BfR and FDA

In Germany products become registered by BfR after testing of various polymer materials to detect residuals of the products. The US FDA describes only residual decomposition products that are not to be found. Future legislation is under preparation by the European Community in this area (Table 2).

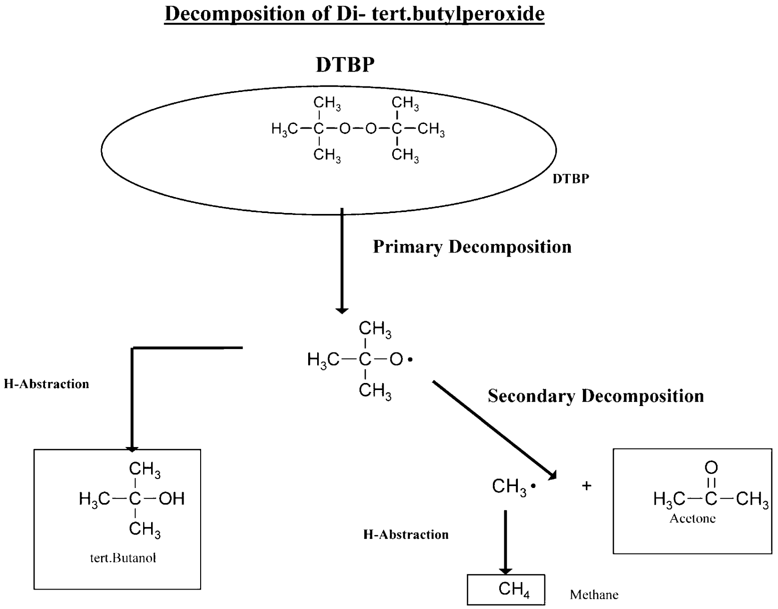


Fig. 8 Dialkylperoxides

3.3 *EINECS/ELINCS*

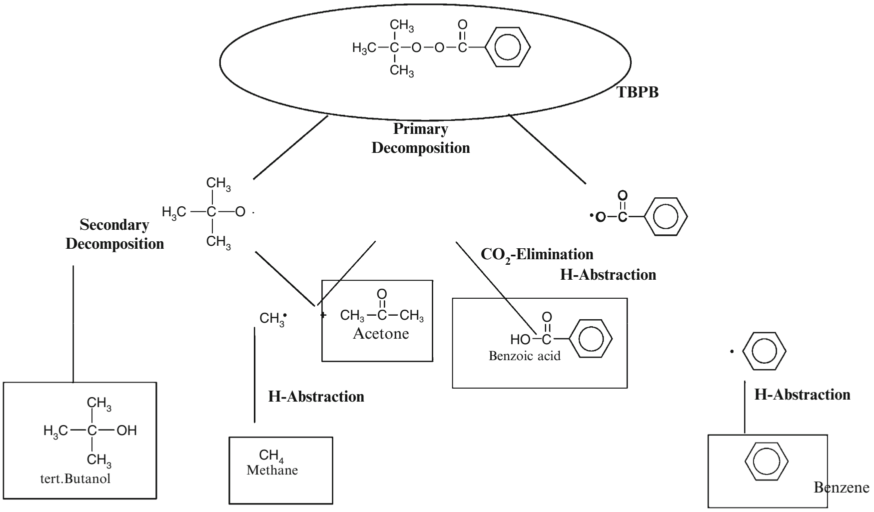
All new chemical substances undergo registration by testing of their toxic properties dependent on a certain annual volume being produced, which is quite costly and prevents a high number of new initiators. In the MSDS sheets the producer refers to the registration if pending.

4 Storage, Transport, and Packaging of Initiators

For safety reasons most liquid organic peroxides are transported as pure materials in small packs of 15–30 kg in HDPE containers (20–30 l) only. After use of the product these containers are usually disposed of. A multiple-use packaging system saves packaging material. There are companies that clean the packaging but a risk of contamination and aging of material remains. A modern concept is to use semi-bulk 1 m^3 IBCs or bulk 15–18 m^3 containers, which even have cooling systems to –15°C integrated.

Most peroxides need to be diluted to about 25–50% strength for safety reasons in appropriate solvents or be emulsified in water (Fig. 11).

Decomposition of tert. Butylperbenzoate
TBPB



Decomposition of tert. Butylperpivalate
TBPPI

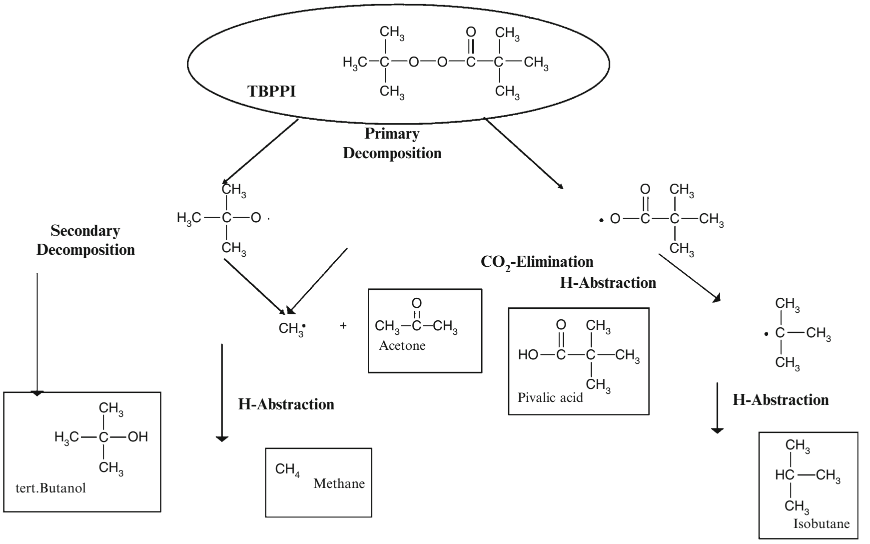


Fig. 9 Perester

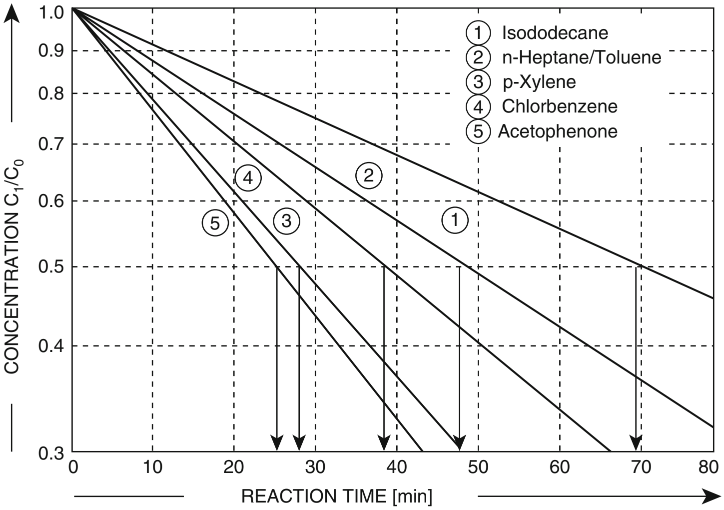


Fig. 10 Influence of initiator concentration on half-life

Table 2 Initiators in food contact

Product	FDA	BfR
DTBP	176.170, 177.2600	III, V, VI, VII, X, XII, XIV, XXXV, XXXVII, XLVI
TBHP	175.105, 176.170	III, V, VI, XII, XIV, XXXV
TBPPI	Not listed	II, III, XIV, XXII, XXXIV, XXXV
BU	Not listed	III, XII, XXII, XXXV
MEKP	1.772.420	XII
BP	133.102, 133.106, 133.111, 133.141, 133.165, 133.181, 183.195, 137.105, 172.814, 175.105, 176.170, 177.2420, 177.2600, 184.1157	II, V, VI, XII, XIV, XV, XXII, XXXIV, XXXV, XLVI
CHPC	Not listed	II, III, XXXIV, XXXV
AIBN	Not listed	II, V, VI, XXII, XXXV, L
APS	Not listed	XIV, L, LI
PAA	172.560, 172.892, 173.315, 173.370, 178.1010	XXXVI, XLVI

5 Polymerization and Processing

5.1 Vinylchloride/PVC

To avoid any contact with the dangerous chemical vinylchloride (cancerogenic) closed-reactor systems became standard and pumpable initiators for automatic dosing were preferred. These can be liquid or solvent-diluted initiators as well as emulsions in water or suspensions of solid initiators in water. The dilution is a safety element to enable proper handling in addition to the fact that most initiators need cooling to avoid decomposition (Table 3).

Fig. 11 Refrigerated bulk transport of organic peroxides

Table 3 Initiators for VC-polymerization

Peroxide	Formulation	Available oxygen [%]	Half-life time 1 h/10 h [°C]	Storage temperature [°C]
CUPND	-50-ENF/1	2.61	55/38	<−15
	-75-AL	3.92		
TOPND	-50-ENF1	2.66	57/40	<−15
	-70-AL	3.73		
EHPC	-50-ENF/1	2.31	61/48	<−15
	-60-ENF1	2.77		
	-75-AL	3.47		
BCHPC	-40-SAQ1(4)	1.61	61/47	+5 to +20
	-75-W	3.01		
CEPC	-40-SAQ1(4)	1.12	62/48	+5 to +20
MYPC	-40-SAQ	1.24	62/48	+5 to +20
TBPND	-50-ENF1	3.27	64/47	<−10
	-75-AL	4.92		
INP	-40-ENF	2.03	78/59	<−10
	-75-AL	3.81		
LP	-40-SAQ1(1) (-40-SAQ4)	1.61	80/62	+5 to +30

Some initiators tend to cause crust formation on reactor walls; such products like ACSP(acetyl-cyclohexyl-sulfonylperoxide) have been eliminated. In addition a special chemical coating is used on the reactor wall and mounted high-pressure cleaning systems are also used.

A short cycle time results in energy saving and higher productivity, but needs high-activity initiators like TOPND (*tert*.-Octylperneodecanoate) or CUPND (Cumylperneodecanoate).

Fogging is a problem especially in automotive use of PVCs. The fogging can be explained by volatile chemical compounds that could be decomposition products of certain initiators especially if they evaporate and are condensed on the cold window surface. Elimination is possible by use of long-chain low-volatility initiators, for example MYPC (Di-myristyl-peroxodicarbonate), or CEPC (Di-cetyl-peroxodicarbonate).

*5.2 Styrene/Polystyrene – BP (Dibenzoylperoxide)TBPB (tert.*Butylperbenzoate)

The most important initiator system for suspension polymerization of styrene has been BP/TBPB (dosage ~0.3 + 0.1%w/w). Upon investigation of the polystyrene it has been found that residual benzene can be detected. As both peroxides contain the benzene molecule they were both suspected. However, it was determined that BP used in the monomer-rich stage of polymerization at 90°C doesn't cause the problem. The radicals become incorporated in the polymer. The origin of the benzene was TBPB which was used to complete the polymerization reaction at 130°C and as styrene is in low concentration the benzene radical abstracts hydrogen and forms benzene. This problem has been eliminated using other initiators not containing the benzene structure, for example TBPEHC (*tert.*-Butyl-ethylhexylcarbonate).

5.3 Crosslinking of Polymers and Elastomers

5.3.1 XLPE, EPM, EPDM, EVA, Smell Problems, Blooming

Crosslinking of polyethylen and its copolymers EPM, EPDM, and EVA is mainly carried out by radicals generated from organic peroxides. Other crosslinking methods like electron-beam radiation and grafting of vinylsilanes assume a smaller role in this process.

The main crosslinker is DCUP (Dicumylperoxide), which generates acetophenone as one of the principal decomposition products. Acetophenone has a strong smell, which is not acceptable in products for human use.

A product that is suitable as a replacement for DCUP is called DIPP (Bis-*tert.* butylperoxy-isopropyl-benzene1,3/1,4). It has much less volatility and no unpleasant smelling decomposition products. The disadvantage of such a product is the slightly higher cost and reduced reaction rate (Figs. 12 and 13).

5.3.2 QM (Silicones)—The PCB Problem

The most important crosslinking agent for pressureless hot air vulcanization of silicone rubber is DClBP(Bis-2,4-dichloro-benzoyl-peroxide) (Fig. 14). It generates decomposition products, which are removed in a post-curing process with air blowing. This product provides the advantage of a fast cure rate and bubble-free cured transparent rubber.

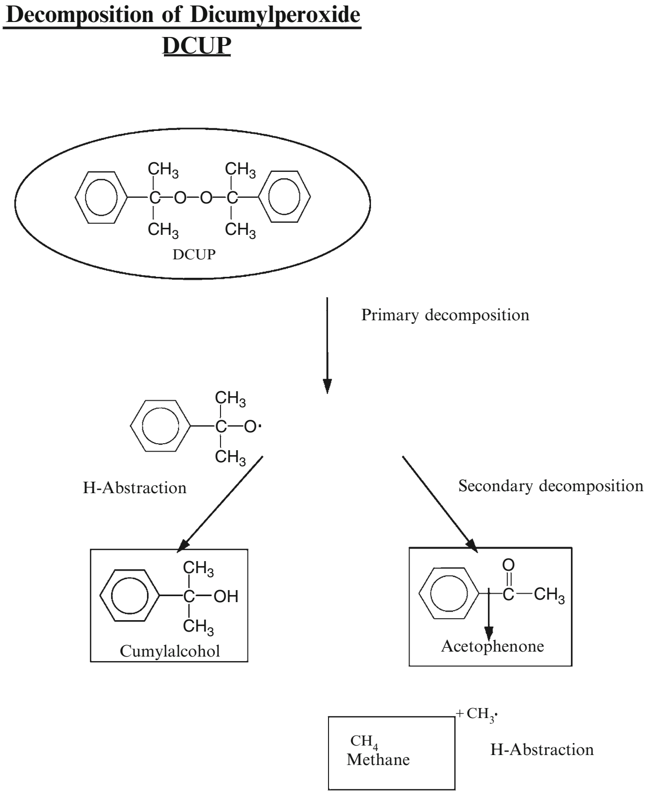


Fig. 12 Decomposition of dicumylperoxide

Its decomposition product PCB—polychlorinated biphenyl—produces an environmental problem. In some countries like Japan DClBP has already been eliminated by law. Replacement products exist, for example PMBP (Bis-4-methylbenzoylperoxide), but its reaction rate is inferior.

5.4 Curing of Unsaturated Polyester Resins

Mainly the car industry but also the food-packaging industry set high standards on emission and extractability of residuals.

5.4.1 MEKP (Methylethylketone Peroxide) Plasticizer Problem

The most important cold curing agent is MEKP, a product made from methylethylketone and hydrogen peroxide. As the pure product is very dangerous, the

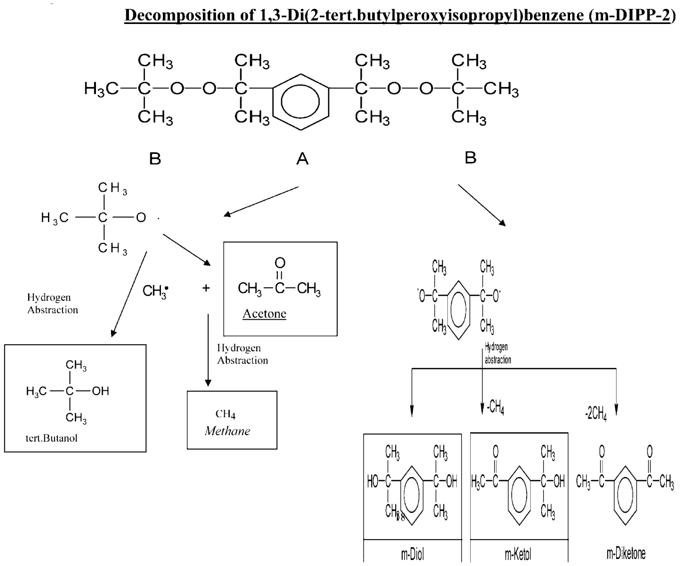


Fig. 13 Decomposition of 1,3-Di(2-*tert*.butylperoxyisopropyl)benzene (*m*-DIPP-2)

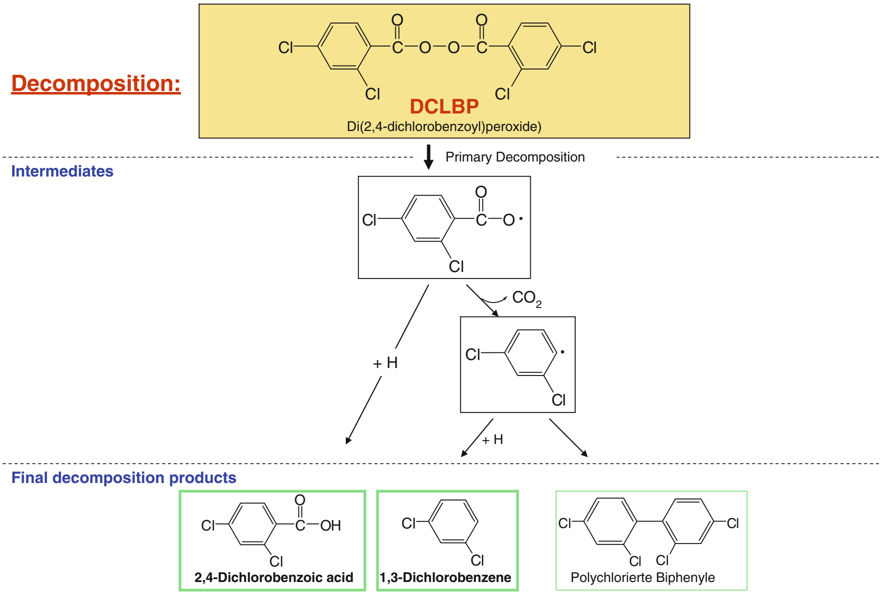


Fig. 14 DCLBP-decomposition

product commonly supplied has dilution to about 50% strength. The solvents used are from the phthalate family, which are widely discussed as an environmental problem for various reasons. Mostly these phthalates remain in the cured plastic article and should not cause problems provided they are not water soluble. Diisobutylphthalate is less water soluble than dimethylphthalate. Phthalate-free formulations have also been introduced to the market using esters like 2,2,4-trimethyl-1,3-pentyl diisobutyrate.

5.4.2 BP (Dibenzoylperoxide)TBPB (*Tert.*Butylperbenzoate)—The Benzene Problem

When these aromatic peroxides are used in thermal curing above 60°C there is a risk of formation of benzene due to excess of initiator (similar to styrene polymerization).

This problem doesn't exist for the main use of BP, which is in aromatic amine accelerated curing at ambient temperature.

5.4.3 Cobalt Metal/Aromatic Amine Accelerators

Cobalt octoate is the main accelerator for ketone peroxides and combined with toluidine amines also useful for BP and TBPB (and other peresters).

Cobalt as a heavy metal has toxic problems and aromatic amines are also suspect. The quantities used are quite small ($<1{,}000$ ppm) and remain in the plastic matrix.

The finished goods in food contact require leaching with diluted acids or use of less critical accelerators e.g., iron salts.

6 Conclusion

Initiators can be found for each application in manufacture and processing of plastic and in any temperature range requested. Modern environmental and health aspects require products that do not cause problems during manufacture, handling, and final use of the plastic materials.

Such solutions are available with the existing product range; but for some products the quantity used needs to be limited and their use avoided in certain applications. Environmental requirements will influence the future development of new initiators or formulations.

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Melt Modification of Polyamides

Dieter Lehmann

Abstract Polyamides are engineering plastics with a wide application area. The first part of this contribution deals with the degradation of polyamides including the discussion of degradation mechanism. The fast, controlled degradation reaction in the melt occurs upon addition of carboxylic acid and carboxylic anhydride compounds. Oligoamides with a defined molecular weight and a narrow molecular weight distribution could be obtained in such a fast melt modification reaction by reactive extrusion. The general degradation mechanism

$$\text{R-COOH} + \text{PA}_1\text{-CO-NH-PA}_2 \rightarrow \text{R-CO NH-PA}_2 + \text{PA}_1\text{-COOH}$$

includes “risk and chances” for reactive extrusion processes and is transferred to several polymer processing systems. By reactive extrusion new polymer materials could be obtained e.g. new graft and block copolymers. It was also possible to transfer chemical reaction into injection moulding processes to increase the bond strength in two-component injection and sandwich moulding processes or to modify the surface properties during an injection moulding process.

Keywords Block copolymers, Interface reactive injection moulding, Polyamide degradation, Polyolefine polyamide graft copolymers, PTFE polyamide materials

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Abbreviations

ε	Elongation (%)
σ	Tensile strength (MPa)
η	Intrinsic viscosity
η_{red}	Reduced viscosity of solution (dl g^{-1})
AAc	Acrylic acid
a_{cN}	Impact strength of notched specimen, 23°C (kJ m^{-2})
a_{cU}	Impact strength of unnotched specimen, 23°C (kJ m^{-2})
DMA	*N,N* dimethyl acetamide
EVA	Ethylene–vinylacetate copolymer
h	Hour
HFo	Formic acid
K_p	Boiling point
MAn	Maleic anhydride
MFI	Melt flow index [240°C/2.16 kg (g/10 min)]
$M_n^{\mathrm{theor.}}$	Calculated molecular weight based on added degradation compound
M_w/M_n	Molecular weight distribution
PA-12	Polyamide 12
PA-6	Polyamide 6
PA-6.6	Polyamide 6.6
PAAc	Polyacrylic acid
PP-gAAc	Acrylic acid grafted polypropylene
PP-gMAn	Maleic anhydride grafted polypropylene
TMAn	Trimellitic anhydride
TPEV^a	EVA-g{[5 wt%]AAc}, EVA with 5 wt% grafted PAAc (homopolymer) chains
TPEV^b	EVA-g{[5 wt%]AAc-co-[5 wt%]S}, EVA with grafted copolymer chains consisting of 5 wt% AAc and 5 wt% styrene
TPU	Thermoplastic polyurethane
wt%	Weight%

1 Introduction: Controlled Degradation of Polyamides by Carboxylic Acids and Carboxylic Anhydrides

After decreasing the research capacity in the fields of liquid crystalline and high-performance polymers at the beginning of the 1990s the emphasis in development work was placed on the improvement of commodities by special polymerisation techniques and the modification of engineering plastics. The basis of successful research was improved macromolecular and engineering know-how including analytical methods.

It is known from Xanthos [1] that the chemical modification of polymers like polymer degradation, introduction of functional groups into polymers, graft reactions and polymer formation processes can be carried out in the melt if the chemical reaction is fast enough. The formation of physical blend or graft polymer was a central question of interest when polyamides were processed with maleic anhydride or acrylic acid-grafted polymers e.g. polyolefines. Different opinions exist with regard to the activity of carboxylic anhydride and carboxylic acid groups towards amide groups in polyamide melt or during melt processing. The first case was the interaction of carboxylic acid groups with amide groups as an explanation of the compatibilisation effect. The second case was the reaction between amino end groups of polyamides and the above-mentioned functional groups [1–4]. A transamidation reaction was not described, because it was generalised from organic chemistry that carboxylic acid groups show low activity. At low temperatures, that means at the boiling temperature of acetic acid ($K_p = 118°\text{C}$) a very slow degradation of PA-6 in excess acetic acid can be observed (Fig. 1) [5].

The following results indicate that not only carboxylic anhydride but also carboxylic acid groups show very high activity during polyamide melt processing at temperatures above 230°C. The controlled degradation of thermoplastic polyamides like PA-6, PA-66, and PA-12 by carboxylic acid and carboxylic anhydride

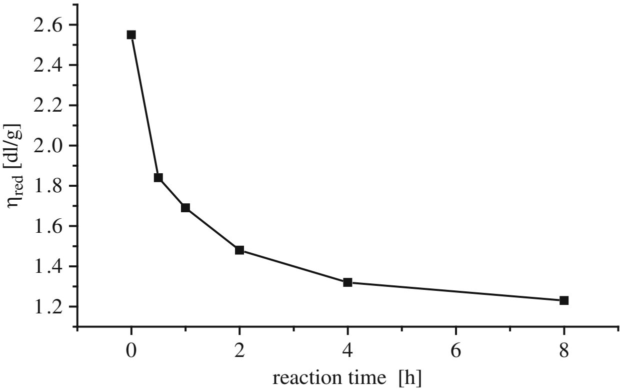


Fig. 1 Degradation of PA-6 in boiling acetic acid

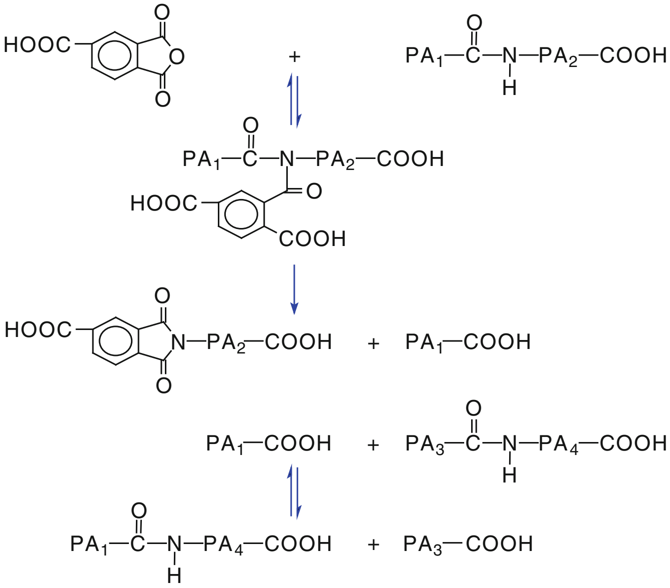


Fig. 2 Reaction mechanism of the controlled degradation of polyamides

compounds is a very fast reaction with a general chemical mechanism (Fig. 2). Adding such degradation compounds into a polyamide melt, a rapid decrease of melt viscosity can be observed after a short time.

The formed oligoamides have a defined molecular weight and show a narrow molecular weight distribution in dependence on the amount of added degradation compound. The molecular weight distribution with $M_w/M_n < 2$ demonstrates the high reaction rate during polyamide melt processing conditions independent of the nature of carboxylic anhydride or carboxylic acid degradation compound. The investigation of the water soluble content of degraded PA-6 shows about 1–3% down to a molecular weight of 5,000 $\mathrm{g\,mol^{-1}}$. Oligoamide 6 products with $M_n^{\mathrm{theor.}}$ lower than 5,000 $\mathrm{g\,mol^{-1}}$ have a higher content of soluble compounds in the water extract consisting of oligoamides, ε-Caprolactam and amino acids as detected by IR spectroscopy [6] (Fig. 3).

Identical results are received with different degradation compounds and different adding procedures (of degradation compounds), which means that if the degradation compound is added together with the polyamide as a solid substance into the melt-mixing equipment (lab mixer, twin-screw extruder) or is added into the polyamide melt during the reactive extrusion process, the same quality of oligoamides is obtained. The advantage of the reactive extrusion is the intensive mixing of the melt components with a narrow residence time. The fast transamidation reaction allows also the preparation of oligoamides with defined end group functionalities in a reactive extrusion process in residence times lower than 5 min.

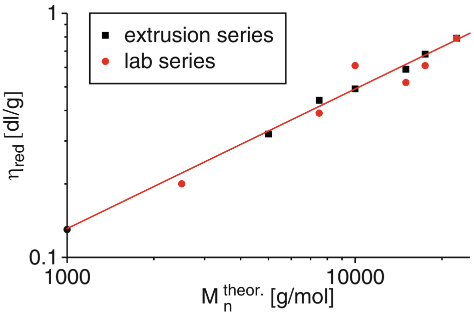


Fig. 3 η_{red}–$M_n^{theor.}$ – relation of oligoamide 6 (controlled degradation by TMAn). η_{red} in o-dichlorobenzene/o-cresol, $c = 0.2\ \mathrm{g\,dl^{-1}}$; *lab series* lab reaction in a stirred glass vessel; *extrusion series* reactive extrusion in a twin-screw extruder (ZSK 28, Werner & Pfleiderer) [5]

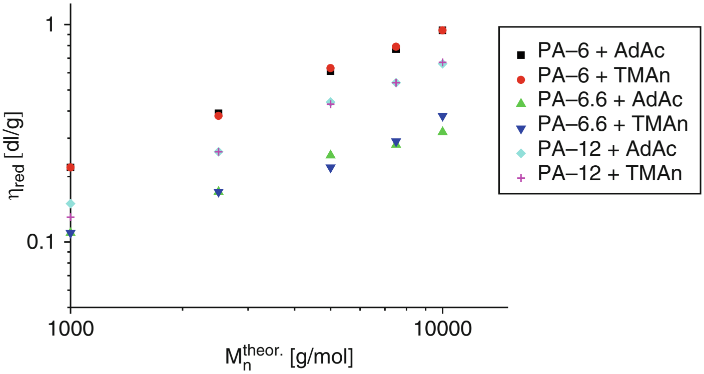


Fig. 4 Comparison of the degradation of different polyamides by adipic acid [AdAc] and trimellitic anhydride [TMAn]

The results of the controlled degradation of several polyamides by trimellitic anhydride and adipic acid demonstrate the reproducibility of the degradation reaction, as shown in Fig. 4.

A general approximation for the intrinsic viscosity $[\eta]$ for low concentrations is the reduced viscosity $\eta_{\mathrm{red}} = (\eta_{\mathrm{red}}-1)\cdot c^{-1}$, shown in (1):

$$[\eta] = \mathrm{K}\mathrm{M}^{\alpha} = \lim_{c\to 0}\,(\eta_{\mathrm{red}} - 1)\ c^{-1}. \tag{1}$$

On the basis of the results of the solution viscosity and the calculated molecular weights the following relation was established for poly-/oligoamide 6:

$$[\eta] = 2.25\cdot 10^{-3}\cdot M_{\mathrm{n}}^{\mathrm{theor.}^{0.584.}} \tag{2}$$

The stability of the molecular weight of the degraded oligoamide 6 is shown by post-condensation tests (Table 1). The base material was extruded once to examine comparable products. The molecular weight of this PA-6 increases in

Table 1 Thermal post-condensation treatment of polyamide 6 and oligoamide 6 products

$M_n^{\text{theor.}}$ (g mol^{-1})	η_{red} (dl g^{-1}) before post-condensation	η_{red} (dl g^{-1}) after post-condensation	Remarks
22,500	1.65	2.25	Base material PA-6only 1× extrusion
17,500	1.36	1.38	COOH end groups
10,000	0.93	0.93	COOH end groups
7,500	0.77	0.80	COOH end groups
5,000	0.46	0.49	COOH end groups

the post-condensation process (8 h, 180°C, nitrogen inert gas atmosphere) by a well-known solid phase condensation reaction of amino and carboxylic acid groups. The controlled degraded oligoamide 6 products after reactive extrusion do not show post-condensation behaviour under the same conditions. There are nearly no amino end groups after the degradation process which was also determined by titration.

The obtained products (oligoamides) show reduced material properties (e.g. tensile strength, impact strength) with increase of the added degradation compound, which means with lowering of the molecular weight. This effect is well known and mostly not desired. By using special functionalised degradation compounds it is also possible to insert special functionalities coupled to the polyamide.

A few publications described the degradation of polyamides in melt using a stirred vessel and a reaction time of 2 h or more [7,8]. Our results open up innovative ways for the melt modification of polyamides by reactive extrusion.

2 Stability of Polyamide 6 Against Hydrolysis During Processing

Hydrolytic stability during melt processing of polyamides is a controversial problem. All producers of polyamides demand the drying of the pellets before extrusion or injection moulding up to 0.1% and preferably to 0.05% moisture. The widely held opinion is the hydrolytic degradation of wet polyamides as a reverse reaction of the polycondensation. One mol water per polymer chain is able to lower the molecular weight rapidly, as has been shown in many chemical contributions. If the reaction of carboxylic acid or carboxylic anhydride groups with amino groups is planned, a sufficient concentration of amino groups should be present or formed in an intermediate step, e.g. by hydrolysis.

Examinations with PA-6 from different producers led to contradictory results and this formed the basis for the following investigation concerning the reason for the different hydrolytic behaviour.

Processing examinations were carried out in a twin-screw extruder ZSK 30 (Werner & Pfleiderer) with three different screw designs, different temperatures (250 and 280°C) and with dried, non-dried and wet PA-6 (Miramid SH3, Leuna AG) without any additives. As we will see later, especially active catalysts from the polycondensation reaction have a strong influence on the molecular weight during melt processing of wet PA-6 [9]. Wet conditions mean that the PA-6 pellets were stored 24 h in water. These wet pellets are processed immediately after removing the water or after a short time drying in air (see Table 3, wet*). A part of the moisture of wet PA-6 steamed out of the metering funnel which means the measured water did not quantitatively pass the extruder. At the vent zone near the dye, steam elimination could be observed as a steam engine. The amount of water could not be detected, but there was enough water/moisture for a hydrolytic degradation during processing. The starting water content was measured by a Karl-Fischer titration before processing.

The screw designs (A) and (B) were segmented like a common compounding system with one and three kneading zones behind the melting zone. The screw design (C) was a specially developed system divided into seven chambers by kneading elements/left elements behind the melting zone. The extruder processing was carried out with a semi-filled screw, which means moisture can separate during processing in the volume above the hot melt. Only in the kneading zones with the structure kneading elements/left elements of the screw with a full-filled region by polyamide melt the moisture passed through together with the melt and an intensive contact or interaction could be assumed. In other regions the moisture would come into contact only with the polyamide melt surface. The extruded materials were dried and injected into a test specimen for the determination of the material properties.

The results are shown in Table 2, 3, 4.

The results show in first approximation no significant hydrolytic degradation of PA-6 under various processing conditions if PA-6 without any active substances is processed. The characteristic values for a hydrolytic degradation are melt flow index (MFI) and η_{red} completed by the tensile strength σ_s and the impact strength a_{cN} of the notched test specimen. Only with the screw design (C) specially designed for these examinations did the wet PA-6 samples show a slight increase of MFI.

For comparison with these results, controlled degraded PA-6 samples of different molecular weights were processed and examined as shown in Table 5.

The characteristic values MFI and η_{red} show a significant degradation of PA-6 during the extrusion process after adding trimellitic anhydride and special oligoamide 6. The results are further evidence for the high activity of carboxylic anhydride and carboxylic acid compounds under polyamide melt processing

Table 2 Processing of dried, non-dried and wet polyamide 6 with screw design (A)

Processing temperature (°C)	Moisture content (%)	MFI 240°C/2.16 kg (g/10 min)	η_{red} (dl g^{-1})	σ_s (MPa)	a_{cN} (kJ m^{-2})
250	0.09 (dried)	33.7	1.60	52.8	25.0
	0.28 (non-dried)	33.3	1.48	53.8	23.3
	10.15 (wet)	33.0	1.59	53.3	23.6
280	0.09 (dried)	34.6	1.55	52.5	25.2
	0.28 (non-dried)	32.0	1.62	52.2	26.1
	10.15 (wet)	34.0	1.65	52.2	24.8

Table 3 Processing of dried, non-dried and wet polyamide 6 with screw design (B)

Processing temperature (°C)	Moisture content (%)	MFI 240°C/2.16 kg (g/10 min)	η_{red} (dl g^{-1})	σ_s (MPa)	a_{cN} (kJ m^{-2})
250	0.08 (dried)	34.4	1.65	54.3	20.6
	0.16 (non-dried)	36.3	1.65	55.0	22.5
	4.15 (wet*)	34.2	1.65	55.0	20.3
280	0.08 (dried)	36.9	1.65	53.5	19.4
	0.16 (non-dried)	35.0	1.61	53.0	22.6
	4.15 (wet*)	34.6	1.65	54.7	20.5

Table 4 Processing of dried, non-dried and wet polyamide 6 with the special screw design (C)

Processing temperature (°C)	Moisture content (%)	MFI 240°C/2.16 kg (g/10 min)	η_{red} (dl g^{-1})	σ_s (MPa)	a_{cN} (kJ m^{-2})
250	0.07 (dried)	35.8	1.70	53.1	23.6
	0.08 (non-dried)	35.0	1.67	51.9	25.1
	8.43 (wet)	38.5	1.60	52.6	23.8
280	0.07 (dried)	32.8	1.66	52.0	25.0
	0.08 (non-dried)	35.1	1.68	52.9	24.6
	8.43 (wet)	40.0	1.61	53.5	22.4

Table 5 Controlled degraded polyamide 6 by TMAn and an oligoamide 6

Degradation agent	Calculated molecular weight $M_n^{theor.}$ (g mol^{-1})	MFI 240°C/2.16 kg (g/10 min)	η_{red} (dl g^{-1})	σ_s (MPa)	a_{cN} (kJ m^{-2})
Without/base material	23,000	34	1.60		
TMAn	20,000	87	1.41	52.5	20.0
	17,500	99	1.37	52.9	15.7
	15,000	130	1.27	54.1	16.0
OA-6[5000/ 2-COOH]	18,000	87	1.40	53.2	18.5
	16,700	90	1.32	53.8	16.8

conditions as mentioned above. It is furthermore evident that controlled degraded polyamides or oligoamides can be used as a degradation agent to adapt the melt viscosity during (reactive) extrusion processing [10]. The chance or rather the advantage of the utilisation of such degraded polyamides as a degradation additive is the completely unproblematic metering as compared to the very low amounts required of low molecular weight degradation compounds like adipic acid or TMAn. It is possible to prepare special oligoamide degradation compounds for every type of polyamide.

Finally, it is necessary to explain the possible causes of the discussed hydrolysis of polyamides during processing. The following test series demonstrates one case of this phenomenon – (residues of) active catalysts from the polycondensation

Table 6 Extrusion of wet PA-6 (Miramid SH3, Leuna AG) with traces of phosphoric acid as model catalyst; processing with screw (A)

Sample	Pre-treatment of PA-6 pellets	MFI 240°C/ 2.16 kg(g/ 10 min)	η_{red}(dl g^{-1})
1	PA-6 (Miramid SH3), base material, dried,1× extrusion, reference sample	27	1.63
2	PA-6 was stored 24 h in excess water before extrusion, after removing the water, wet PA-6 was processed	30	1.58
3	PA-6 was stored 24 h in excess water + 10 ml conc. phosphoric acid (c ≈10 ml/10 l water + PA-6) before extrusion, after removing aqueous solution, wet PA-6 was processed	39	1.42
4	PA-6 was stored 24 h in excess water + 10 ml conc. phosphoric acid (c ≈10 ml/10 l water + PA-6) before extrusion, after removing aqueous solution without washing, PA-6 was dried and processed	34	1.61
5	PA-6 was stored 24 h in excess water + 10 ml conc. phosphoric acid (c ≈10 ml/10 l water + PA-6) before extrusion, after removing aqueous solution, the pellets are washed with aqueous $NaHCO_3$ solution, after washing wet PA-6 was processed	29	1.61
6	PA-6 was stored 24 h in excess water + 10 ml conc. phosphoric acid (c ≈10 ml/10 l water + PA-6) before extrusion, after removing aqueous solution, the pellets are washed with a solution of 10 l water + 100 g $NaHCO_3$, after washing PA-6 was dried and processed	29	1.61
7	PA-6 was stored 24 h in excess water + 100 ml conc. phosphoric acid (c ≈100 ml H_3PO_4/10 l water + PA-6) before extrusion, after removing aqueous solution, wet PA-6 was processed	62	1.52
8	PA-6 was stored 24 h in excess water + 10 ml conc. phosphoric acid (c ≈100 ml H_3PO_4/10 l water + PA-6) before extrusion, after removing aqueous solution, the pellets were treated 10 min with pure water, after removing the water, wet PA-6 was processed	64	1.33
9	PA-6 was stored 24 h in excess water + 10 ml conc. phosphoric acid (c ≈100 ml H_3PO_4/10 l water + PA-6) before extrusion, after removing aqueous solution, the pellets were washed with a solution of 10 l water + 500 g $NaHCO_3$, after removing the aqueous solution, wet PA-6 was processed	31	1.65

process or additives with acidic groups. The used PA-6 (Miramid SH3) has no active catalyst. The PA-6 was stored for 24 h in water, the water was removed and the pellets were processed without drying.

Table 6 shows the effect of traces of mineral acid concerning the hydrolytic behaviour of PA-6 during processing. Active mineral acids catalyse the hydrolysis. It is assumed for sample 4 and 8 that during the water treatment, traces of phosphoric acid were absorbed by PA-6, which then became active during processing. If bases ($NaHCO_3$) were added for neutralisation and deactivation of the acid catalyst before extrusion, almost the MFI and η_{red} values of the starting material were observed after processing.

The examination shows that wet PA-6 without active catalysts or catalytically active additives can be processed by extrusion as wet material with water contents higher than 4%. The amide bonds have a high resistance against hydrolysis in the short residence time of the compounding processes. If active mineral acids, traces of active catalysts or additives with active catalytic groups are present during processing, then the polyamide materials have to be used as pre-dried products. Another possibility is to add a neutralising agent for the deactivation of such active groups.

This result could not be transferred to injection moulding processes because wet materials lower the surface quality of the component parts.

The above-described results demonstrate that several publications with postulated hydrolytic degradation steps during reactive extrusion processes should be evaluated critically. Not only amino groups can react with anhydride groups and carboxylic acid groups. The transamidation reaction of carboxylic acids with amide groups is a very fast reaction under polyamide melt processing conditions similar to the reaction of carboxylic anhydride with amide groups. These reactions are much faster than the hydrolytic degradation. Therefore mechanisms in which the first step is the formation of amino groups by hydrolysis, followed by the second reaction as a bond-forming process are often postulated – examples are reported in [1,11].

3 Formation of Polyolefine Polyamide 6 Graft Copolymers

Examination and knowledge of the actual reaction mechanism during melt processing form the basis for the development of new materials and innovative technologies and could be used for process optimisation. On the basis of the degradation of polyamides by low molecular degradation compounds the mechanism was transferred to polymer degradation compounds with carboxylic anhydride and carboxylic acid groups. The incompatibility of polymers like polyolefines and polyamides are often problematic. Melt-mixing equipment has to be used to realise the interaction of the functional groups and following the chemical reaction.

Maleic anhydride and acrylic acid-grafted polyolefines are used as well-known compatibilising agents in blend processing with polyamides. No publication overview shall be given here – but a discussion of published mechanisms. The mainly discussed and published coupling mechanism is the reaction of amino end groups of polyamide with the grafted anhydride or acid groups [1–4]. A widely used technology to lower the colouring tendency of polyamides during melt processing is the blocking/capping of amino end groups e.g. by acylation; that means, the concentration of active amino groups for a coupling reaction is decreased. The question whether polyamides without amino end groups can be used for coupling reactions with polymers functionalised by carboxylic acid or anhydride groups has to be

Table 7 Solubility of PA-6/EVA and PA-6

Sample	PA-6 content (wt%)	EVA/TPEV content (wt%)	Remarks – solution behaviour
PA-Ex 1	80	20 (EVA)	EVA non-modified, physical blend;dissolves in HFo very fast with a quantitative separation into the pure polymers, PA solved and EVA solid powder sediment
PA-Ex 2	90	10 (TPEV[a])	Gel particles in HFo solution without a phase separation, gelic solution
PA-Ex 3	80	20 (TPEV[a])	Gelic HFo solution without phase separation, pellets swell very slowly after days to such a gelic system
PA-Ex 4	70	30 (TPEV[a])	Pellets after days in HFo unchanged (phase inversion with a EVA surface)
PA-Ex 5	90	10 (TPEV[b])	Behaviour like PA-Ex 3, no phase separation
PA-Ex 6	80	20 (TPEV[b])	Only swollen pellets in HFo, pellet structure could be observed
PA-Ex 7	70	30 (TPEV[b])	Behaviour like PA-Ex 6, but swelling degree is lower

Table 8 PA-6/EVA or PA-6/TPEV blend compositions for quantitative separation

Sample	Blend composition for quantitative separation(all samples contain 80 wt% PA-6)
PA-Ex 8	20 wt% EVA (non-modified), physical blend for comparison
PA-Ex 9	13 wt% EVA (non-modified as diluent)+7 wt% TPEV[c]
PA-Ex 10	20 wt% TPEV[c]
PA-Ex 11	20 wt% TPEV[a]

answered with yes – a coupling reaction takes place by the transamidation reaction. Carboxylic anhydrides and carboxylic acids both react – besides the reaction with amino groups – also with amide groups. After melt processing of such polymer systems graft copolymers could be detected as will be shown in the following [12].

Published results mainly deal with material properties, changes in material and rheological properties and morphological phenomena. The formation of copolymers consisting of polyolefine-grafted polyamide chains can be detected by IR spectroscopy. First results from an investigation on the quantitative chemical separation are published in [12]. After processing of acrylic acid-grafted ethylene–vinylacetate copolymer with PA-6 by reactive extrusion in a twin-screw extruder the products in Table 7 were examined for their solution behaviour.

The physical blend dissolves and separates very fast. The reactive blended products did not show a phase separation. After these pre-examinations several blends shown in Table 8 were separated quantitatively. This proved to be very difficult and time-consuming work.

These results demonstrate the chemical linkage between TPEV and PA-6 by graft polymer formation during the reactive extrusion process (Fig. 5).

The physical blend could be separated into pure polymers as shown by IR spectroscopy. With increase of the TPEV content or even better by increasing the

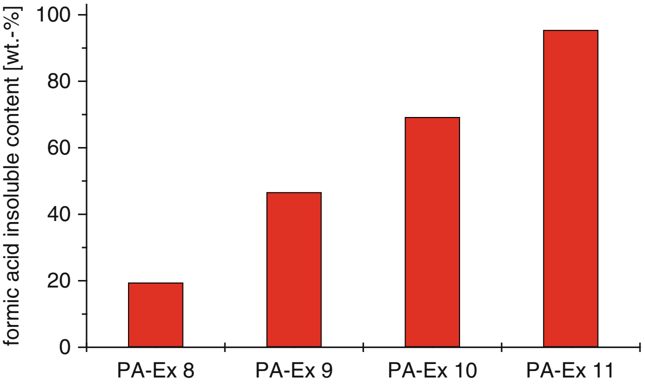


Fig. 5 Insoluble contents of PA-6/EVA and PA-6/TPEV blends after separation of the formic acid soluble PA-6 contents

Table 9 Material properties of polypropylene and polyamide 6 blends after reactive extrusion

Sample	σ_S(MPa)	ε_S(%)	σ_R(MPa)	ε_R(%)	E_t(MPa)	a_{cU}(kJ m^{-2})	a_{cN}(kJ m^{-2})
E 0	25.7	12	11.9	331	1,060	178.7	4.6
E 5	23.6	12	10.3	395	848	103.2	4.3
E 10	24.3	12	14.1	490	885	179.4	4.4
E 20	24.9	11	19.9	526	950	198.1	5.0
E 30	26.0	11	21.2	454	996	208.1	6.0
S 0	37.0	6.7	31.1	22.4	1,870	51.2	4.6
S 5	37.3	6.9	36.0	9.7	1,850	43.5	3.4
S 10	37.3	6.1	36.3	8.3	1,830	48.6	3.3
S 20	37.9	5.7	35.9	9.6	1,840	46.5	3.3
S 30	41.7	4.6	39.8	7.3	2,180	48.1	3.3

concentration of grafted acrylic acid in the reaction system, an increase of the formic acid insoluble content was observed. PA-6 is very well soluble in formic acid. The insoluble content consisted of EVA and grafted polyamide as was detected by IR spectroscopy. Sample PA-Ex 11 with a composition of 20 wt% TPEV and 80 wt% PA-6 is nearly insoluble. These results demonstrate the possibility of the transfer of a reaction mechanism for polymer degradation to the development of new materials from well-known commercial products by reactive extrusion.

The problem of physical blends is not only the formation of a stable morphology. A more important problem for the users of such materials is the changing and most often the lowering of material properties. Table 9 [13] lists the effect of the reactive compatibilisation of polypropylene PA-6 blends of different compositions:

E0	100 wt% PP-gMAn
E5	95 wt% PP-gMAn + 5 wt% PP-6
E10	90 wt% PP-gMAn + 10 wt% PP-6
E20	80 wt% PP-gMAn + 20 wt% PP-6

E30	70 wt% PP-gMAn + 30 wt% PP-6
S0	100 wt% PP-gAAc
S5	95 wt% PP- gAAc + 5 wt% PP-6
S10	90 wt% PP- gAAc + 10 wt% PP-6
S20	80 wt% PP- gAAc + 20 wt% PP-6
S30	70 wt% PP- gAAc + 30 wt% PP-6

The reactive compatibilisation between PP and PA-6 retain the material properties of the starting material PP without lowering the properties with increasing PA-6 content. Sometimes a slight improvement could be observed.

4 Polyamide Block Copolymers: Formation and Properties

By a similar degradation and graft copolymer formation mechanism block copolymers could be obtained by reactive extrusion. A prerequisite is the presence of functional groups and the interaction of these groups with immiscible polymers during melt processing. Several polyamide block copolymers are synthesised by a melt-modification process.

To improve the miscibility of polymer systems, a well-known method is to add compatibilisers or to form compatibilising compounds during processing. These substances are located in the interface layer and improve the blend morphology and the material properties.

The chemical structure of polyamides and polyester involves only few chances for a reactive compatibilisation during melt processing with short residence times [14]. Controlled degraded polyamides could be used in a three-step extrusion process to form compatibilised polyester polyamide blends. After degradation and functionalisation of the polyamide with increase of the carboxylic acid concentration (see Chap. 1) a transesterification reaction was carried out in the melt. The carboxylic acid groups of the polyamide block react with the ester bond of the polyester with a low reaction rate. The gross reaction rate depends on the processing temperature and the quality of mixing the immiscible polymers. A low molecular block copolymer was formed as has been shown by ^{1}H- and ^{13}C-NMR investigations. To improve the material properties the terminal groups of these block copolyesteramides were condensed by adding special substances like diisocyanates, diurethanes or bisoxazolines to high molecular weight polymers. The increase of the molecular weight occurs in both phases through formation of strong chemical bonds between the blend components. Further investigation on process optimisation showed that this three-step process could be condensed to a one-step process [15]. The degradation and transesterification steps are carried out in the first part of the reactive extrusion. The first results regarding the material properties of the blends demonstrate a successful increase of the characteristic values. This one-step process is a very interesting method for the recycling of mixed PET/PA post-consumer waste.

Another example of a reactive compatibilisation during melt processing is the formation of polyarylether polyamide blends. Used polyarylethers (e.g. polysulfone and polyethersulfone) were synthesised with functional groups (pendant carboxylic acid and carboxylic anhydride groups, terminal carboxylic anhydride groups). By an in situ reaction of functionalised polyarylether with polyamide in the melt the compatibility of these immiscible polymers was improved by copolymer formation causing a change in the morphology and the improvement of the mechanical properties of such reactive blended materials [16].

The reactive blending of PA-6 and polycarbonate and especially the effects of PA-6 terminal groups was described in [17]. Amino end groups show a very high reactivity in contrast to carboxylic acid groups. Terminal carboxylic acid groups do not react significantly with polycarbonates – as it turned out in the examinations. Similar to the block copolyesteramide formation [14] controlled degraded polyamides could be used for the synthesis of polyamide polycarbonate block copolymers [18].

The gross reaction rate of carboxylic acid groups with polyester and polycarbonate materials is low compared to the reaction rate of amino groups, but it is fast enough to form block copolymers by reactive extrusion as shown by GPC. With the beginning of the block copolymer formation of these immiscible polymers in the melt this compatibilisation effect improves increasingly the mixing quality of the blend components thus causing a continuous increase of the gross reaction rate. This complex reaction system under melt processing conditions is very difficult to describe. The reaction rate during the reactive blending is strongly influenced by the reaction and processing conditions (concentration of carboxylic acid groups, temperature, mixing quality).

Such final block copolymer products are described and used as compatibilised chain extender additives for the modification of melt viscosity of polyamides during compounding by reactive extrusion [10] (Fig. 6).

The chain extension modifier reacts completely already in the first processing step based on optimised additive properties. The melt viscosity increases to a high level after the first processing step and decreases just parallel to the standard polyamide later on (Fig. 7). For practical applications most additives could never be used without problems in reproducibility and uncontrollable cross-linking reactions because these compounds have a too high activity and the reaction rate is faster than the proper additive distribution in the melt. Therefore, the practical value of these commercial additives was limited and still is. With a lowering of the reaction rate and improvement of the distribution properties during reactive extrusion a controlled polyamide chain extension could be realised. The attained levels of melt viscosity are quite stable also under multi-extrusion conditions.

A highlight of the reactive compatibilisation of extremely incompatible polymers is the chemical bonding between the anti-adhesive PTFE and the polar polyamides. It had been assumed for a long time that a chemical bonding between PTFE and polyamide is impossible because there was no appropriate reaction mechanism. PTFE is a highly crystalline polymer which could only be processed by using special equipment. The utilisation in tribological systems is a well-known

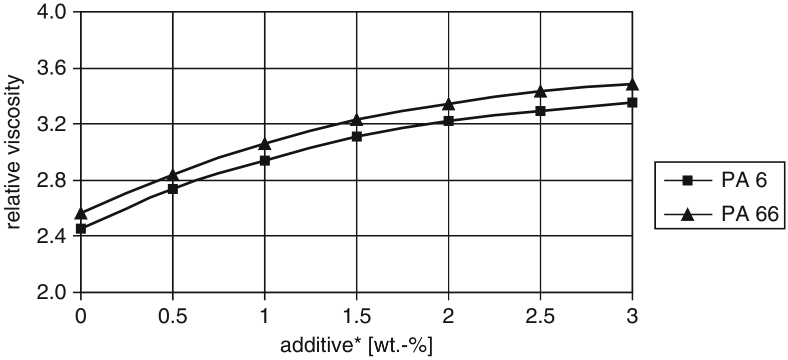


Fig. 6 Increase of relative viscosity of PA 6 and PA 66 depending on the added amount of chain extender BRÜGGOLEN® M 1251[10]

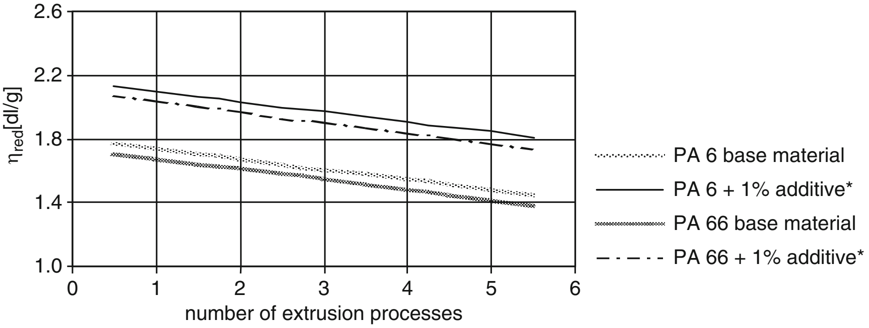


Fig. 7 Effect of multiple processing on reduced viscosity of PA 6 and PA 66. Additive* ... BRUGGOLEN® M 1251 (Copolycarbonateamide) [10]

field of application. It is also well known that PTFE decomposes by means of high-energy irradiation [19,20]. Commercial PTFE micropowders modified with carboxylic acid groups are obtained by electron-beam irradiation of PTFE in the presence of oxygen. The generated carbonyl fluoride groups are transferred into carboxylic acid groups by hydrolysis post-treatment (e.g. ZONYL MP 1100, DuPont).

The use of modified PTFE micropowder in combination with the mechanism of the controlled degradation of polyamide and the utilisation of melt-mixing devices like a lab melt mixer or twin-screw extruders are the basis of the reactive compatibilisation of the completely immiscible polymers. On the basis of the discussed mechanism PTFE polyamide block copolymers are formed by reactive extrusion:

Reaction mechanism of PTFE polyamide block copolymer formation by transamidation

$$\begin{aligned}\text{PTFE-COOH} + \text{R-[PA}_1\text{]-CO-NH-[PA}_2\text{]} \rightarrow\ & \text{PTFE-CO-NH-[PA}_2\text{]} \\ & + \text{R-[PA}_1\text{]-COOH}\end{aligned}$$

R = H_2N- and/or Ac-NH-; $PA_{1,\ 2}$ polyamide chain segments.

In order to form PTFE polyamide block copolymers high shear rates are necessary under melt processing conditions, to receive a good distribution and a further break down of PTFE micropowder particles. The particle size of the added PTFE micropowder is in the order of 2–8 µm. The crucial point for a successful coupling reaction is the contact between the carboxylic acid groups on the surface of the PTFE microcrystals and the amide groups of the molten polyamide matrix. As a result, a very homogeneous distribution of PTFE in the PA matrix is observed after reactive extrusion [21–23].

Upon dissolution of physical mixtures (blends) of PTFE micropowders (without carboxylic acid groups) and PA-6 in formic acid, pure PTFE separates very fast from the solution. If the new melt-modified PTFE polyamide materials (PTFE irradiated: 2,000 kGy) are dissolved in formic acid, the separation is very difficult. After separation of the insoluble content by centrifugation and elimination of the soluble pure polyamide, the presence of an amide bond $\boldsymbol{R_f}$**-CF_2-CO-NH-CH_2-PA*** between the PTFE and e.g. PA-6 was proved by IR spectroscopic investigations. The 1,708-cm^{-1} band in the IR difference spectrum (Fig. 8 blue line) deriving from the direct PTFE polyamide linkage was in agreement with the IR spectra of low molecular model substances.

No IR absorption bands of R_f-COOH and R_f-CO-F are detectable in IR spectra of the PTFE PA-6 product after reactive extrusion. Additionally, spectra of an unirradiated PTFE (black line) and an irradiated PTFE (1,000 kGy) (red line) are shown for comparison in Fig. 8. All spectra were normalised to the CF_2 band at 2,365 cm^{-1}. IR spectroscopy can be used for the determination of the turnover of carboxylic acid groups after reactive extrusion.

Another interesting phenomenon – the fractionated crystallisation of PTFE – could be observed by DSC. PTFE melts near 325°C and crystallises near 310°C. The crystallisation behaviour of the dispersed PTFE phase in a PA matrix is influenced by the melt viscosity of the polyamide matrix, the processing conditions in twin-screw extruders and the irradiation dose of PTFE. With increasing

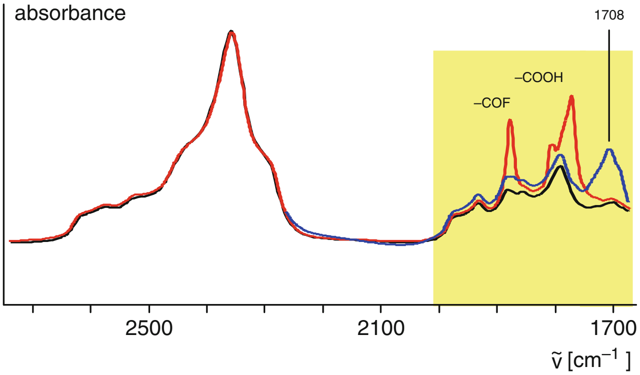


Fig. 8 IR spectra – evidence of the chemical coupling between PTFE and polyamide 6

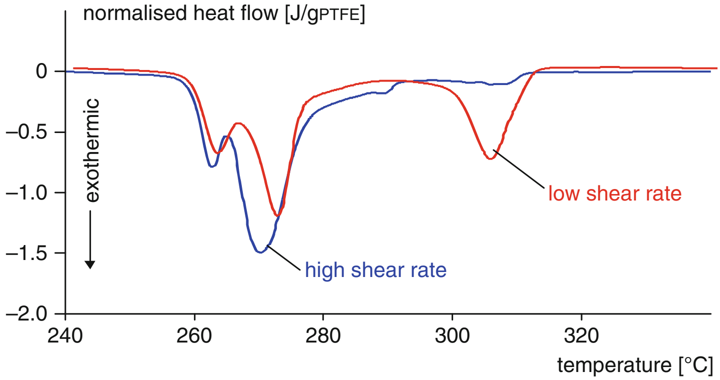


Fig. 9 Influence of the shear rate during the extrusion on the crystallisation behaviour of the PTFE phase

irradiation dose in the presence of oxygen, the concentration of generated carboxylic acid groups of PTFE as the basis for the chemical bonding between PTFE and polyamide increases. With decomposition of PTFE the melting as well as the crystallisation point decreases.

Figure 9 shows DSC-curves of PTFE PA-6 materials of the same composition but produced under different processing conditions (two different screw designs). With increasing shear rate the intensity of the peak for bulk crystallisation (310°C) decreases and the intensity of the peak for fractionated crystallisation (260°C) increases. Furthermore, DSC and SEM investigations have shown that the particle size of the dispersed PTFE component depends on the shear rate during processing. In this way, the degree of the fractionated crystallisation is a helpful tool for the estimation of the efficiency of the in situ reaction causing the compatibilisation of the blend components.

It was found that the degree of the fractionated crystallisation grows with the increase of the melt viscosity, shear rate and radiation dose. Electron microscopy and AFM investigations indicate that the added PTFE micropowders are reduced in size to very small particles.

WAXS investigations of irradiated PTFE and PTFE PA-6 materials after melt processing show that the crystallinity of PTFE samples does not change. A change in PA-6 crystallinity was observed after processing with the irradiated PTFE. With increasing shear rate during the melt processing a lowering of the PA-6 crystallinity was detected.

The material properties of the reactive-processed PTFE-PA-6 products show a very surprising behaviour caused by the chemical coupling of the incompatible polymers. The tensile strength of PTFE-PA compounds obtained by reactive coupling decreases when increasing the added PTFE content to a lower degree than comparable physical blends. The E modulus is nearly constant although with PTFE a soft material was added.

Table 10 Notched impact test of PTFE polyamide 6 materials in dependence on irradiation dose

Material	PTFE (500 kGy) a_{cN} (kJ m^{-2})	PTFE (1,000 kGy) a_{cN} (kJ m^{-2})	PTFE (4,000 kGy) a_{cN} (kJ m^{-2})
PA-6 base material	(25.0*)		
PA-6+7.5 wt% PTFE	21.7	33.2	107
PA-6+15 wt% PTFE	17.1	40.7	133
PA-6+30 wt% PTFE	12.0	119	127

With increasing PTFE micropowder content, irradiated with 500 kGy, the value of the impact strength of the notched test specimen a_{cN} decreases (Table 10). With addition of PTFE with a higher irradiation degree, a rapid increase of the value could be observed. The material properties are strongly influenced by irradiation dose and processing conditions. These phenomena are also an indication of the chemical coupling between PTFE and polyamide. The PTFE segment in the PTFE PA-6 block copolymer irradiated by 4,000 kGy acts like an impact modifier.

The melt flow index of PTFE-PA-6 materials decreases with increasing amount of added PTFE micropowder but the MFI also demonstrates the processability of such compounds.

These new PTFE-PA materials can be processed without any problems on commercial processing equipment like twin-screw extruders and injection-moulding machines. The specific adjustment of the melt viscosity could be realised through additives (lowering of MFI: additive [10,18]; increase of MFI: acid-terminated oligoamides [9,10]). The new materials combine the good material properties of PTFE and polyamide with the processability of polyamide and are particularly well-suited for wear-resistant maintenance-free bearings.

The tribological investigation of the chemically bonded PTFE-PA materials shows that besides the low friction coefficients the high wear resistance is the most important property of such products. Examinations with several different PTFE polyamide materials certify this predicate. This phenomenon could be explained by the chemical coupling of the PTFE distributed in PA. The compatibilisation of PTFE by “block copolymer” formation causes a better connection to the PA matrix as compared to physical blends.

Interesting results are obtained by atomic force microscopy (AFM, adhesive mode) after tribological wear and tear tests like the disc on wheel system. The surfaces of the disc and also the wheel were investigated by adhesive mode to determine the influence of PTFE.

As seen in Fig. 10 the steel surface of the wheel is modified by PTFE-PA material. The surface morphology is the same as the disc surface (used the PTFE-PA-6 test specimen). The examined PTFE PA-6 material consisting of 15-wt% PTFE micropowder (= 8.1 vol%) has only a small volume content but the AFM picture shows nearly 50% of the area of low adhesion. This means a surface modification takes place during tribological application. PTFE particles are degraded, removed and distributed on the surface by wear and tear and fixated on PA

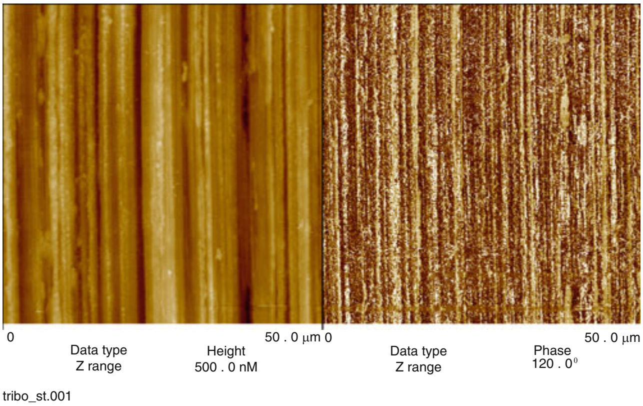


Fig. 10 Atomic force micrograph (adhesive mode) – surface examination after wear and tear of PTFE polyamide 6 compound (wheel surface). *Tribological system* disc on wheel; *light* low adhesion; *dark* high adhesion

rich areas by anchorage with chemically bonded polyamide chains of the PTFE. A higher concentration of PTFE is observed at the surface than added.

The tribological investigation of the chemically bonded PTFE-PA materials shows that besides the low friction coefficients the high wear resistance is the most important property of such products. Examinations with several different PTFE polyamide materials certify this predicate [21–23].

5 Interface Reactive Injection Moulding

PUR-RIM and PA-RIM are reactive polymer formation processes with reactive low molecular starting materials. The interface reactive injection moulding is not comparable to these RIM processes – these processes are an independent development. The aim is the improvement of interface or surface properties of commercial plastics by utilising injection-moulding machines as a “reactor system” similar to reactive extrusion with the melt energy to activate fast chemical reactions. The application of chemical reactions in injection moulding processes has not been described so far and it was doubted by chemists and engineers that this would be possible. Chemical reactions are mostly carried out in dilute solution over several hours – such short time reactions seemed to be impossible. The reason was that nobody estimated or even took proper notice of the processing conditions. Melt modification reactions take place in the melt, i.e. in a highly concentrated system at melt temperatures mostly above 200°C. These are optimal conditions for very fast chemical reactions (shown by reactive extrusion processes) which are necessary to create chemical bonds between different materials or for a surface modification.

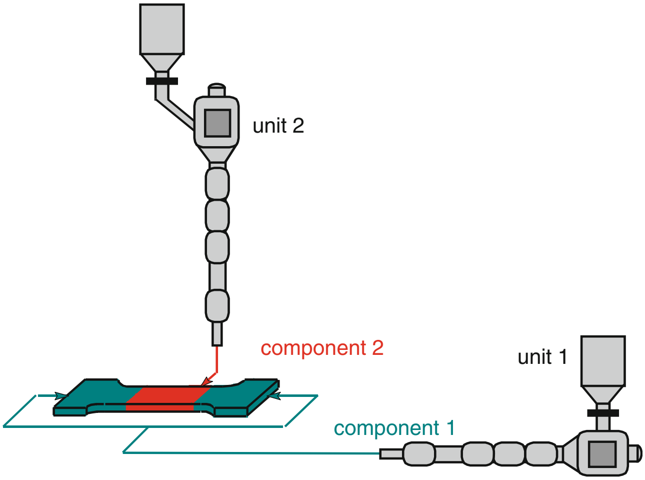


Fig. 11 Two-component injection moulding (formation of test specimen with two boundary layers/interfaces)

Table 11 Combination of polyamides – composite strength depending on PA-6 modification

Sample	Material	Unit	Boundary layer	s (MPa)
H3022	PA-6	1	Smooth	11.9
	PA-6 $T_m = 250°C$	2		
H3027	PA-66	1	Smooth	12.8
	PA-66 $T_m = 275°C$	2		
H3012	PA-6	1	Smooth	11.2
	PA-66 $T_m = 275°C$	2		
H3025	PA-6 mod.	1	Smooth	22.6
	PA-66 $T_m = 275°C$	2		
H3013	PA-66	1	Smooth	no connection
	PA-6 $T_m = 250°C$	2		
H3028	PA-66	1	Smooth	16.6
	PA-6 mod. $T_m = 250°C$	2		

The first results of degradation of polyamides shown above are based on fast melt modification reactions. The determination of the gross kinetical reaction rate was impossible. Only a very vague estimation could be made during reactive extrusion processes.

The first results of an interface reactive injection moulding by two-component injection moulding (Fig. 11) are listed in Table 11.

It is shown that the composite adhesion or bond quality is dependent on the PA-6 modification as examined by tensile test. The processing parameters are not optimised to obtain the highest values for the tensile strength. The aim of this investigation was the determination of the influence of the increase of carboxylic acid concentration in modified PA-6 during the two-component injection moulding processing at comparable conditions.

The injection of the polymer of unit 2 with a higher melt temperature than the melting range temperature of the solidified material 1 (unit 1, shoulder parts) causes a thin sheet of molten material 1 in the interface region and a possible interdiffusion could increase the composite adhesion (pure substances: samples H3022, H3027; mixed polyamides: samples H3012, H3025). Chemical reactions could not be excluded as shown by H3025 in which the tensile strength values are two times higher than for H3012. If the melt temperature of material 2 (unit 2) is lower than the melting temperature of the solidified material 1 no interdiffusion is possible as shown by sample H3013 – no connection could be observed. With use of the modified PA-6 after the controlled degradation to a molecular weight of $M_n^{\text{theor.}} = 15{,}000\ \text{g mol}^{-1}$ and a much higher concentration of carboxylic acid end groups a better adhesion could be observed than with the samples of pure polyamides (H3022 and H3027) or H3012. The adhesion of sample H3028 could be explained only by very fast chemical reactions – the transamidation reactions discussed above – in the interface region and the very high value of sample H3025 demonstrates the additional effect of interdiffusion and chemical reaction. These results are useful for the estimation and give evidence for very fast melt modification reactions.

These results formed the basis for the developments detailed below.

5.1 Interface Reactive Two-Component Injection Moulding (Core-Back Process)

This special process was first developed for the increase of the bond strength of hard–soft composites by interfacial connections via chemical bonds in the system polyamide TPU (thermoplastic polyurethane) [24–30]. The TPU component was modified by reactive extrusion with the addition of diisocyanate compounds. It was found that with the addition of up to 5 wt% no free diisocyanate could be detected and that no increase of the melt viscosity or network formation was observed. The added diisocyanate could not be detected as free compound after melt processing or after injection moulding. The very active isocyanate groups are reactivated during the injection moulding process in the melt. A two-component test specimen was formed and the bond strength was examined by tensile test. The first component was the hard material polyamide forming the shoulder parts – the second component was the pure or the activated TPU (see Fig. 11).

The aim of the investigation was the estimation of the influence of chemical and processing conditions on the bond strength by chemical reactions during interface formation. Besides the connection by adhesion and interdiffusion processes the controlled initiation of chemical bonds for an improvement of the bond strength was used for the first time in a two-component injection moulding process. An increase in bond strength to 150% and higher not depending on the type of TPU

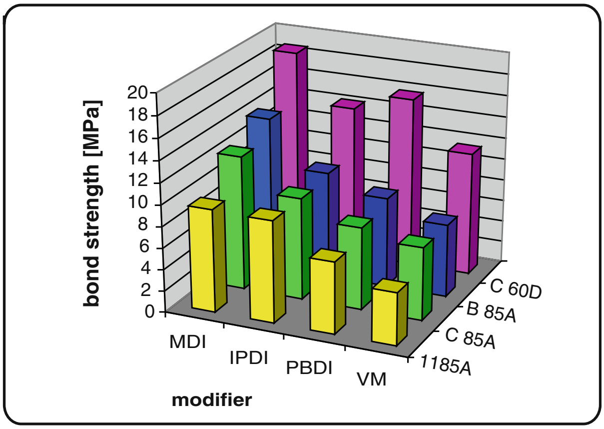


Fig. 12 Interface reactive two-component injection moulding – bond strength in dependence on the type of diisocyanate and TPU elastomer. Bond strength between PA-6/TPU. *PA-6* Ultramid B3S; *TPU* Elastollan 1185A, Elastollan B 85A, Elastollan C 85A, Elastollan C 60D. Modifiers: diisocyanates: MDI, IPDI, IPDI-Uretdion, PBDI, Oligomer-TDI-DI. Addition of 1 up to 5 wt%; *VM* virgin/base material

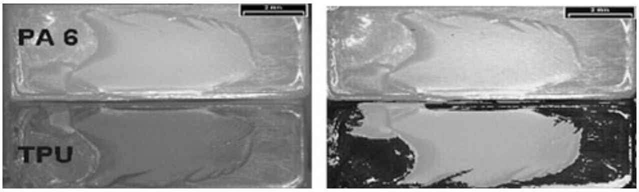


Fig. 13 Interface reactive two-component injection moulding – image of fractured specimen after tensile test, polyamide bulk material on the TPU fracture surface (right – fracture with coloured TPU part for differentiation)

elastomer and diisocyanate used (Fig. 12) could be shown. A tensile test showed that the interface is not a weak spot. The fracture was located in the bulk region in the vicinity of the interface. With additional chemical bonds the interface bond strength was so high that bulk material was pulled out (Fig. 13).

The mechanism was discussed based on extensive analytical examinations [27,29]. Not only are polyamide residues observed on the TPU fracture surface, TPU residues are also detected on the polyamide surface after removal of the soluble TPU residues by DMA (Fig. 14). The presence of insoluble or connected TPU residues can only be explained by chemical bonds.

The influence of the processing parameters on the bond strength was described in [28]. The consequences of polyamide modification by different terminal groups were discussed in [30].

A further example of improvement of the bond strength by chemical coupling can be observed upon the combination of chemically bonded PTFE polyamide

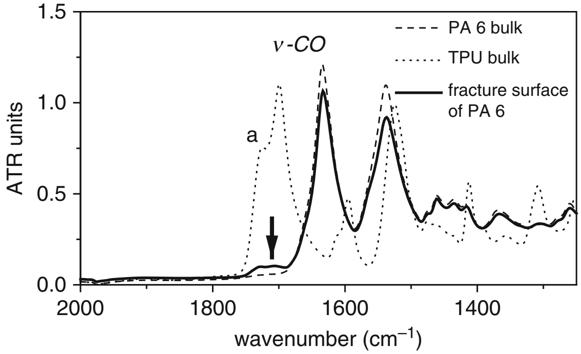


Fig. 14 Interface reactive two-component injection moulding – IR spectra of the polyamide part of fractured specimen after tensile test, TPU residues on the polyamide surface after separation of the soluble part of TPU (a ν-CO absorption band of TPU)

compounds (described in Chap. 4) with pure and glass fibre-reinforced polyamide materials. The background of utilisation of two-component injection moulding is the decrease of costs by reducing the amount of expensive PTFE polyamide materials used and the combination of the PTFE polyamide compounds as the functional material with reinforced and/or filled polyamides as the construction material. Upon increasing the PTFE content in such compounds the concentration of carboxylic acid groups increases, but the anti-adhesive influence of the PTFE also increases. This phenomenon can be demonstrated by the contact angle (water droplet) of PTFE PA-6 materials with PTFE contents > 30 wt% which is higher than 105°. Surprisingly we found excellent bond strength values in the boundary layer between the PTFE polyamide compounds and polyamides or glass fibre-reinforced polyamides which can only be explained by additional chemical bonds in the interface as discussed above (compare Table 11) [21–23,31,32].

Similar to the system PA-6/TPU the interface was found not to be the weak spot, but the fracture was located in the PTFE polyamide bulk region in the vicinity of the interface (Fig. 15).

The following PTFE weight% to volume% relations demonstrate the composition conditions in PTFE polyamide materials:

PTFE PA-6 material with 15 wt% PTFE = 8.1 vol%
30 wt% PTFE = 17.7 vol%
50 wt% PTFE = 33.3 vol%

Table 12 details the first results of the bond strength between different polyamide materials after the tensile test.

The tests were carried out under comparable processing conditions without optimisation, which led us to expect higher values for bond strength after process optimisation.

In all cases PTFE polyamide residues can be observed on the fracture surface of glass fibre-reinforced polyamide materials. These results are the basis to transfer

Fig. 15 Interface reactive two-component injection moulding – image of fractured specimen after tensile test, PTFE polyamide bulk material on the fracture surface of the polyamide material

Table 12 Interface reactive two-component injection moulding – bond strength between different polyamide materials [32]

Component 1	Component 2	Bond strength after tensile test (MPa)
PA-6 EG 6	PA-6	36.5
PA-6 EG 6	PA-6+5 wt% PTFE	34.6
PA-6 EG 6	PA-6+30 wt% PTFE	25.4
PA-6 EG 6	PA-6+50 wt% PTFE	31.6
PA-66 EG 6	PA-6	9.2
PA-66 EG 6	PA-6+15 wt% PTFE	17.7
PA-66 EG 6	PA-6+30 wt% PTFE	7.7
PA-66 EG 6	PA-6+50 wt% PTFE	11.7
PA-6	PA-66 EG 6	25.0
PA-6+15 wt% PTFE	PA-66 EG 6	35.3
PA-6+30 wt% PTFE	PA-66 EG 6	13.6
PA-6+50 wt% PTFE	PA-66 EG 6	12.3

this mechanism of interface reactive two-component injection moulding to sandwich moulding processes since the melt contact time and thus the reaction time is longer than it is in the two-component injection moulding process.

5.2 Interface Reactive Sandwich Moulding as a Special Two-Component Injection Moulding System

On the basis of these results, the sandwich moulding process was investigated by use of the controlled formation of chemical bonds for the improvement of the bond strength in the interface of the two components – the skin and the core component. The advantage of this process is a longer melt contact time during the mould filling period.

Component parts with PTFE polyamide materials as the skin component and reinforced polyamides as the core materials made by sandwich moulding will lower the material and processing costs and reduce the amount of PTFE polyamide

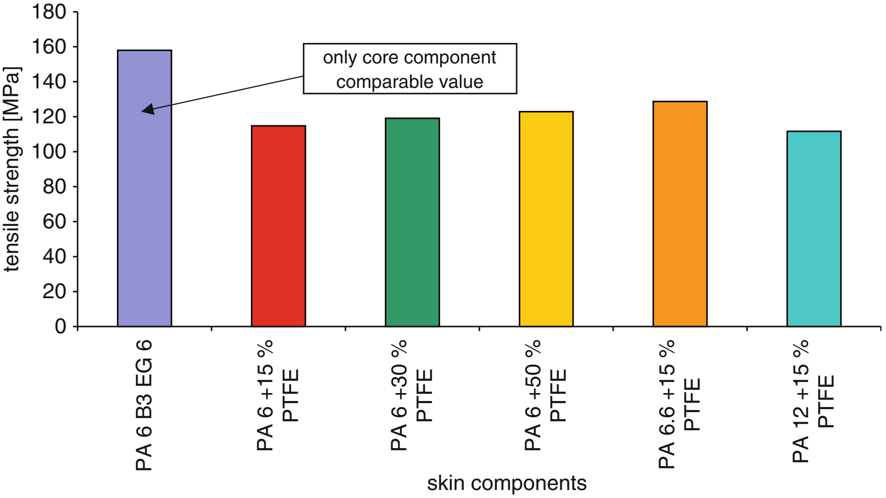


Fig. 16 Reactive sandwich moulding – image of fractured specimen after tensile test, PTFE polyamide bulk material on the fracture surface of the polyamide material

material used similar to two-component injection moulding. A main requirement in tribological application fields is safe use without any skin delamination. The basis for that is the reproducibility of the process and excellent bond strength between the components.

Figure 16 shows the values for the tensile strength of the sandwich test specimen (skin component: PTFE PA-6 with different contents of PTFE micropowder; core component: reinforced PA-6 with 30% glass fibre). The tensile strength is mainly determined by the reinforced material, the PTFE polyamide material contributes only to a lesser degree. In a first approximation it is possible to calculate the skin content and the skin thickness.

After the tensile test no delamination between skin and core was observed in the fracture region, demonstrating the excellent bond strength (Fig. 17).

No skin parts form deformed or stretched lips. The separation of the components by the peel test or by splitting with a wedge and the determination of the bond strength between skin and core component by measuring methods was not possible.

This example shall demonstrate the possibilities of optimisation by a controlled use of chemical reactions in engineering fields to improve material and component part properties.

5.3 Reactive Surface Modification Injection Moulding

The last part of this contribution deals with an innovative process for surface modification derived from the fundamental research of the results mentioned

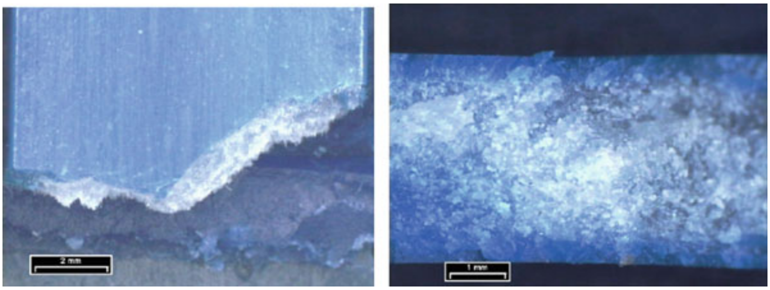


Fig. 17 Reactive sandwich moulding – image of fractured specimen after tensile test, no delamination between the skin and core components was observed

above. The request for a surface modification in connection with the moulding process of plastic materials has a long history. The change of surface properties for follow-up processing steps by polymer surface treatment for printing, painting or sticking is usually carried out by plasma treatment, by flame treatment or by pickling treatment. It is well known that the thus-modified surfaces often have no permanent properties. The component parts have to be processed on-line during the modification process.

The first fundamental examinations with polycondensates like polyamides and polycarbonates were carried out in an interdisciplinary cooperation between chemists and engineers as published in [33–35] by use of fast in situ chemical reactions at high melt temperature. It is well known that the gross kinetical reaction rate decreases very fast with decreasing temperature.

Therefore the reaction rate for an in situ surface modification during a moulding process has to be very fast, as can be concluded from the model assumption in Fig. 18. The chemical coupling of substances has to be finished after a very short time because at the moment of contact of the hot melt front with the tempered or rather "cold" mould surface the temperature drops rapidly and as a result an exponential decrease of the reaction rate should be observed (Arrhenius equation).

It was found to be of advantage to use functionalised polymers rather than low molecular compounds as modifiers in a very low concentration. Only a few bonds or connections of the modifier macromolecule on the melt surface are necessary for a permanent surface modification of a component part. The residual functional groups can be used for follow-up processes as indicated in Fig. 19 in which the polymer surface is a simplified model.

The use of high molecular modifiers prevents the penetration of the connected functional compounds into the bulk surface region and forms the basis for a permanent surface modification.

The application of low molecular substances as a modifier for polycondensates is also possible but the efficiency is low. The concentration of functional groups is too low when using diluted solutions. For polyamide and polycarbonate materials it could be shown, that with increasing modifier concentration an increase of

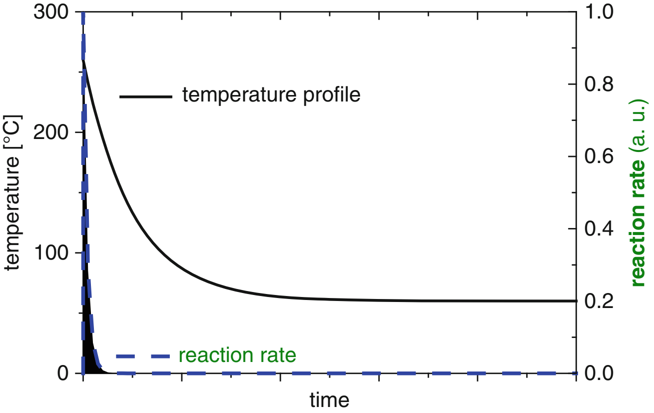


Fig. 18 Reactive surface modification injection moulding – assumed model for the reaction rate profile in dependence of the temperature profile and time

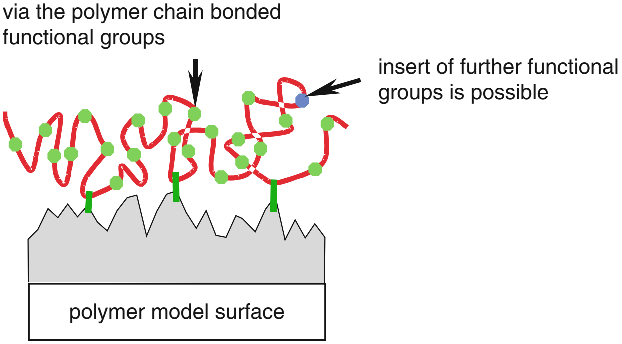


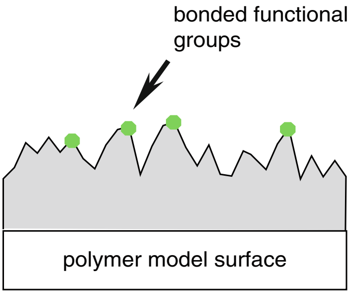
Fig. 19 Reactive surface modification injection moulding – assumed model for the modified surface after mould filling process

functional groups can be detected, but at the same time the formation of oligomers by a decomposition reaction in the surface region of the material leads to a lowering of the material properties. A possible insertion of coupled low molecular modifier compounds was not examined (Fig. 20).

The investigative process for evidence of reactive surface modification was carried out in the following process steps:

1. A defined concentration of a modifier (diluted modifier solution) was sprayed into the mould.
2. After evaporation of the solvent from the tempered mould surface the mould was closed.
3. The hot plastic melt was injected into the mould followed by a fast reaction with the modifier on the mould surface by a polymer surface modification.
4. After cooling the component part with a modified surface was eliminated.

Fig. 20 Reactive surface modification injection moulding – assumed model for the modified surface after mould filling process



The described process is simple. The aim was to provide the first evidence for such a reactive surface modification injection moulding process. A transfer to a production system requires an optimisation of the modifier adding process. The principle of the surface modification injection moulding process can also be transferred to extrusion processes for the manufacture of semi-finished and profile products.

It could be shown for polyamides and also for polycarbonates that an in situ surface modification leads to a permanent modification. The following chemical equations demonstrate the reaction mechanism:

- Polyamide surface modification:

$$\text{PA-NH-CO-PA}^* + \text{P(COOH)}_n \rightarrow \text{PA-NH-CO-P(COOH)}_{n-1} + \text{PA}^*\text{-COOH}$$

- Polycarbonate surface modification:

$$\text{PC-O-CO-O-PC}^* + \text{P(OH)}_n \rightarrow \text{PC-O-CO-O-P(OH)}_{n-1} + \text{PC}^*\text{-OH}$$

or

$$\text{PC-O-CO-O-PC}^* + \text{P(NH}_2\text{)}_n \rightarrow \text{PC-O-CO-NH-P(NH}_2\text{)}_{n-1} + \text{PC}^*\text{-OH}$$

The presence of modifier compounds on the surface was proved, after removal of non-bonded compounds, by analytical methods e.g. IR spectroscopy and zeta-potential measurements.

The mechanical properties of the surface-modified products were examined by a special shear test. After reactive surface modification under optimised chemical and technological conditions, the test specimens were cut and the pieces were bonded by special adhesives. The connected pieces were examined in a shear test and the shear strength was determined in dependence on the chemical and processing conditions. The best results for polyamides were obtained for polyacrylic acid as the modifier with an increase of the shear strength from 28 MPa (non-modified polyamide) up to 37 MPa for polyacrylic acid-modified polyamide surfaces.

The increase of the measured values of the shear strength of polycarbonates was 34 MPa (non-modified polycarbonate) up to 43 MPa. The tests were repeated after months giving the same results, which means the surface modification is stable over a long time period.

In conclusion the published results shall demonstrate risks and chances associated with melt modification of polyamides which may lead to the opening up of innovative research areas by a controlled use of chemistry in engineering fields. These results are a beginning – the investigation will be continued.

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Biodegradable Polymers: Properties, Possibilities, and Limits Considering the Synthesis, Processing, and Application of Poly(2-Hydroxypropionic Acid) and Poly(3-Hydroxybutyric Acid)

G. Schmack

Abstract Biodegradable polymers, like poly(2-hydroxypropionic acid) (PLA) and poly(3-hydroxybutyric acid) (PHB), are described with respect to possibilities and limits of their synthesis, degradation, processing, and application. The chemical structure and the processing as well as their influence on property spectrum are especially discussed for PLA and PHB multifilaments spun by an on-line spin-drawing process. This processing route was chosen, since it poses extremely high demands on the deformation ability of polymer melts, and the high deformation rates lead to a broad spectrum of different structures. Structure–property relationships are discussed including stress-induced crystallization, influence of differently crystalline modifications and various physical properties. Finally, economic aspects of PLA and PHB are addressed with respect to medical and technical applications.

Keywords Biodegradable polymers, Poly(2-hydroxypropionic acid) (PLA), Poly (3-hydroxybutyric acid) (PHB), Processing, Structural characterization

Contents

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Abbreviations and Symbols

α	Crystallinity
ω	Shear frequency
η^*	Complex melt viscosity function
γ_a	Density of the amorphous part
γ_c	Density of the crystalline part
ε_H	Elongation at break
ΔH_o^M	Equilibrium heat of fusion
3HB	3-Hydroxybutyric acid
3HV	3-Hydroxypentanic acid
AFM	Atomic force microscopy
D-LA,D-2-Hydroxy-propionic acid	(D-Lactic acid)
DR	Draw ratio
DSC	Differential scanning calorimetry
E	E-Modulus
G′	Storage modulus
G″	Loss modulus
LA	2-Hydroxypropionic acid, (Lactic acid)
L-LA	L-2-Hydroxy propionic acid, (L-Lactic acid)
M_w	Weight-average molecular weight
P2HA	Poly(2-hydroxyalkanoic acids)
P3HA	Poly(3-hydroxyalkanoic acids)
PEO	Poly(ethyleneoxide)
PET	Poly(ethylene terephthalate)
PHA	Poly(hydroxyalkanoic acid)
PHB	Poly(3-hydroxybutyric acid)
PHB/PHV	Copolymer based on 3HB and 3HV
PLA	Poly(2-hydroxypropionic acid), Poly(lactic acid)
PL-LA	Poly(L-2-hydroxypropionic acid), Poly(L-lactic acid)
PVAc	Poly(vinylacetate)
PVC	Poly(vinylchloride)
R_H	Tenacity at break
t	Time of conditioning
T^G	Glass transition temperature

T_o^M	Equilibrium melting temperature of an infinite crystal
WAXS	Wide-angle X-ray scattering

1 Introduction

During the last years a large number of monographs and publications [1–7] have been published which cover biodegradable polymers of the different material groups (e.g., polysaccharides, polypeptides, polyesters, and polyisoprenoides), as well as their copolymers and blends.

This contribution places the emphasis on aliphatic polyesters and, as the main protagonists, on poly (2- and 3-hydroxyacids). Poly(2-hydroxypropionic acid) and poly(3-hydroxybutyric acid) which can be regarded as their prototypes, will be specially comparatively discussed concerning their chances and risks. Herein they will be called polylactic acid or PLA and PHB.

The reason for choosing this polymer group can be explained from the point of view that extensive fundamental research of generation, processing, characterization, application, and disposal have already been undertaken. Therefore, all relevant aspects can be examined, economic and ecologic, as well as technical and scientific ones.

But, both polymers, PHB and PLA, lead to conflicts in the context of assigning them as biodegradable polymers, because these are naturally occurring polymers, which like PHB were evolved in natural material cycles. However, in the case of PLA only the monomer, L-2-hydroxypropionic acid, (L-Lactic acid) can be found in the natural material cycle. On the other hand, both of them can be generated on a natural nonpetrochemical basis, with renewable resources, and they are degradable. This common denominator should justify the discussion of both polymers herein and makes a comparison meaningful.

Degradable/resorbable polymers have been well established in the field of medicine, for example, as surgical sutures, implants, and bone plates, since the 1960s and 1970s [8]. They attracted attention as the rapidly expanding production and the use of plastic materials created massive problems in the area of waste disposal. Hence integrated waste-management concepts are seeking to minimize the waste and/or to exploit the plastic waste from material and energy aspects. These ideas were recognized as a chance for a stronger commercial exploitation of renewable resources as a basis for biodegradable polymers and biodegradable materials. During the oil crises biodegradable plastics were even esteemed as the key object to solve the waste-disposal problem. With this in mind research on biodegradable polymers, like poly(3-hydroxybutyric acid) (PHB) and poly(2-hydroxypropionic acid) (PLA), was intensified in the 1970s and 1980s.

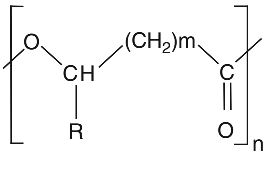
In 1996, the so-called “economic circulation and waste law” was introduced in Germany. It was orientated towards different possibilities of plastic waste exploitation: recycling by thermoplastic processing, conversion into low molecular weight substances, or alternatively gasification in order to use the synthetic gases or to use the energy content by incineration. Under the given circumstances, the kind of exploitation that is chosen has to be economically and ecologically reasonable. A total balance should give enlightenment about both, material and energy expenditure of all products and processing.

Biopolymers have to meet these requirements too. But, in contrast to oil-based polymers, biologically generated polymers offer an additional possibility concerning their waste management, they are compostable. Another important aspect is the stabilization of the CO_2 content in the environment, which is believed will avoid the progressive greenhouse effect, because the composting of "growing again" resources releases only as much CO_2 as it has bound from the atmosphere during the growth phase. Other advantages of biopolymers consist of saving fossilized resources and in the possibility of opening markets for agricultural products and their remains, if polymers, synthesized on an oil-derived basis, are substituted by polymers based on the "growing again" raw material.

2 Polymer Structure

Aliphatic polyesters show a wide spectrum of potential molecular structures. The variations of esterification permitted by the large number of available monomers led to a broad range of aliphatic homopolyesters and copolyesters. The basic structures of the aliphatic polyesters are depicted in Fig. 1.

The property spectrum of this material group can be varied in a wide range referring to the monomer units, e.g., different lengths of side chains R, different positions of hydroxyl groups within the polymer chain, which results in the number of CH_2-groups, m, and the incorporation of double bonds and other functional groups (Fig. 1). R may represent, besides the CH_3- and CH_3–$(CH_2)_x$-groups, about 90 different components. In this way, the properties of these polyesters can be varied in a wide range from hydrophilic to hydrophobic, from hydrolytically degradable to moisture-resistant, from highly crystalline to amorphous, from



m = 0,		Poly(2-hydroxyalkanoic acids)	(P2HA)s
m = 0,	R = CH_3	Poly(2-hydroxypropionic acid)	(PLA)
m = 1,		Poly(3-hydroxyalkanoic acid)s	(P3HA)s
m = 1,	R = CH_3	Poly(3-hydroxybutyric acid)	(PHB)

Fig. 1 General structures of poly(hydroxyalkanoic acid)s (PHA)s

brittle and rigid to flexible and flexural, without losing their biodegradability [9]. The generated polymers are more elastic and less crystalline the longer the side chains of the PHAs are. A fundamental difference exists between P2HAs and P3HAs or in general the m-PHAs. The P2HAs have not been detected in the natural cycle of materials yet, since they cannot be generated biotechnologically. The detection of m-PHAs in the natural cycle of materials succeeded only in the range from $(1 \leq m < 5)$ until now.

3 Synthesis

The production of aliphatic polyesters can principally be realized both, by conventional chemical synthesis or by using biotechnological fermentation processes, excluding P2HAs and long-chain PHAs. In this connection one has to emphasize that the basic materials, the monomers of both production processes, the biotechnological production as well as the conventional chemical synthesis, can be generated on a petrochemical basis but also on the basis of renewable resources.

3.1 Biosynthesis

Already in 1925 Lemoigne [10] had isolated PHB, from the bacterium *Bacillus megaterium*. His invention, the class of naturally occurring PHAs, did not find scientific interest until the 1960s and 1970s. Special interest was shown to the point of view that a large number of different aliphatic polyesters can be biotechnologically produced on the basis of renewable resources by means of microorganisms. A broad variety of bacterial species are capable of composing and storing these polymers as a carbon and as an intracellular energy source. Up to now PHAs have been detected in approximately 100 bacterial species, among them genetically engineered bacterial species, fungi, and animal cells. However, only five bacterial species have been used in pilot plants for fermentation. Since PHB has also been detected in cells of plants, genetically engineered plants can be seen as another possible source of PHB.

While the first efforts [11, 12] of the biotechnological generation of aliphatic homopolyesters and random copolyesters have been restricted essentially on monomers from 3-hydroxybutyric acid (3HB) and 3-hydroxypentanic acid (3HV), newer investigations concentrate on monomers with branches in the range of medium chain length, the so-called thermoplastic elastomers [13–15]. Steinbüchel et al. [3] catalogued more than 100 hydroxyalkanoic acids as constituents of biosynthetic PHAs.

The fundamental method of biotechnological production can be explained by the ability of certain microorganisms to produce PHAs when nutrients are limited and carbon sources are available. The growth of the microorganisms can be limited by the depletion of an essential nutrient such as N_2, O_2, P, S, or Mg. The intracellular metabolism of these microorganisms was detected as a cyclic process in which different enzymes take part, varying in dependence on the type of microorganism and the carbon source [16].

The structure of PHAs, regarded as homo- or copolymers can be varied in a wide range by choosing the microorganism and the type and concentration of carbon substrates. The fermentation conditions, concerning concentration or limitation of nutrients, the temperature profile, the pressure conditions, especially the O_2 partial pressure, the pH-value, the residence time, and the adjustment of sterile or nonsterile and aerobic or anaerobic conditions are important factors influencing also the structure of the PHAs. The structure, the degree of polymerization, and the stereoregularity of the generated PHAs determine the corresponding processing behavior and the property profile of the samples. In order to use the accumulated PHAs at a large scale, a lot of research work has been done to increase the accumulation rate and yields of the PHAs and simultaneously reduce the price of the carbon sources. In this connection biogas was tested as a potential source [17].

In general, two-step fermentation processes are realized. In the first step, the breeding of the biological material takes place, and in the second step the accumulation of the PHAs takes place by limiting essential nutrients like N_2, O_2, P, S, or Mg. In order to isolate and purify the produced polymers out of the bacterial cells, a process of centrifugation and freeze drying can be executed after the harvest.

PHB: The PHB is extracted from the dried cells by means of suitable chlorinated solvents and subsequent precipitation of the PHAs. As an alternative, the cell components can be dissolved in an appropriate oxidizing solvent or by using enzymatic decomposition of the cells including the cell components and sonic oscillation. However, enzymatic decomposition should be preferred taking into account the risks of using chlorinated solvents.

LA: Starting product for PLA is 2-hydroxypropionic acid (lactic acid, LA), which also can be produced biotechnologically. Basic materials for LA are agricultural raw and waste materials; these will be converted by means of a bacterial fermentation process into L-2-hydroxypropionic acid (L-lactic acid, L-LA).

3.2 Chemical Synthesis

PHAs can also be produced by conventional chemical synthesis. A chemical synthesis is basically possible in two ways: by polycondensation starting from hydroxyacids as well as by ring-opening polymerization starting from cyclic esters. In both cases hydroxyacids can be the starting monomers. They also can be produced by chemical synthesis on a petrochemical basis or by means of bacterial fermentation from renewable resources. Only the last route ensures high stereochemical purity through a careful choice of producing strain.

The polycondensation involves the removal of the split water by using solvent under high vacuum and temperatures. In this way, low to intermediate molecular weight polymers are generated. A higher molar mass can be reached by the polymerization concept. Cyclic esters are starting products which are used for the catalytically initiated ring-opening polymerization. They can be derived from monomers, such as 3-butyrolacton, or dimers, such as lactide, depending on the chain length of their hydroxyacids.

PHB: PHB can be polymerized with anionic or cationic initiators on the basis of 3-butyrolacton by ring-opening. The step of the ring-opening polymerization defines the stereoselectivity and consists of the insertion of one monomer in the terminal polymer initiator complex. With the aid of achiral or chiral initiators and racemic or enantiomeric pure 3-butyrolacton one can create *iso*-, *syndio*-, and *atactic* PHB [16].

PLA: Cyclic dimers of lactic acid, so-called lactides are the starting product for the polymerization of PLA. These lactides are obtained from lactic acid by using a combined process of oligomerization and crystallization. This generated crude lactide has to be purified with regard to residual water and free acidity. During the catalytically initiated ring-opening polymerization of the lactide either Lewis-acid catalysts or metal-alkoxide initiators being used.

Because of the selection and concentration of the stereoisomeric L-, D-, or *meso*-lactide it is possible to receive a wide range of molecular weight.

The ring-opening polymerization of PLA is traditionally realized during a discontinuous batch-process, but recently continuous processes have been developed. As another alternative to continuous polymerization processes the reactive extrusion of PLA was realized. By combining Lewis-acid catalysts with cocatalysts it is possible to increase the catalytic activity and to reduce the polymerization time [18].

4 Properties

Physical properties of PHAs are determined by monomer units, which are predominantly responsible for the molecular interactions, the molecular weight, and the molecular weight distribution. In addition, different crystalline modifications and processing conditions have a considerable effect on the achievable property level of the samples. For this reason, only the basic material data are listed and compared: the glass transition temperature (T^{G}), the equilibrium melting temperature of an infinite crystal ($T_{\mathrm{o}}^{\mathrm{M}}$), the equilibrium heat of fusion ($\Delta H_{\mathrm{o}}^{\mathrm{M}}$), and the densities of the amorphous (γ_{a}) and crystalline (γ_{c}) parts (Table 1).

PHB of biosynthetic origin is partially crystalline, thermoplastic and optically active. It is presented as an optically active D-form with a high level of crystallinity. By analyzing crystal structures, two crystalline modifications have been reported, the orthorhombic (α-modification,) described by Yamamoto et al. [19] and the hexagonal (β-modification) described by Orts et al. [20].

From X-ray diffraction patterns it was found that PHB of biosynthetic origin can adopt a 2/1 left-handed helix as well as a planar zigzag conformation. Under tension

Table 1 Physical properties of PHB and PLA [23, 27, 30]

Properties	PHB	Reference	PLA	Reference
T^{G} (°C)	4	[23]	25	[30]
T_{o}^{M} (°C)	197	[23]	215	[30]
ΔH_{o}^{M} (J g^{-1})	146	[23]	93.6	[27]
γ_c (g cm^{-3})	1.260	[23]	1.290	[30]
γ_a (g cm^{-3})	1.177	[23]	1.248	[30]

Glass transition temperature (T^{G})
Equilibrium melting temperature of an infinite crystal (T_{o}^{M})
Equilibrium heat of fusion (ΔH_{o}^{M})
Densities of the amorphous (γ_a) and crystalline (γ_c) parts

the repeat unit of PHB can be changed, most probably because either the helix or the amorphous regions transform into a zigzag conformation.

The crystals of the PHB of biosynthetic origin have no center of symmetry, so charges can arise at their interface by means of mechanical pressure or tensile stress. This property is described as piezoelectricity.

If PHB is crystallized by slow cooling from the melt, it will form thin lamellar crystals which will be organized in large banded spherulites. Because of this PHB is a relatively brittle material with poor mechanical properties. Since highly purified PHB does not include any impurities, which could act as heterogeneous nucleation agents, and the crystallization rate of PHB is very low, it consequently can be quenched into a glassy state by rapid cooling from melt to temperatures below 0°C. From a dilute solution PHB can be precipitated into thin lamellar arrow-shaped single crystals. The thickness of the lamella is a function of the crystallization and annealing temperatures and the molecular weight. Highly drawn fibers show fibrillar structures.

PLA: An important feature of the lactic acid is its ability to exist in two optically active forms: L- and D-isomers. Lactic acid derived from fermentation consists of 99.5% L-isomer and 0.5% D-isomer. The production of the cyclic lactide dimer intermediates results in three potential L-, D-, and L/D (*meso*)-forms and a racemic equal mixture of D- and L-forms. The L- and D-forms are optically active while the *meso*-form and the racemic mixture are optically inactive (Fig. 2).

The chirality of the PLA-chain is an essential property. It allows a certain adjustment of the polymer degradation speed. By controlling the ratio and contribution of the D, L isomers and the *meso* (D, L diastereoisomer) in the polymer chain, it is possible to induce different melting points and degrees of crystallinity, because the concentration of D- or *meso*-segments in the PL-LA strongly influences the chain mobility and arrangement and due to this crystallization rate.

Wide-angle X-ray scattering (WAXS) studies of PL-LA revealed the existence of two crystalline modifications. De Santis [21] described the structure of the α crystalline modification as pseudoorthorhombic with the chains in a 10/3 left-handed helix. Hoogsteen [22] reported a β orthorhombic crystal structure, characterized by a 3/1 left-handed helical conformation.

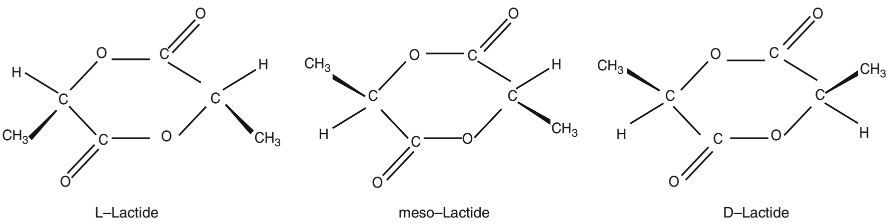


Fig. 2 Stereoisomers of PLA

PL-LA crystallizes from the melt into spherulites, from dilute solution into lamellar single crystals, and in highly drawn fibers into a fibrillar extended-chain structure.

5 Degradation

Even in the decomposition behavior there are considerable differences between P2HAs and P3HAs, which are manufactured biotechnologically.

There are two temperature ranges of particular interest, the low-temperature range where the degradation proceeds very slowly, and the high-temperature range, where the decomposition can proceed within a short time period. The first range is important for application, and the second for processing.

In principle, many factors affect the rate of degradation of PHAs. They include the properties of the polymers, such as the molecular composition, the resulting intermolecular interactions, hydrophilic and hydrophobic behavior, the structural parameters, like degree of crystallinity, level of orientation, surface structure, and molecular weight. Concerning biopolymers, the related factors are the growth of microorganisms, especially the pH-value, temperature, aerobic or anaerobic conditions etc.

In general, both P2HAs and P3HAs, are subjected to acid-based catalyst hydrolytic decomposition in a low-temperature range, and only biotechnologically produced PHAs are subjected in addition to enzymatic decomposition due to extracellular enzymes. Some microorganisms excrete extracellular depolymerases to degrade microbial PHAs and to utilize the decomposed compounds as nutrients.

PHB: Under optimum conditions, in the accumulation phase during the fermentation process, the rate of the enzymatic degradation of this amorphous PHB is extremely fast, within a few hours. In contrast to this, extracted or processed, partially crystalline PHB is attacked relatively slowly over periods of weeks. The enzymatic decomposition, for example, of the PHB test specimen, leads to a slow surface erosion, while the volume body remains unchanged for some time, so the whole weight and the properties change slowly. The enzymatic degradation occurs at the surface of the PHB material and the rate of the surface erosion is strongly dependent on both the structure and the composition.

A pure hydrolytic decomposition of hydrophobic PHB is, in contrast to the enzymatic decomposition under the same experimental conditions, about 2–3 times slower, but increases with growing pH-value and temperature. Under high-temperature conditions, above the melting point, the PHB is subjected to the formation of linear oligomers as a result of ester cleavage and/or a β-elimination, and this resulted in crotonic acid.

From a medical point of view, it should be noted that a healthy human tissue does not contain bacteria utilizing PHB. But experiments [23] have suggested a difference between the rate of hydrolytic degradation in vivo and in vitro. The interpretation is that enzymes from the body itself catalyze the hydrolytic degradation process in vivo. During the degradation, PHB molecules decompose into 3HB. It is found in human blood and can be metabolized by the body.

PLA: The acid-based catalyst hydrolytic decomposition of PHAs in general and of P2HAs in particular is considered to be controlled by diffusion.

Depending on the hydrophilic character of the PHAs and of the diffusion rate of the water, a statistically random hydrolytic chain scission of the ester groups takes place, which can directly lead to a fast loss of mechanical properties of the test objects of PLA. The diffusion process happens primarily in the noncrystalline regions. Therefore, it can be controlled by the degree of crystallinity and with this the chirality within limits. The degradation of PLA is a function of several variables, among them the temperature. The onset of fragmentation occurs after about 9 days at 60°C [24], which is the approximate temperature of active compost. Above melting point PLA produces mainly cyclic oligomers owing to intermolecular ester exchange, the transesterification. At low to moderate humidity level the shelf life at room temperature is several months. During the degradation in the human body PLA decomposes into lactic acid which is naturally present in the human body as a result of metabolism.

6 Processing

PLA and PHB may be processed because of their thermoplastic properties in the usual thermoplastic processing systems by using extrusion, injection molding, melt spinning, blowing film, and melt-blown techniques.

But it should be noted that the respective processing windows are quite narrow for aliphatic polyesters, and especially for PHB, which are thermally more sensitive, and the process control has to be adapted in relation to temperatures, residence times, and shear.

6.1 Melt Spinning

A comparison of results of the thermoplastic processing characteristics of PHB and PLA is particularly expressive, if they are obtained using the same equipment.

For this comparison, a melt-spinning process was chosen. Each special thermoplastic process influences the structure and thus the properties of the obtained polymer samples differently. This is particularly pronounced for fibers, since especially melt spinning is a process which makes extremely high demands on the deformation ability of the polymer melts at high deformation speeds. Particularly the tensile stress within the fiber formation zone is a very important factor to reach a high orientation of the macromolecules along the fiber axis and a stress-induced crystallization. This crystallization should be discussed in relation to PLA and PHB multifilaments, and at the same time the general property spectrum of these polymers should be represented.

The fibers were spun using a spin-drawing process. The structure formation of the fibers is caused especially by the forces of gravity, air friction, and inertia. These forces act against the rheological force which consists of an elastic and a viscous part of strain, equivalent to the storage (G')- and loss (G'')- moduli, respectively. These parameters provide a rheological characterization which is sensitive to differences of the structure, the monomer composition, and the molecular weight of the PHB and PLA.

The viscosities of polymer melts, calculated from the storage modulus and the loss modulus, have to be within a range to resist the applied forces, which act against the rheological forces. But they should not be as large as to prevent the necessary deformation before the start of sodification. The elastic part of deformation has to be small since an elastic deformation happens more rapidly than a viscous one. Therefore, a considerable elastic deformation can lead to a cohesive fracture of the fiber in the molten state. The ratio of the viscous to the elastic energy of the polymer melt may be seen as one of the most important factors for the spinnability of polymers. For the usual commercially used spinnable polymers, such as, for example, poly(ethylene terephthalate), the ratio is about $G''/G' > 10$ [25]. The master curves G'' versus G' for PHB and PLA and the straight line $G''/G' = 10$ are displayed in Fig. 3.

Differences between both polymers are especially distinct in a high-module range. While the tested PLA provenance is proved to be relatively well spinnable, the spinning behavior of PHB is clearly worse.

Differences in the processing behavior between PLA and PHB may be seen because of their different thermal stability, as the comparison of melt viscosities of both polymers shows. Figure 4 gives details of the melt viscosities of the PLA and PHB pellets and as-spun fibers as a function of the shear frequency during a measuring period of about 15 min.

The measurements were carried out from higher to lower shear frequencies to observe the thermal degradation occurring during the measured time, since by measuring in the other direction, the degradation of the polymers resulting in a viscosity decrease would be overlapped by the decrease of the complex viscosity function as a result of the structure-viscous behavior.

PHB: The decrease of the melt viscosity of the PHB at lower shear frequencies indicates substantial degradation during the rheological measurement. From this it is obvious that the thermal degradation is enhanced at a residence time above 5 min,

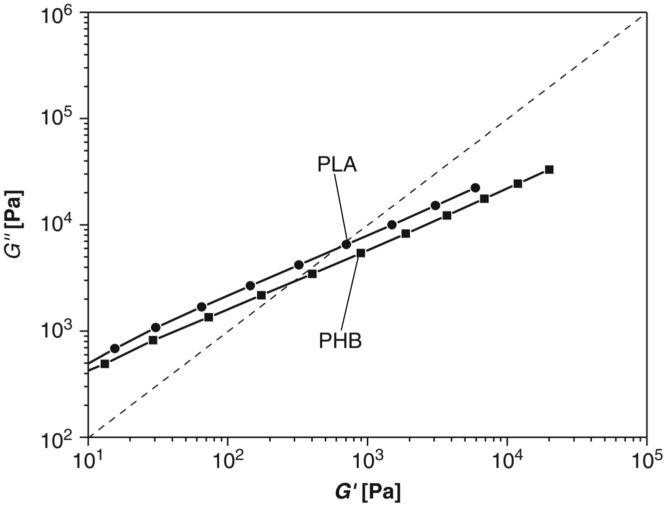


Fig. 3 Loss (G'')- and storage (G')-moduli dependence on PHB and PLA

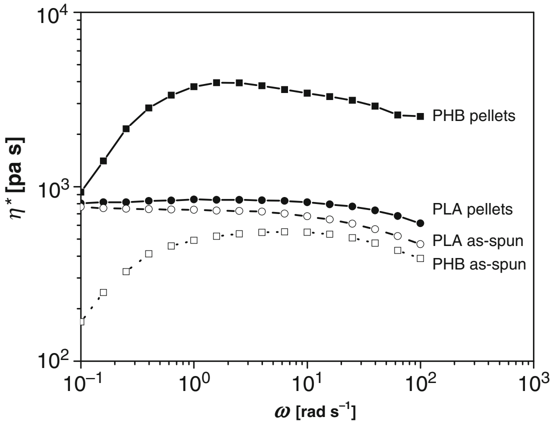


Fig. 4 Complex melt viscosities (η^*) of the PHB and PLA pellets and as-spun fibers as a function of the shear frequency (ω)

corresponding to a frequency range of <1 rad s^{-1}. Those measurements show that thermoplastic processing and especially a melt-spinning process of PHB can only be carried out during very low residence times of the melt in the extruder of about <4 min. Holm [23] has already referred to this problem by means of melt index measurements. The differences between the functions of the complex viscosity of the pellets and the as-spun fibers also clearly show the thermal degradation originating from the existing thermal processing of the melt spinning.

PLA: The viscosity functions of PLA show the relative stability of the PLA pellets and of the as-spun fibers during rheological measurements. The differences between both functions of the complex viscosity show a low thermal degradation

Table 2 Textile physical properties of drawn PHB und PLA fibers [31–33]

Spin-drawn fibers	E (GPa)	R_H (MPa)	ε_H(%)	α (%)
PHB	4.0	304	36	60
PLA	7.4	503	24	50

E-Modulus (E)
Tenacity at break (R_H)
Elongation at break (ε_H)
Crystallinity (α)

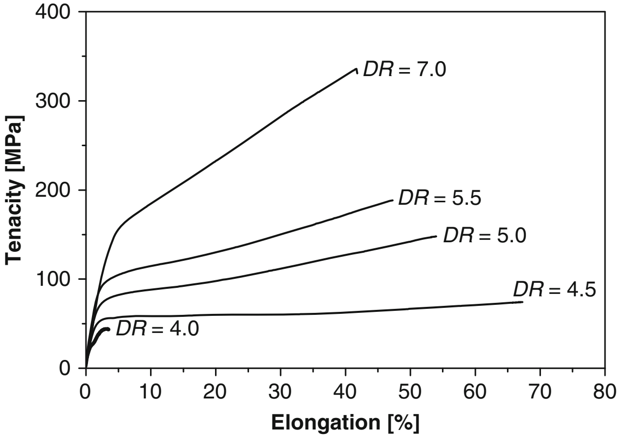


Fig. 5 Stress–strain curves of PHB fibers at different draw ratios (*DR*)

originating from the existing thermal processing of the melt spinning and show the good thermal stability of PLA.

The results of spin-drawing experiments of both polymers should be compared here for illustration. Polyfilaments have been generated consisting of 12 monofilaments with a respective diameter of 30m at a take-up speed of 2,000 $\mathrm{m\,min^{-1}}$. Table 2 shows the textile physical parameters and data of the crystallinity of the PHB and PLA multifilaments.

PLA fibers show a considerably higher level of strength at a lower elongation at break than PHB fibers. Differences in the crystallization and orientation behavior during the structure formation are seen as the cause.

PHB: Characteristic for PHB fibers within the context of knowledge about structure formation are considerable deviations of changes within the textile physical values of PHB filaments which had been spin drawn using different draw ratios. Figure 5 shows the stress–strain curves of the spin-drawn fibers at different draw ratios in the range of 4.0–7.0.

The draw ratio is known to be determined by the degree of chain extension and the molecular orientation relative to the fiber axis. The spin drawing of fibers is based on sliding processes of chain segments. During this process crystallites are formed due to increasing parallelism and orientation. These crystallites work as crosslinkage points and lead to higher alignment of tie-molecules by increasing tensile stress. Usually filaments which have been spun under the same conditions but at different levels of draw ratios show a continuous decrease of remaining elongation and a clear increase of the level of strength.

However, an extraordinary difference exists between the curves of the PHB fibers drawn at a draw ratio of 4.0 and 4.5. The PHB fibers drawn at a draw ratio of 4.0 have no significant elongation at break and no tensile strength and are brittle. First a draw ratio of 4.5 allows the production of fibers with an acceptable elongation at break. Higher tenacity values and lower elongations at break were reached in the range of higher draw ratios.

Those serious differences in fiber properties can be illustrated by the means of fiber structures as they can be derived out of the results of WAXS and atomic force microscopy (AFM) images.

Typical X-ray diffraction patterns of the equatorial scattering areas for spin-drawn fibers spun at draw ratios of 4 and 7 are shown in Fig. 6a and b.

Both equatorial X-ray scattering areas show reflexes which have to be assigned as helical α-modification. Differences result in the degree of orientation of the crystallites which increases with the draw ratio and is documented in the form of the crystal reflexes. At draw ratios $DR > 4$, which are demonstrated on fibers at a $DR = 7$ here, an additional crystal structure exists; this can be assigned to the hexagonal β-modification. At the draw ratio of 4.0, no reflections of the hexagonal β-modification could be detected. The appearance of both crystalline modifications for highly oriented fibers indicates that PHB chains can crystallize in a helical, as well as in a planar, zigzag conformation. Obviously, the stress reached during the process of fiber formation determines the amount of crystalline modifications. The stress, resulting from the process conditions at $DR = 4$, seems not to be high enough to start a stress-induced crystallization, which is the case in fibers spun at higher draw ratios as shown in Fig. 6b.

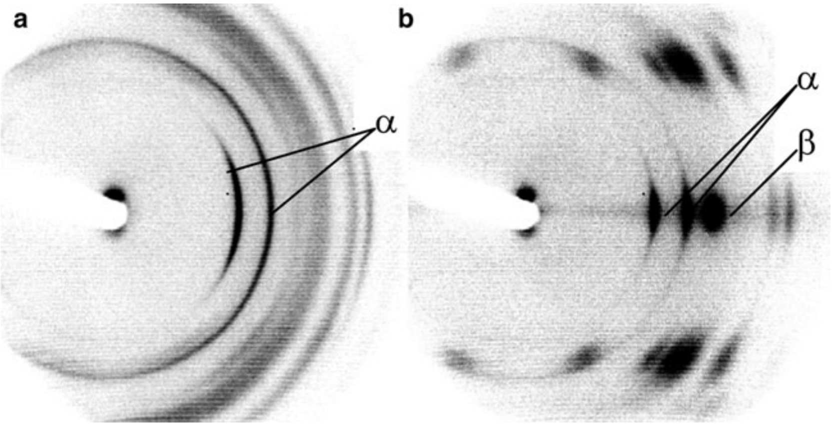


Fig. 6 (**a**) and (**b**): The equatorial X-ray scattering area near the $\alpha(020)/(110)$ and $\beta(100)$ reflections for PHB fibers, spun drawn (**a**) at $DR = 4$, (**b**) at $DR = 7$

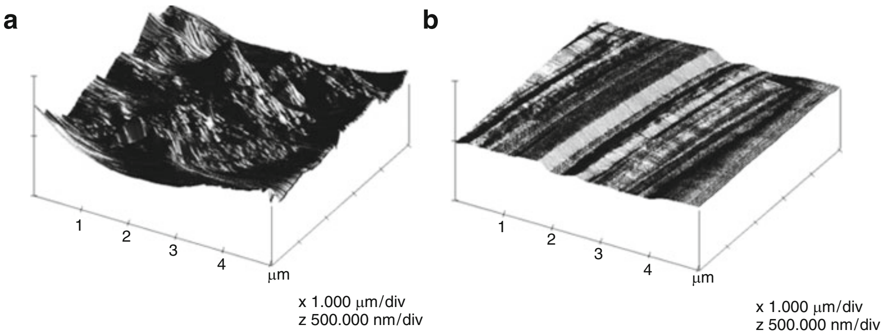


Fig. 7 (**a**) and (**b**): Three-dimensional surface topographic images of PHB fibers, drawn (**a**) at *DR*=4, (**b**) at *DR*=7

Figure 7a and b show typical three-dimensional surface topographic images of the PHB fibers drawn at a draw ratio of 4.0 and 7. The surfaces of the fibers differ considerably. Depending on the draw ratio, spherulitic or fibril-like surface structures were formed. The textile physical properties of the fibers can be explained by these different structures. The fibers, spun at a draw ratio of 4.0, are brittle without a sufficient elongation at break visible in the stress–strain curve (Fig. 5). The fibers spun at a draw ratio of 7 show a completely different stress–strain behavior with a sufficient elongation at break and a sufficient tenacity, as can be seen from the stress–strain curve (Fig. 5).

In the absence of the high molecular orientation, which appears to be the case in the filaments spun at a low draw ratio of 4.0, the crystallization velocity of PHB is so slow, that the PHB fibers are easily quenched to a noncrystalline, amorphous state. The crystallization will be developed only in the postcrystallization process during the conditioning. With rising draw ratios a molecular orientation is developed in the spinline and the crystallization velocity increases and is sufficient to compensate the cooling rate in the spinning process. As a result, PHB is able to crystallize at a definite draw ratio due to stress-induced nucleation, as the relatively highly oriented crystalline fraction shows.

These results show explicitly the influence of different processing, especially spin drawing, conditions on the structure–property relationships of samples, especially fibers.

Figure 8 shows DSC-scans of PHB and PLA pellets and fibers. The scans illustrate the shift of melting temperature maxima, the changes of the distribution of the crystallite sizes, and the degree of crystallinity of the pellets relating to the processed polymers, in this case of drawn fibers. The comparison of the DSC-scans of the pellets with the drawn fibers illustrates a narrower distribution of crystallite sizes, a higher degree of crystallinity and a distinct shift of the melting temperature maximum to higher values. These changes indicate fundamental dependence of these parameters on the processing conditions.

Table 3 repeats the textile physical properties of PHB and PLA fibers conditioned at room temperature for 3 months in relation to the original state.

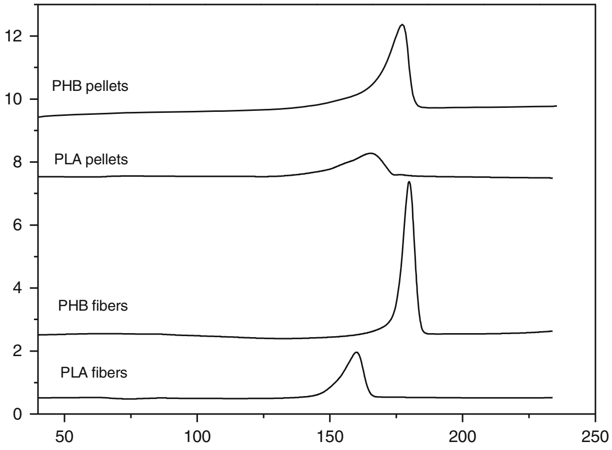


Fig. 8 DSC-scans of PHB and PLA pellets and fibers, respectively

Table 3 Textile physical properties of conditioned PLA und PHB fibers

Spin-drawn fibers	*t* (month)	*E* (GPa)	R_H (MPa)	ε_H (%)
PLA	0	7.4	503	22
PLA	3	7.4	484	23
PHB	0	5.1	262	37
PHB	3	7.2	278	31

Time of conditioning (*t*)
E-Modulus (*E*)
Tenacity at break (R_H)
Elongation at break (ε_H)

The PLA fibers show neither embrittlement nor deterioration of properties due to the secondary crystallization, which means that the structures of PLA fibers are stable at these conditions and during this time. The reason for this could be the high crystallinity and the high orientation of the polymer chain of the highly drawn fibers to avoid the secondary crystallization.

For PHB fibers certain variations concerning the E-modulus can be seen, which may be connected with a slight recrystallization within the noncrystalline areas, whereas the tenacity and the elongation at break are not changed in the context of limit of error.

These results, which were obtained from highly drawn PHB fibers with a molecular weight of $M_W = 175{,}000\ \mathrm{g\,mol^{-1}}$, contrast with those from solvent-cast and hot drawn films [26], whose stability and reproducibility referring to a secondary crystallization are very strongly dependent on the molecular weight and are given only by a molecular weight of more than $3 \times 10^6\mathrm{g\ mol^{-1}}$.

6.2 Further Spinning Methods

Possibilities for optimizing the structure and thus the physical properties result, appropriate to the theory, in extremely slow processes of fiber formation. Thereby high molecular provenances with narrow molecular weight distribution under high tensile stress are spun, predominantly out of a solution.

PLA: Fambri et al. [27] compiled a list of present literature data on PLA fibers, which were spun under quite different technological conditions, dry spinning, solution spinning, melt spinning, and spin drawing.

Values of the tensile strength and the E-moduli were obtained within the ranges from 2.3 up to 9 GPa, at partly quite low spinning and drawing rates of only a few meters per minute.

PHB: Holmes [23] has found for PHB that gel spinning is the most appropriate spinning process. Typical properties for highly drawn gel-spun PHB have been indicated by him, using appropriate high molecular solutions with a module of about 8 GPa and a high tensile strength of about 0.9 GPa.

These experiments are interesting as they show the possibilities of structure formation. A possible extension of these spinning processes to an industrial application is extremely limited. Problems result, on the one hand, under unacceptably low spinning speeds, and on the other hand, in the difficult lavish solution processes of high molecular provenances and the used chlorinated solvents.

7 Modification

The physical and mechanical properties of the degradable polymers can be controlled by blending with synthetic or natural polymers and copolymerization.

Its β-substituted structure makes PHB thermally unstable and, as a result, the thermoplastic processing difficult. A way to reduce this problem and to increase the size of the processing window is through the use of copolymers, based on 3HB and 3-hydroxyvaleric acid. With increasing parts of 3HV in the PHB/PHV-copolymer, there is a decrease in the melting point, so the processing temperatures can be lowered and the risk of thermal degradation can be reduced. By increasing the concentration of 3HV, the glass transition temperature decreases, and allows one to use the copolymer at lower temperatures without embrittlement. With growing toughness also the values of the notched impact strength rise. A very important property of the PHB/PHV-copolymers is their high crystallinity for all compositions; they are isomorphic.

PHB is miscible to the same degree with a number of polymers such as PEO, PVAc, PVC, and polysaccharides because of the hydrogen bonding. P3HAs comonomers are internal plasticizers for PHB and improve its mechanical and processing properties [1].

A comfortable pathway for improvement of the crystallization of poly(3-hydroxybutyrate) in a melt-spinning process is the use of nucleating agents like electron-beam irradiated PHB [28] or the reactive extrusion with peroxide [29].

The property profile of PLA can also be changed by blending with other polymers and copolymerization with D- and *meso*-types of isomers to adapt to the relevant processing and application conditions.

8 Application

Biodegradable thermoplastics, like PHB and PLA, can be processed by conventional thermoplastic processing technologies, such as extrusion, injection molding, melt spinning, blowing film, and melt blown, for a wide range of application as environmentally friendly materials and for medical applications.

The obtained products find numerous possibilities of application, especially taking into account the point of view of their degradation behavior and their compliance with the disposal and environmental concept, for example in packing and the fishing industries. Furthermore, they are promising candidates for disposable goods, like hygiene products. In agriculture and as geotextiles they are mainly interesting as cover fleeces and carrying materials where they are used as retard materials for the purposeful release of agrochemicals and seed.

The chirality of the monomer units of microbiologically generated polyesters is of great interest for the chemical and pharmaceutical industry. They are considered to be the pool of chiral building blocks, which receive optically active derivates for the construction of enantiomer-pure products.

In addition, other properties of PHB can be used for example the excellent gas barrier effect, especially against CO_2, and its biological efficiency for nitrate elimination during drinking water purification.

Applications in medicine take advantage of the combination of such properties as biocompatibility and degradability. Neither the polymers themselves nor their degradation products can set free toxic materials or cause tissue-damaging processes.

Both 2-hydroxypropionic acid and 3HB are intermediates of metabolism and can be metabolized by the body. Since 3HB is found in human blood, PHB has always been referred to as a biocompatible polymer.

Additionally for PHB their piezoelectric properties are characteristic, which can have a stimulating effect, for example, on bone growth.

But the different degradation processes, PHB catalyzed by enzymes and acid–base catalyst and PLA just by acid–base catalyst, determine to a considerable extent the degradation and/or resorption times of both materials and therefore the areas for human and veterinary medical use. These materials are used in human or veterinary medicine, or they are presently being tested in the in vitro phase, for example, as resorbable sutures, for blood vessel repair, drug-delivery systems, bandages, scaffolds for producing retard materials for coupling active substances, cells and epithelial materials, resorbable patch implants and supportive materials in the shape of bone plates. The properties of PHB encourage medical applications where slower absorption is desirable.

But they can compete only with petrochemically derived synthetic polymers for special application where biodegradability is the primary criterion.

9 Outlook

During the search for efficient and ecologically justified waste-management concepts, the use of biodegradable polymer materials was repeatedly made a political demand. Next to the arguments of a partial solution to the waste-disposal problem by natural degradation, the conservation of the petrochemical resources, the reduction of CO_2-emission, and the use of renewable resources are a point of discussion.

The possible ways of using biopolymers are determined by the achieved property level of the end products, the extrudate, the injection-molded solids, films, fibers, and textiles but also and most of all from the view point of costs both regarding polymer production and thermoplastic processing.

According to the laws of the market PHAs will have to fit into two price ranges, that of the low price product and that of the high price product.

The prerequisite for the readiness of the industry to use these polymers in the range of low-price materials has to result from the relation between reached property profile and the price of striven-for products.

Both criteria have to be appropriate to synthetic polymers which were used hitherto and have to be substituted. Legal framework conditions, for example the different costs of waste disposal in pricing, allow the possibility of appropriate price relations within narrow limits.

But when the deviations are too extreme, the products will find no entrance in the market. The skepticism of the consumers is then, among others, an argument of the producers or marketing manager to ignore they.

The application of high price materials, for example, in the medicine and pharmaceutical industry, requires the achievement of appropriate special property profiles that may justify the price and therefore the use.

The readiness of the industry to use PHB in the range of low price materials has failed during the last years because of the costs of PHB. Production of PHB or the PHB/PHV-copolymer under the trade name Biopol for technical use was abandoned, while in the last years efforts to use PHB for the medical sphere and niche products have continued.

In contrast, the use of PLA in the medical sphere, for example Vicryl as a PGA/PLA copolymer, is now supplemented by the development of PLA with technical qualities under the trade names Lacty, Lacea, and EcoPLA. Production and price of PLA with technical quality should allow one to find areas for PLA use also outside medicine. The property profile reached and the striven-for costs are decisive. The latter should adjust to those of PET in the coming years. Consequently the inclusion of the disposal costs in the price statistics makes prospectively the use of PLA even economically sensible.

In addition to the above-mentioned polyesters on the basis of renewable resources the industry will use their scientific and most of all technical capacities in a growing manner to synthesize degradable polymers, polyesters, and polyamides like Bionolle, BAK, Eastar Bio, Materbi, Eastman on a petrochemical basis. These polymers will be considered to be low price materials on the market and to take the striven-for disposal concepts into account and show the advantages of synthetic materials referring to constant quality independent from seasonal and territorial fluctuations and the low costs in their best light.

However, environmental considerations concerning the CO_2-emission, the use of renewable resources, and the substitution of petrochemical raw materials are not considered.

10 Summary

The aliphatic polyesters PHB and PLA are generated using different mechanisms of synthesis, PHB by biosynthesis and PLA by chemical synthesis on the basis of biotechnologically generated monomers.

For the thermoplastic processing the differences between PLA and PHB referring to their thermal stability during the melting are essential. By using PHB, the residence times of the melt have to be kept to less than 4 min to limit thermal degradation. PLA turns out to be relatively thermally stable under similar conditions.

Referring to hydrolytic degradation, PLA and PHB are subject to different mechanisms, PLA hydrolysed by acid–base catalysts and PHB by enzymatic and an inferior range of the acid–base catalysts. Because of the different degradation mechanisms, differences occur between the degradation times and temperatures.

Further differences result in the crystallization behavior. Under high stress which may be reached in a spin-drawing process, PLA crystallizes in the course of an orientation initiating mechanism in one defined crystalline modification, regarding PHB two crystalline modifications have been detected in the course of the stress-induced crystallization.

PLA fibers show a considerably higher level of strength at a lower elongation at break then PHB fibers do. Differences in the crystallization and orientation behavior at the structure formation are seen as the cause.

The comparison of the chances that both polymers can achieve production and processing at favorable prices and to an appropriate property level show that the advantage lies decisively with PLA. PLA can play an important role in reducing the waste-disposal problems, because it is widely accepted as a future packaging material.

According to current knowledge, biotechnologically generated pure PHB compared to PLA and other degradable polymers will be able to find application only in the medical sphere and for niche products.

To summarize it can be said that biodegradable polymers can be considered as a sensible complement to the traditional raw material source. However, effusive expectations should be curbed and the subject should be responsibly arranged in social context.

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Product Design and Processing: Adhesive Technology

Otto-Diedrich Hennemann

Abstract An overview of the state of the art in adhesive technology and the different kinds of adhesives, their components, and their preferred applications including industrial production processes is given. The components of the adhesive systems are regarded in view of their potential risks for the environment and human health. Legal regulations concerning the handling and the processing of adhesives with respect to their hazardous components complete the mainly technical viewpoint of the paper. Future developments are discussed in an outlook including natural products based adhesives and the improvement of the compatibility of existing adhesives as well as their industrial applications with the environment.

Keywords Adhesive applications, Adhesive components, Joining technology, Primers, Risk minimization

Contents

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1 Perspectives of Adhesive Technology

The joining of materials and structural components is a basic operation in production engineering. Adhesive technology has assumed a special position among irreversible joining techniques during the past 50 years. It is necessary to distinguish between nonstructural and structural adhesive joining, nonstructural adhesive joining has been practiced for centuries – as a matter of fact for a number of millennia. This category includes adhesive joining in the consumer and home handyman markets. The resulting adhesive joints need not be as strong as in industrial applications, but they must be very reliable, i.e., private users expect adhesive products to be easy to handle and require adhesive bonds that are long-lasting. Regarding the use of adhesives in these areas, ecological concerns are becoming increasingly important. In this regard, sealing techniques employing liquid and paste polymers must also be mentioned, since the principal function of these is also an adhesive one. Whether one speaks of sealant adhesives or adhesive sealants, the basic materials are the same. Construction adhesives, in particular mixtures of cement-bound minerals and polymer bonding agents, are among the nonstructural adhesives with a wide area of application.

Back injection of plastic structural parts with PUR and the slush technique used to produce a decorative "skin" on such structural components are also elements of adhesive technology in the widest sense, since the polyolefins and polyurethanes used in them are functional adhesives that develop a strong adhesion to the substrate while they cure. The Inmold labeling technique (IML) is also an adhesive engineering process, in view of the fact that during the injection molding process the surfaces of labels, but not the entire film material of the labels, are melted and bound up with the injection-molded structural component. The labels are composite films or copolymer films. The melting temperatures of the materials involved are so different that only the inner surfaces of the labels, and only a few regions within the macromolecules of the copolymers, are melted. The basic material of these inner layers is comparable to that of polyolefin-based hotmelts. Among other factors, development of this technique arose from difficulties with labeling using organic and aqueous adhesives. The IML technique is thus an example of production risks leading to new solutions.

In recent years, the concept of light construction has led to the development of hybrid structural parts. Using parts made of pure plastic runs into repeated difficulties because of the material's low modulus of elasticity, since the only way to compensate for this drawback is to use much thicker structures. Combinations of sheet metal materials with plastics facilitate new solutions that do justice to the concept of lightweight construction and provide new properties at the same time (sound insulation, thermal conductivity, dynamic stability, corrosion protection). The precondition for successful development of such hybrid structural parts is a reliable bond between the two materials. In certain cases, this must be realized by adhesives that are flexible with regard to the α problem (different heat expansion coefficients of the materials), but still provide high strength levels.

The adhesive joining of hybrid constructions can be considered an example of the transition from nonstructural to structural adhesive technology.

Microsystems technology and miniaturization represent additional new challenges for adhesive engineering. The diminishing sizes of structural components present problems for all heat-intensive joining techniques, since the components tend to warp rapidly and the thermal load on adjacent components quickly reaches excessive levels. A good example is provided by production of electronic structural components and sensors. High thermal loads applied during board assembly can damage the chips. Of course there is the alternative of enlarging the protective encapsulation and thus enhancing the thermal insulation effect, but the industry is now no longer willing to accept this approach. Low-heat adhesive technology is therefore often used so that structural components can be made even smaller. Advances in the microinjection molding of plastics also require adhesive technology to mount the structural components. These fields of application may not be characterized by large production volumes in the future, but they will lead to highly engineered and refined adhesive technology solutions.

The adhesive bonding and sealing of structural components serving the purpose of heat insulation represents a special field of application for adhesives that is frequently neglected in evaluations of adhesive technology. The primary ecological objective of reduction of energy consumption can be realized in a number of different ways. One method is to avoid energy losses, for example when transporting goods, in particular foods. By application of suitable adhesives, the cargo unit designs for refrigeration trucks have been changed in recent years so as to increase cargo space and/or improve insulation properties (refrigeration means fuel consumption, so lower mass means better fuel economy).

Structural adhesive joining requires in particular high-strength, reliable adhesive bonds that hold securely under industrial conditions and meet certain design specifications. The selection of adhesives and adhesive technology by design engineers should be supported in this field by mathematical equations and a set of recognized process selection rules. Another criterion is the heat and temperature resistance of adhesive bonds. Using a number of adhesives (thermosetting phenol-formaldehyde resins, polyimides, polycyanurates), bonds can be obtained with a temperature resistance of up to 250°C (brief heatup to test temperature) and heat resistance up to 150°C (long-term heating, utility temperature). These are niche products with risks that can be controlled during processing. Hot-curing phenol-formaldehyde resins in particular were still the decisive basic materials in the adhesives used in aircraft construction and mechanical engineering 20 years ago, when demands for better environmental compatibility resulted in development of new adhesive types with comparable properties.

Figure 1 shows a highly demanding structural component in terms of structural adhesive joining. Careful selection and placement of the adhesive bond ensure that the telescope mirror dimensions remain virtually uniform, despite the enormous diameter, under the influence of temperature changes. The coefficient of expansion of the entire system is kept at zero for all practical purposes.

The entire field of adhesive technology is comprised of 15% structural adhesive joining and 85% other fields of application, which is also reflected in the development of basic materials for adhesive technologies:

- 44% Liquid adhesives
- 22% Adhesive tapes and adhesive films
- 19% Adhesive sealants
- 15% Designer adhesives with polymer content

Sales volumes in the different product segments have developed markedly over the past 20 years. Total sales grew from 900 million to 2.5 billion € and is thus currently 237.600 €/branch employee. This is far above the average for other

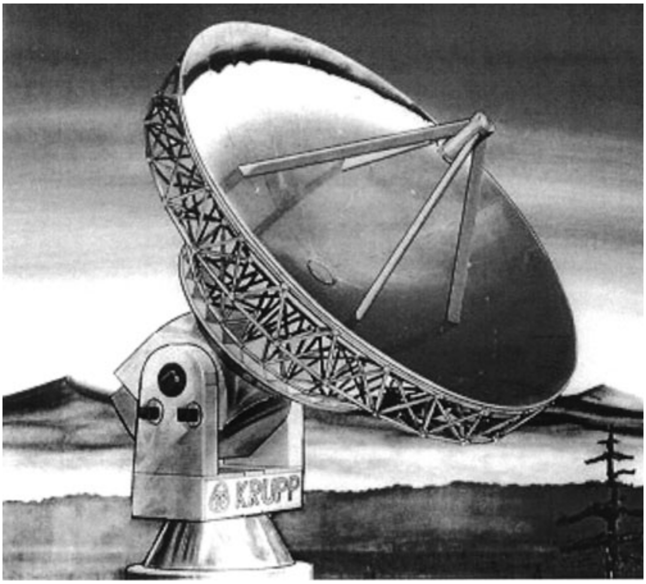


Fig. 1 Radiotelescope with adhesively joined structures comprising CFP segments

industrial branches, emphasizing the attractiveness of the adhesives industry. Taking general price developments into account when assessing the sales curve, it becomes apparent that these increases also reflect the increasing interest of other industries in adhesive technology. The relatively small margin of average price changes for adhesives, from 2.04 to 1.95 € kg^{-1}, once again underlines the innovation potential represented by the adhesive technology industry.

About 10% of the adhesives marketed worldwide are produced in Germany. Adhesives consumption in this country, 6.5 kg/inhabitant, is higher than in any other European country. This fact reflects a long tradition of use and innovations as well as the levels of industrial, business, and private interest in adhesive technology. This also applies to other industrialized countries such as Switzerland, Denmark, Belgium, Sweden, and the Netherlands. Regardless of developments in other European countries, it can be assumed that Germany will be a major player, if not the leader, in future technological developments in this field.

Worldwide growth in the adhesives market will reach 4% by 2004, again exceeding average industrial growth rates.

Of course developments in the adhesive industry cannot be seen in isolation from developments in other areas. Figure 2 shows the most important market segments for adhesives.

Figure 2 shows that adhesives, as mentioned above, are used mainly in the field of nonstructural adhesive technology. The automotive, shipbuilding and aircraft industries, in which mainly high-strength adhesive bonds are used, are included

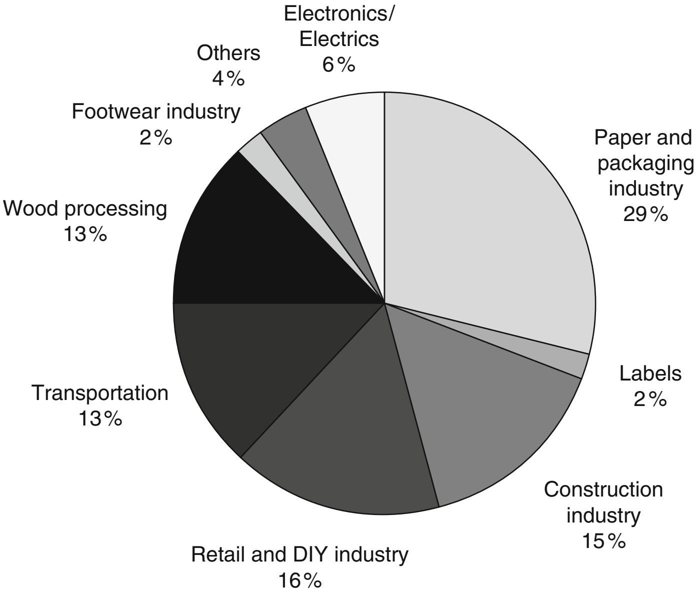


Fig. 2 Principal market segments for adhesive applications. *Source*: Industrial Adhesives Association, Düsseldorf

under the transport segment. There are a number of interesting aspects of this classification scheme:

- When using high-strength adhesives it can be assumed that the process condition will be monitored and optimized on a continuous basis and that the risks of adhesive use are known and will be minimized. Use of a specific adhesive is normally proceeded by a qualification procedure in which strength, process-related environmental contamination, and possible emissions during utilization are taken into consideration.
- The largest volumes of adhesives are used in applications involving direct human contact with the adhesive (home handyman application, construction industry, paper and packaging industry, wood processing) and varying work-place conditions.
- Electro engineering, the chemical industry, and motor vehicle production are the growth branches, the construction and furniture industries are showing a downwards production index curve. Adhesive manufacturers will therefore concentrate development efforts on the first-mentioned areas.
- The largest sales volumes are achieved in so-called low-cost areas in which adhesives with high emissions rates are still used.
- Besides the adhesives manufacturers, European machine manufacturers are also leaders in their fields (wood processing, labeling, packaging, printing), providing a favorable basis for further developments in the field of adhesives.
- The high standard of living and purchasing power in the private sector will ensure growth in adhesives use in the private and home handyman markets, assuming ecological aspects are given due attention.

These tendencies can only be transformed into practical results if existing and future laws, regulations, and framework conditions are taken into account. The European legislative process, and the expansion of the European Union, will play important roles, in particular the “chemical policies” product liability laws. The particular relevance of these aspects to the adhesives industry and development of new adhesives, and the chances and risks involved, are treated in greater detail later.

The perspectives for adhesive technology must increasingly be considered in terms of whether they allow and provide for integration of additional new functions. Besides power transfer, other important functions include sealing, improvement of structural component dynamics, sound insulation, electrical insulation and electrical conductivity (as dependent on adhesive modification), combinability with other joining and bonding technologies (welding, clinching), and radiation filtration.

The automotive industry, although it does not currently account for a high percentage of industrial adhesive use, is a key industry for the future of adhesive technology. In the past 40 years, the percentage of steel and iron used in cars has been reduced from 76 to 61%, while that of aluminum has increased from 2 to 7.5% and plastics from 2 to 14%. Some companies have already exceeded these levels: At AUDI AG, the share of plastics in some models is at 22.5%, and Al 34%. These developments in material use are due to demands for lighter vehicles and also result from changes in production processes. The wide variety of materials used, and increased use of nonmetallic materials, now require joining techniques that were not needed in earlier production processes. In many cases, adhesive technology has proven to be the only viable alternative to the older welding processes, resulting in extensive developmental efforts on the part of adhesives manufacturers, users, and mechanical engineers (reliable dosage, computer-controlled application, SPC, heating furnaces, etc.). Adhesive technology not only makes for lighter vehicles, it also facilitates application of completely new design principles, Fig. 3.

Adhesively fixed transverse members can bear much greater loads assuming essentially equivalent mass (3) or can be made much lighter to bear the same load.

Adhesive technology will continue to open up new applications if the following advantages are fully exploited:

- Joining and bonding to other materials (potentially unlimited material combinations)
- Uniform, full-surface transfer of power
- No influence on material structure because of avoidance of excessive heatup
- Joining of highly heat-sensitive materials
- No structural component warpage due to thermally induced tensions
- Low-cost adhesive joining of both large and small structural components will present few difficulties
- Material strengths fully utilized by designs in keeping with adhesive potentials
- Combination of adhesive jointing and sealing in a single process step
- Combinations with other functions

Strength and thermal load play an important role in metals, glass materials, and oxide ceramics, so that limits to adhesive technology do become apparent here.

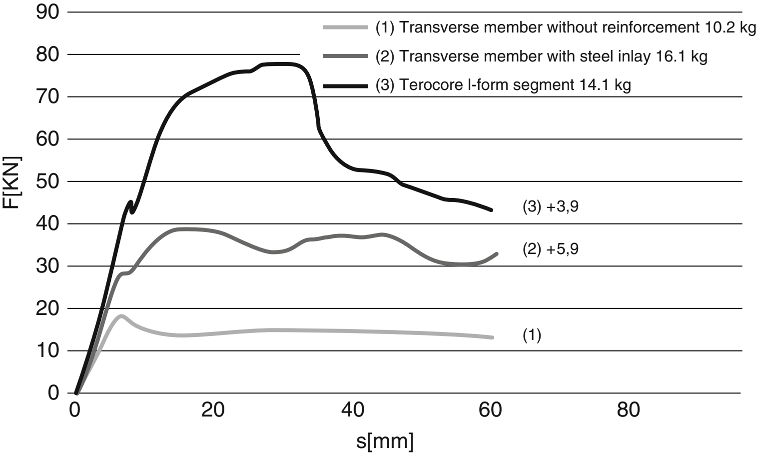


Fig. 3 Strength of transverse members. *Source*: Henkel Teroson Heidelberg

On the other hand, especially in bonds of plastics to other materials, the thermal resistance of the plastics and adhesives is equivalent, for which reason such applications are bound to grow in importance.

The following unsolved problems in adhesive technology are considered risks that are slowing down the increased use of adhesives and related technologies:

- Basis of calculation still uncertain.
- Limited repair potentials [with the exception of pressure-sensitive adhesives (PSAs)].
- Stress cracking susceptibility in adhesives containing solvents.
- Surface morphology and topography of adhesive substrates are highly variable, resulting in so many parameters that potentially influence adhesion that sufficiently reproducible production processes are a difficult challenge.
- In some cases, considerable time and effort go into production, especially pretreatment processes. Integration of the adhesive process in other process steps is desirable.
- The general knowledge in the field of adhesion and its improvement do not apply uniformly to all materials, but rather vary widely for metals, glass, and plastics.
- Personnel require a higher degree of qualification.
- Insufficient inline test methods for process control.

The chances of adhesive technology could be exploited more fully if advances to counter these risk factors could be made. The reactive and physically setting adhesives will be used mainly in the field of construction, with natural adhesives used more often in the areas of consumer goods, foodstuffs, and packaging. Water-based adhesives will continue to replace solvent-based products, a process supported in particular by the food processing and packaging industries.

2 Adhesive Joining as a Production Process of the Future

Product manufacture in the coming years will be characterized by a number of framework developments:

- Products will become smaller, lighter and more complex
- Material variety within a product will increase
- Increasing aesthetic and functional demands will be met by coatings and paints that are only compatible with low-heat joining techniques
- The properties of the structural components must be maintained without any follow-up treatments
- The joining technology must be integrated in the production process so as to facilitate mechanization or automated production
- Useful product life must be extended to improve sustainability

In the future, new joining technologies should restrict thermal loading to very small areas (microsystems technology, actuators, electronics, sensor technology).

In some cases, no thermal loading can be tolerated at all (chip integration in structural components). In many cases, laser welding technology provides a solution but, for nonmetallic materials and small joining surfaces, adhesive technology is often the only alternative, especially if no heat can be applied. The requirement for a long product life is at the same time always a demand for greater reliability and a reduction of failure quotas. Since the likelihood that a product will fail is highly dependent on the joining technology used, adhesive engineering must do what is necessary to improve the reliability of adhesive bonds.

When it comes to large structural components and mass products, light construction is a target parameter, since this is one way to reduce the burden on material resources and produce more products from the same material volume. The automotive industry is a typical example. It is well known that the ecological burden generated by automobiles is 85% fuel consumption-related, a factor that depends to an essential degree on vehicle weight. Advantages in the area of light construction therefore at the same time represent progress in reduction of CO_2 exhaust. Analyses have shown that use of plastics have reduced fuel consumption in Germany by 470 million $l\ a^{-1}$ and CO_2 exhaust by 1.7 billion $kg\ a^{-1}$. Integration of multiple functions in a single structural component in connection with the light construction concept will require new joining solutions in the automotive industry. Adhesive technology would be an attractive method of joining materials in cases where simplified dismantling is to be ensured, in which cases adhesive technology would be categorized as a detachable joining system.

3 Adhesive Types and Their High-Risk Components

The use of adhesives began early in human history. The adhesive qualities of natural substances from the environment were made ready use of. The first industrial applications of adhesives involved use of tar products to render ships leaktight. In this application, both the efficient ceiling function and cord adhesion to the wood were made use of. In the course of history, more and more products were found in the natural environment with adhesive properties, for example dextrin, starch, cellulose, casein, and proteins. Both vegetable and animal products provided the basic materials for adhesives. A well-known example is the bone glue (glutin) derived from the collagens obtained by boiling animal body parts. A quantum leap in the development of adhesives was the discovery that natural rubber could be made into an adhesive with interesting properties by means of a specific modification. The resulting material was used in development of new industrial bonds and consumer goods. For instance, the first sticking plasters were made of natural rubber. The real breakthrough in adhesive technology came with the development of synthetic adhesives. Parallel to this, material engineering was developing in leaps and bounds, and the number of materials intended for combination use increased continuously in the second half of the last century in particular. New ways to join and bond these materials had to be found.

This challenge was the engine that drove adhesive technology. Many synthetic adhesives developed during this period are now still found in everyday articles. Looking back, it is interesting to note that it was a branch of industry that places the very highest demands on joining and bonding technology, the aerospace industry, that has been most conducive to advances in adhesive technology. Since reliable adhesion took precedence over adhesive costs in this industry, it became possible to finance developments the results of which then benefited other industrial branches as well. The aircraft construction industry uses light metals that would lose 50% of their strength if welded – forcing designers to make them oversized. Using adhesive technology, the light structures were developed that eventually made today's jumbo aircraft feasible. Of course this development also resulted in a greater fuel economy. To this extent, adhesive technology has contributed a great deal to our current ecological potentials regarding transport of large volumes of goods and large numbers of passengers. Adhesive technology can of course not be made responsible for increasing demand for global transport and the absolute increase in CO_2 exhaust, but it can make a significant contribution to its reduction.

Figure 4 provides an overview of the main groups of adhesives. The market is dominated by synthetic adhesives, but there's also a large market for adhesives based on natural primary substances (so-called natural adhesives).

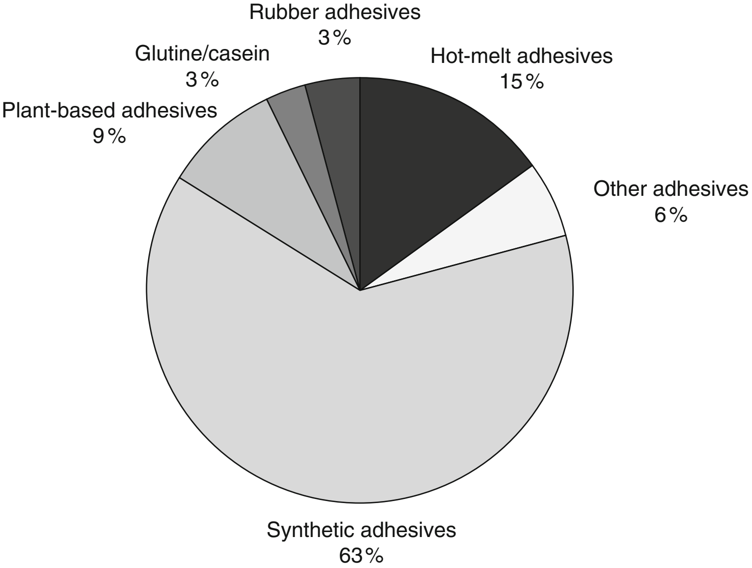


Fig. 4 Adhesives market according to product groups. *Source*: Industrial Adhesives Association, Düsseldorf

The main differences between synthetic and natural adhesives are:

- Natural adhesives show excessive variability in their adhesive properties
- Natural adhesives are based on products some of which are taken from the food market
- Low environmental burden levels of natural adhesives, assuming primary products do not undergo extensive chemical modification
- High adhesive strength of synthetic adhesives, making them the only suitable choice for structural applications
- Synthetic adhesives involve a greater risk potential in their production (usually not evident to consumer), processing (greater expenses involved in workplace design and higher process design expenditures), and application (emissions, fogging)
- Difficulty in dismantling high-strength adhesive bonds, thus limiting recycling potential

Today, it is no longer feasible to categorize adhesives according to unique characteristics and properties, since modern adhesives always share the qualities of multiple groups.

As seen in Table 1, adhesives can be classified into groups by way of risk assessment.

The chemical basis of crosslinking adhesives is always a reaction subject to the laws of chemical kinetics. The reactive process depends heavily on the stoichiometric ratios, the reaction temperature, and the primary materials (resin and curing agent). Two-component adhesives are those in which the reactive components are mixed before processing (2C adhesives). Heat-curing 1-component adhesives (1C adhesives) are those in which curing is initiated thermally. In this case, the resin and curing agent is mixed with other components in the so-called prepolymer state. At room temperature, the components are either not reactive or the reaction is so gradual that it results in no disadvantages for the adhesive function. If crosslinking

Table 1 Overview of adhesives

Chemically curing	Physically setting	Adhesives with special setting characteristics
Epoxy resins	Melt adhesives	Postpolymerization possible
Polyurethanes	Contact adhesives	
Silicones	Dispersion adhesives	Postpolymerization possible
Saturated polyesters	Solvent adhesives	
Methacrylates, peroxide crosslinking	Pressure-sensitive adhesives	Tack variable
MS polymers	Adhesive films, heat activating	Activation temperature variable
Phenol-formaldehyde resins		
Polyimides		
Acrylates and epoxides, radiation-crosslinkable		
Rubber adhesives, crosslinking		

is initiated by moisture (polyurethanes, silicones, cyanacrylates) or radiation at specific wavelengths (acrylates, epoxies, UV-crosslinking PSAs), one also refers to 1C adhesives.

The decisive factor in the evaluation of 2C adhesives is that if the stoichiometric ratio (mixing ratio of resin to curing agent) is off in either direction, the excess resin or curing agent remains in the adhesive. The unused resin or curing agent residues often have the effect of a “plasticizer.” This type of reaction will influence the adhesion to some degree, in particular leading to migration of the unused reaction partner and possible risks in the later utilization period. In 1C adhesives, the risk of emissions is especially high during the heatup phase to “starting temperature.” As soon as the curing (crosslinking) reaction begins, the reaction partners are bound chemically into the macromolecular structures (in prepolymers), after which they can no longer give off emissions.

A typical characteristic of physically setting adhesives is the evaporation of solvents or heatup to a molten state. Application is then in liquid form (solvent adhesives, contact adhesives, dispersion adhesives, hotmelt adhesives) or from the solid phase (adhesive films, laminate adhesives). In all of these types there is a liquid state during processing from which emissions are always a possibility due to the volatility of the basic polymer or other adhesive components.

Workplace studies on processing of PUR adhesives have revealed that, with extraction, the TLVs (threshold limit values) for isocyanates were not exceeded in any case, Fig. 5. Extraction can reduce the risks significantly. Extraction combined with absorption or deactivation is preferable.

3.1 Adhesive Types

Adhesives are nonmetallic substances used to join two surfaces by means of surface adherence (adhesion) and inherent strength (cohesion), DIN 16920. This definition of adhesives does not cover water glass adhesives, adhesive ceramics, or adhesive mortars. The substances used as adhesives are polymers that go through a liquid phase at least once (reactive adhesives) or more than once (hotmelts, thermally activated adhesives). The liquid phase can also be achieved by dissolution in suitable solvents (nonreactive adhesives). In dispersion adhesives, the polymer molecules are dispersed (finely distributed) in a liquid – usually water – whereby the polymer molecules themselves are not dissolved, Fig. 6. These adhesives are also known as “water-based or aqueous” adhesives. It must be remembered that solvents are contained in these adhesives in addition to the water. “Genuine” aqueous adhesives contain less than 5% solvents in the liquid phase. The dispersions contain, in contrast to the solute adhesive molecules, additional substances, disposal of which requires specific additional measures. Since the dispersions represent stable systems in water, the water-resistance of such adhesives is reduced. Their thermal and water resistance can be increased by additional crosslinking (usually with isocyanates).

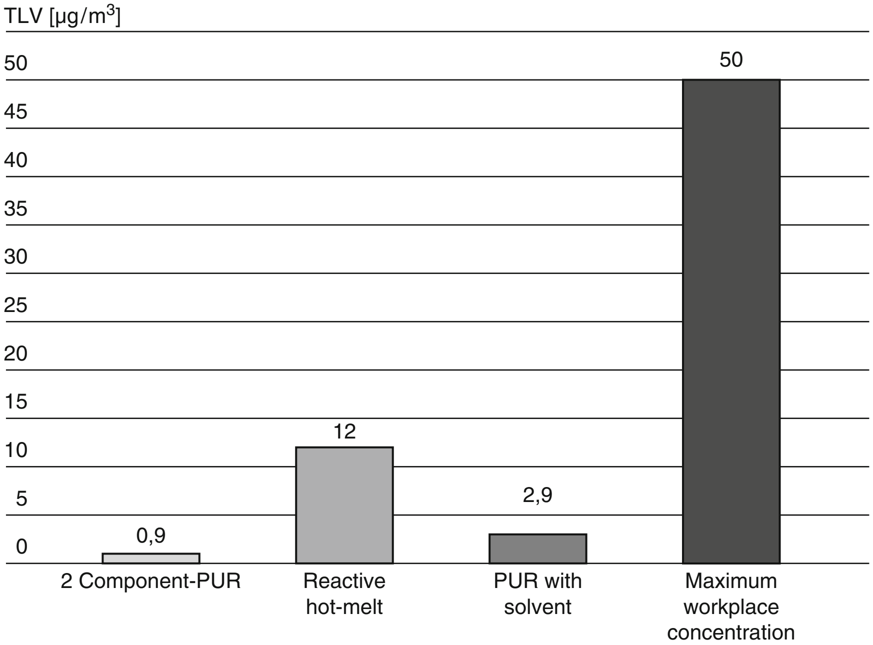


Fig. 5 Outgassing rates at different workplaces and from different adhesive types. *Source*: IFAM Bremen

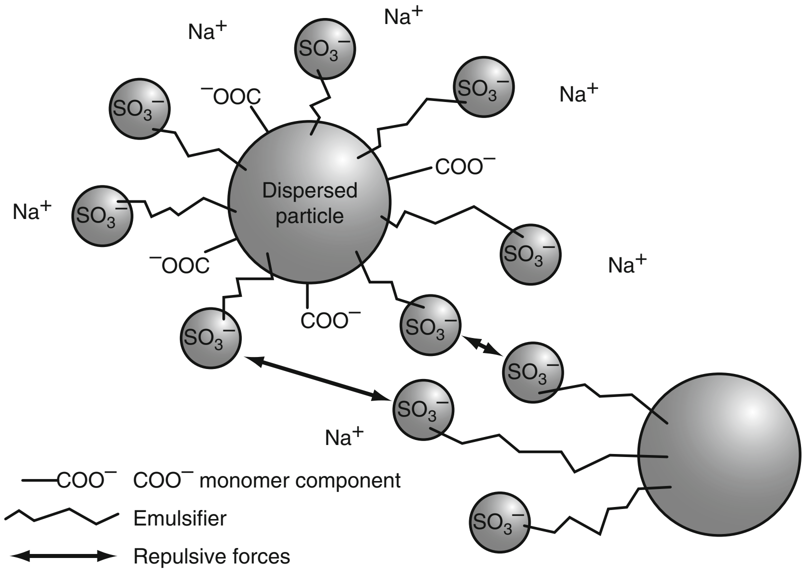


Fig. 6 Dispersion of adhesive molecules, water-compatible dispersants and emulsifiers

Pure solvents such as methylene chloride are not true “adhesives”, but certain solvents are called adhesives or adhesive varnishes due to their effects. The most important primary materials and substance groups for adhesives are:

- Vegetable substances: dextrin, starch, cellulose
- Products of animal origin: animal glues, casein
- Chemically reactive prepolymers and intermediate products of monomeric substances (1C and 2C adhesives)
- Polymers dissolved in solvents (many rubber adhesives, contact adhesives)
- Meltable polymers (hotmelts)
- Polymers that are dispersible in water or organic liquids (dispersion adhesives)

3.2 Epoxy Resins (1C and 2C Systems)

In a chemical sense, the EP resins are intermediate products of bisphenols with epichlorohydrines. These two primary products are allowed to react until suitable intermediate products (resins) are produced that can enter into further reactions. The reaction of the bisphenols and epichlorohydrines with the intermediate product – also known as a prepolymer – is readily controlled so that high molecular and low molecular EP resins result. The resulting EP resins, usually from bisphenol A, have various viscosities that can be influenced by diluents, for example glycidyl ether. The diluents, which may account for up to about 50%, react during the crosslinking reaction with the EP resins so that no formula component is lost. They are then designated as reactive diluents (e.g., 1.4-butandioldiglycidyl ether). The result, on the one hand, is a so-called 100% solid adhesive with little shrinkage and on the other hand a highly fluid adhesive that wets substrate surfaces efficiently or can be readily worked into the fillers. The hazard potential of the raw materials in the polymers is eliminated in the reaction of the starting materials.

The actual EP resins are diglycidyl ether of bisphenol A and epichlorohydrine and prepolymers with different molar masses. The epoxy group with highly reactive oxygen bonded to two carbon atoms is typical. The crosslinking reaction of the two-component, cold-curing adhesives is initiated by a curing agent containing active hydrogen atoms. The curing agents are mainly aliphatic and aromatic amines, thio compounds, and polyaminoamides. The high reactivity of the primary amines is responsible for the hazard potential of resin-curing agent mixtures, so that the cold-curing mixtures (frequently used in consumer products) in particular require special protective measures up to the end of the crosslinking reaction.

Higher temperatures are required to process warm or thermosetting prepolymers. The curing agents are dicyandiamines and the anhydrides of aromatic carboxylic acids, for example phthalic acid anhydride or hexahydrophthalic acid anhydride. Some EP adhesives are also termed high-temperature adhesives. If the melt temperatures of the curing agent and the molar masses of the prepolymers are very high, solid mixtures result at room temperature that have to be melted before processing.

The adhesive components can also be produced as layers on films or textiles or without carrier materials if they form solid films at room temperature. For this purpose, they are applied warm, in thin layers, or in solute form, to foils and textiles and the carrying materials (preferably made of glass fibers, carbon fibers, or metal netting) are integrated into the bonding joint after the thermosetting process. The adhesive films frequently contain fillers made of Al oxide, Cu, Ag, Al, etc.

The resin-curing agent mixture ratios required to maintain the stoichiometric conditions are usually between 10:1 and 1:1, whereby a 1:1 ratio is the most suitable for mixing and dosing purposes. In any case, thorough mixing is important since curing only takes place where sufficient curing agent is locally available to the EP resin for crosslinking.

Among the decisive criteria in processing EP adhesives are:

- Storage stability
- Viscosity
- Mixing ratio
- Temperature of the mixture and thoroughness of mixing
- Processing and fixing time
- Process temperature and curing time

In all 2C EP resins it must be remembered that, for application purposes, it is the viscosity of the mixture and not the viscosity of the components that is important, so that highly viscous resins, mixed with low-viscosity curing agents, can result in mixtures that wet efficiently. These curing agents with a "diluent function" are often highly volatile, so cautious handling and disposal must be ensured.

In all cold-curing 2C EP resins, crosslinking begins immediately after resin and curing agent are mixed. Since the crosslinking reaction is always exothermic, i.e., with an energy excess, and is always most rapid at the beginning, the viscosity drops somewhat at first, only to rise again when crosslinking sets in. When viscosity is lowest, the resin and curing agent (as well as all other components) should be thoroughly mixed once again since the mixing effect is greatest at this point.

During the crosslinking reaction, the adhesives pass through the states liquid → gelatinous → rubber elastic → solid.

In practice, it is important to note that the adhesives can only be processed up to just before they turn gelatinous, i.e., positional corrections are only possible up to this point. The time between first mixing and the transition to the gelatinous state is known as the "potlife" – an expression that reflects in a concrete manner how long a mixture can be used "in the pot." Any application of a 2C adhesive after the potlife is over means a loss of strength, which also applies to any positional correction or readjustment after this point.

Since crosslinking reactions are always exothermic and the reaction rate rises with temperature, there is an "explosive" rise in temperature if the reaction mixture starts out at a very high temperature and the reaction heat is not dissipated quickly enough. The reaction may then take place so quickly that the adhesive overheats in an undesirable manner, in which case the potlife would be drastically shortened. The product of such a reaction is then a brittle, hard adhesive with reduced adhesion and long-term stability. It is therefore important to prepare small batches of highly exothermic reacting 2C adhesives, to cool the mixture of resin and curing agent if required and to stir it from time to time to dissipate the heat generated at the core. Aside from the quality problems, there is a particular risk during the phase of exothermic overheating that some of the curing agent might evaporate or become highly volatile. If personal protection measures are insufficient the products will be deposited on the skin or equipment and may cause damage to health, either immediately or at a later time. If the material is processed properly there is no potential hazard, since completely crosslinked adhesives are only normal “household waste.”

The potlife – or working life – of the mixture is not a universal parameter, but depends on the type of adhesive involved. It is about 20 min for rapidly reacting adhesives, which are usually prepared in small amounts, and several hours for adhesives that have to be mixed in large-volume batches. As soon as the adhesives are applied in thin layers, the positive reaction heat loses its significance because of the relatively efficient dissipation from the thin layer.

In addition to the cold-curing EP resins there are also 2C systems that require a minimum temperature so that the crosslinking reaction can take place within a technically acceptable timeframe. The advantage of these thermosetting 2C adhesives is that their curing times can be varied. If the materials to be bonded and the technical conditions allow, the curing time can be shortened with increasing temperature. Phased or constant temperature increases represent an important adjustment parameter for production times. In the cases of plastics it is of course impossible to raise the temperature without limit, since the properties of the plastics themselves change drastically with rising temperatures. Even if high-temperature curing is understood as an additional tempering effect that shortens the production time, the higher temperatures also mean greater cooling tensions and greater tension factors in contact with other materials due to differences in the coefficient of expansion (the so-called α problem).

To eliminate errors resulting from mixing or due to the exothermic reaction heat, so-called 1C adhesives were developed. These EP resins are only single-component adhesives in a procedural sense: Chemically they are still two-component or multiple-component adhesives. These resins frequently contain additional catalysts that influence the course and kinetics of the reaction.

Primers, sometimes called “self-adhesive resins” or adhesion promoters, can be used to improve adhesion, for instance Self-Adhesive Resin EP 2440, Hüls AG, Marl. The resin is soluble in many different solvents and can thus be readily applied before the adhesive. It is also used as an adhesion promoter for polyester and ketone resins. Other adhesion promoters include 0.5% silanes in methanolic solution. They are mixed directly into the adhesives or applied to the adhesion surfaces.

The shearing strength of most EP adhesives is around 15–40 MPa depending on the nature of the test sample and material used, for methacrylates 15–22 MPa and for PUR 5–20 MPa, i.e., maximum strengths can be expected with EP adhesives compared to the other types.

3.3 Polyurethane (1C and 2C Systems)

PUR adhesives have shown the most annual growth of all adhesive types at 3.5%. The absolute volume/year for these products exceeds that of all other reaction adhesives. As is the case in all PUR chemical applications, the PUR adhesives show a variety not found with other reaction adhesives.

The basic reaction of all polyurethane adhesives is the reaction of diisocyanates (isocyanate group –N=C=O, curing agent, B component) with polyvalent alcohols (OH groups, resin, A component). Many different diols or polyols (bivalent aliphatic or aromatic alcohols, e.g., adipic acid, butylenes glycol, hexantriol) are used as resins. The hydrogen atoms of the OH group are the so-called active hydrogens. The adhesive character and curing curve can be influenced by the selection of the isocyanates diols and polyols, resulting in the urethane group –NH–CO–O–, also known as carbamide acid ester, which has given this product group its name. In the polymeric state, the PURs consist of flexible soft segments and rigid hard segments. The soft segments can crystallize and hydrolyze, i.e., they are moisture-sensitive.

Linear PURs are made from diphenylmethane-4.4′-diisocyanate (MDI) and 1.4-butylene glycol. Aliphatic polyols are cheaper and more reactive, but have a lower level of thermal stability; the aromatic polyols are more expensive, less readily reactive and have a higher level of thermal stability. TDI is the classic substance used for crosslinking of the polyols. TDI is toluene-2.4-diisocyanate (CH_3–Ph–$(NCO)_2$). This crosslinking or curing agent is the least hazardous of all diisocyanates.

Further attachment of 1.4-butylene glycol to the intermediate products made of MDI or TDI with diols or 1.4-butylene glycol results in chain accretion. The attachment of the diols to the isocyanate group results from an atomic rearrangement: hydrogen attaches to the nitrogen atom, the oxygen atom to the carbon atom:

$$\mathrm{R - NCO' + OH - R1R - NH - CO' - O - R1.}$$

The basic process of crosslinking can be accelerated or delayed, i.e., the production time can be determined by adhesive selection. On the other hand, the reaction with water is also possible (OH–H), whereby the following group would result: R–NH–CO–OH. The compound is unstable and continues to react by splitting off CO_2 and forming an amine R–NH_2 or a diamine. The CO_2 is a foaming blowing agent, not desirable in adhesives, since the CO_2 formation would produce an adhesive layer containing bubbles. The resulting amine also continues to react. This results in “hard,” inflexible, high-melting polyurea segments (R–NHCO–NH–R1–NH_2) within the PUR, which are frequently undesirable. Aromatic PURs are most frequently used as the basis of PUR adhesives, of which there are two types: the polyester polyurethanes and the polyether polyurethanes.

Polyester polyols are the esters of dicarboxylic acids with bivalent alcohols, resulting in intermediate products with two terminal or functional OH groups (diol). The dicarboxylic acids may be either aliphatic or aromatic, which is also true of the esterifying alcohols. The polyester polyols contain fewer OH groups (about 8–10). The adhesives have a high polarity/volume and therefore adhere well to many different materials. The polyether polyols result in low-viscosity, hydrolytically stable adhesives.

Blocked isocyanates are also used for thermosetting 1C PUR adhesives: When the R–NCO group react with OH–Ph (phenol), the result at low temperatures is RNHCO–O–Ph. At higher temperatures, the product "disintegrates" into the starting materials, whereby most of the phenol is also integrated in the PUR. Since there are still residues, however, the primary adhesive products result in adhesives that are thermally activated by blocked isocyanates, the toxicity of which must be checked carefully. Most 1C thermosetting PUR adhesives contain so-called latent curing agent (e.g., Tivoli Hamburg: Tivo 9551).

The most important reaction in all PUR adhesives is the crosslinking of the prepolymers with air moisture. This results in moisture-hardening adhesives and end products of the entire reaction (1C adhesives) with very long curing times. The products are packaged in Al cartridges or composite films, since contact with moisture must be avoided by all means. The crosslinking reaction is not stoichiometric, since water is once again produced during crosslinking. In terms of application, this means that the crosslinking process cannot be stopped once it has started. Then again, the reactions are very gradual, so that crosslinking in thick layers may take several weeks.

1C, moisture-crosslinking PUR adhesives are silicone-free sealants and adhesives that can be painted over after application and can be used "overhead" due to their thixotropy. Rapid skin formation in sealing applications ensures product reliability.

With their close resemblance to the properties of most plastics, polyurethanes are particularly well-suited for bonding of plastics such as PC and PMMA. The adhesives are ductile, have a low glass transition temperature, a lower inherent strength level than EP adhesives, and a highly variable potlife.

Typical data for 2C PUR adhesives:

Mixing ratio (resin) A: (curing agent) B	3:1–5:1
Viscosity component A	5.000–25.000 mPa s
Viscosity component B	1.000–4.000 mPa s
Density (depending on type and amount of filler)	1.30–1.60 g cm^{-3}
Potlife	60–240 min
Setting strength	8–20 h
Final curing strength	16–48 h

The 2C PUR adhesives are generally slow-reacting adhesives that require a longer period until the reaction is completed: In practice, this means long fixing times, high equipment costs and workplace safety expenditures unless booster systems are used. To increase adhesion, primers based on special condensation resins are used, applied in solvents with a high hazard potential, for example the primer 8310 (Kleiberit Klebchemie Weingarten), a 2.5% resin solution in methylene chloride.

The use of diisocyanates should be kept as low as possible due to their carcinogenic potential (whereby the classification of isocyanates as carcinogenic or genotoxic according to TLV (*MAK*) III A and B is still incomplete and therefore speculative) and adhesive manufacturers have therefore made considerable efforts to find substitutes. Prepolymeric urethanes with silyl groups are products that do not require isocyanate groups for crosslinking and are therefore suitable for special applications in adhesives and sealants on the basis of toxicological considerations (MS adhesives).

An example of an application of these special adhesives is their contribution to the construction of liquid gas tanks and tanker gas transport. Worldwide transport of this fuel would not be feasible from an ecological point of view without this adhesive technology, since the construction of large-scale tankers was first made possible by development and use of suitable insulation and bonding applications. The adhesives had to yield high-strength bonds, for instance at temperatures down to −160°C. This specification was met by use of these specially modified adhesives with an interpolation of PUR and silicone adhesives (MS adhesives), see details in Sect. 3.6.

The formulations of the PUR adhesives not only make for excellent adhesion to many substrates, their electrophilic reactivity is also a source of potential hazards to humans and the environment. It is therefore necessary to identify the emissions from the different types in this class of adhesives in particular, whereby not only the emitted substance is important, but also their absorption tendency and residual reactivity, since the substance alone is not potentially hazardous.

Outgassing chambers with a volume of approx. 2 l, Fig. 7, are suitable for analysis of the adhesive emissions. Outgassing chambers make it possible to measure specific

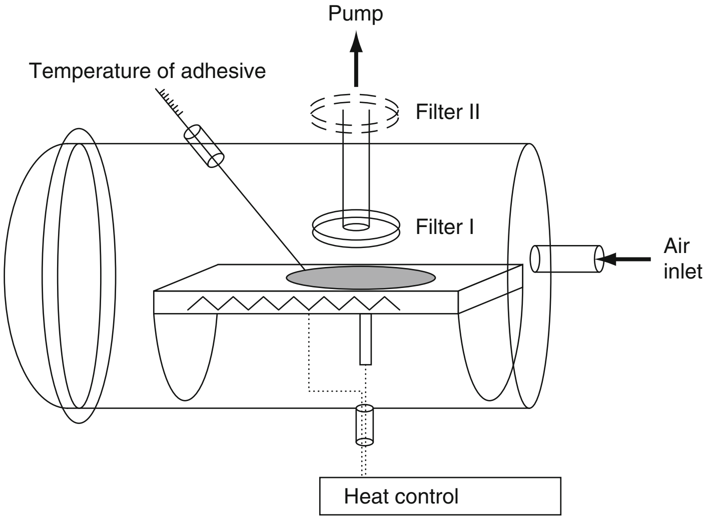


Fig. 7 Apparatus for analysis of the outgassing of adhesives

outgassing rates (μg m^{-2} h). The outgassing substances are derived and separated by means of HPLC. The individual substances can then be identified analytically, for example by means of fluorescence and UV detection. Outgassing is gas phase-controlled in the first phase after mixing, i.e., the process depends on the ambient air pressure. After a network structure has been generated, it is diffusion-controlled, i.e., the process depends on the layer thickness. What this means in practice is that the mixtures must be prepared under extraction hoods, in large rooms or with strong ventilation. Such measures would greatly reduce the hazard potential after the initiation of the crosslinking reaction, so that curing will not require so much ventilation.

The emission rates for thermosetting PUR adhesives can be expected to be higher than for cold-curing adhesives by a considerable margin, since gas phase-controlled outgassing occurs up until the start of the crosslinking process and volatility of course increases with temperature.

In isocyanates, the hazard potential depends to a considerable extent on air moisture. Because of the high level of reactivity, with water among other substances, the primary products show rapid chemical changes in moist air and lose their toxicity. It is therefore always better to work under conditions of high humidity and to wipe off the adhesive joints with a wet rag after fixation if possible. Outgassing in 1C and 2C PUR adhesives are reduced to practically zero within 10% of the total curing time.

3.4 Polyester Resins

In addition to the saturated polyesters (the best known of which are the thermoplastics PET and PBT) there are also unsaturated polyesters which, dissolved in styrene, are typical adhesives for polyester laminates and similar duromers. The decisive thing for these adhesives is the integration of the styrenes in the polymer structure after curing so that the styrene makes it possible to apply the liquid adhesive, but need not evaporate. The styrene content is between approx. 20 and 30% by mass. Styrene has the effect of a diluent and thus has a significant effect on the working viscosity. The crosslinking of the polyester resins and styrenes is a radically initiated copolymerization, whereby the reaction is initiated by catalysts (peroxides, preferably cyclohexanone peroxide for cold-curing adhesives and benzoyl peroxide for thermosetting adhesives) and accelerators/cocatalysts (preferably cobalt accelerators), in which case one would have cold-curing, two-component adhesives. Some adhesives do not require an accelerator, but have to be heated to between 80 and 120°C to initiate radical formation and thus copolymerization. The styrene in the adhesive links the polyester molecules that are lengthened by polymerization, so that no cleavage products occur during crosslinking. This reaction does, however, involve up to 10% shrinkage of the resin. The addition of fillers and short glass fibers not only reduces shrinkage, it also avoids internal stresses and raises both the modulus of elasticity and load-bearing capacity of the bonds.

One characteristic of adhesives is gelling after the reaction starts or after the catalyst and accelerator are mixed. The time interval between mixing and the termination of gel formation is called the gelling time. During this time, the viscosity of the adhesive has already increased (gelatinous state), but the structural component can still be shifted. Once the gelling time is past, further shifts in position will result in considerable loss of adhesive strength, i.e., the fixation of the adhesion surfaces must be completed within the gelling time.

The crosslinking reaction has a pronounced exothermic character, so that the amount of adhesive mixed should always be as small as possible. A small overdosage of catalysts or accelerators results in a sharp rise in the temperature of the adhesive mixture. These problems are not experienced with thermosetting adhesives, since the decomposition temperature of the catalysts (radical formers) is required at any rate. As the temperature rises, the crosslinking time can be shortened, so that the process times can be adjusted by means of the temperature level. The curing times of thermosetting adhesives range from 2 to 10 min and are thus much lower than those of cold-curing adhesives (several hours). At excessively high temperatures, the high levels of cooling stress and energy requirements must be taken into account.

Aside from a number of problems associated with the application of these adhesives (low flash point, strong styrene odor, high levels of expenditures to ensure compliance with styrene TLVs, highly exothermic reaction), they are frequently used to bond large-surface laminates made of fiber-reinforced unsaturated polyesters (UP) or epoxy resins (EP) or to repair such structural components. The extremely high costs caused by the strong odor of the styrene vapors have led to development of polyesters with different solvents as chain extenders, also reducing the hazard potential of the adhesive mixtures (or laminating resins).

3.5 Silicone Adhesives (1+2C Systems)

Silicone adhesives are crosslinking prepolymers that cure with air moisture or contain latent curing agents and are therefore processed as single-component adhesives. Two-component systems are those in which the curing agents have to be added prior to processing. In the silicone adhesives, the polymeric skeleton is not made up of carbon, but rather comprises a silicon-oxygen chain (siloxane structure). This structure has a high level of thermal stability, so that the silicone adhesives are among the heat-stable adhesives.

When silicone adhesives react with air moisture they are called RTV-1 silicone adhesives (RTV: room temperature vulcanization). The RTV adhesives have a “rubber-like” character. The term vulcanization is not technically correct, but is rather an historical reference. Silicones are elastomers and were at first crosslinked like other elastomers, albeit not with sulfur. In the integrated state, silicones contain blocked crosslinking agents that lose their blocking function upon contact with moisture. There are various different types of crosslinking agents with different cleavage products, for example acetic acid, amines, or oximes. These cleavage products determine the odors given off in the crosslinking process and are the decisive factors determining the hazard factors of the adhesives. The cleavage products are released during crosslinking and afterwards, so that environmental contamination can occur even after a number of weeks. The crosslinking of RTV-1 adhesives is diffusion-controlled, i.e., in wide gaps complete curing can take a long time.

RTV-2 adhesives are solidified with a curing agent like all two-component adhesives. This reaction is not diffusion-controlled, so that the adhesives are suitable for bonding (and sealing) large adhesion gaps. There are two different reaction types for initiation of crosslinking: condensation reaction and addition reaction. The end products differ in their chemical structures.

Because of their high level of elasticity, which changes little until a temperature of approx. 150°C is reached, these adhesives are particularly suitable for use with metal–plastic bonds exposed to wide temperature variations (compensation for dimensional changes).

3.6 Silane-Modified Polyoxypropylene

The oxypropylene chains (polyether groups) of these adhesives include so-called alkoxysilyl groups at the ends of the chains capable of crosslinking with moisture like 1C silicones. The MS adhesives are therefore classified between polyurethanes and silicone adhesives. Because of their hybrid structure, they adhere strongly to many different substrates (PA, PC, PP, EPDM, GFP, practically all metal and glass types), even without primers. These adhesives are resistant to UV radiation and weather influences.

3.7 Methacrylate (1C and 2C Systems, A/B Systems)

Methacrylates, in combination with peroxide curing agents and accelerators, result in adhesives that react very quickly and are notably transparent. They are therefore preferred for bonding of transparent plastics such as PMMA, PS, PET, or PC. The resin to curing agent to accelerator ratio in these adhesives can vary within certain limits. Polymerization of methacrylates is radical-based, i.e., in principle the reaction is initiated by the curing agent. On the other hand, the amount of curing agent determines the reaction rate and polymer chain length, so that a certain amount of influence can be exerted on the adhesive strength. If the peroxide concentration is too high, relatively brittle adhesive layers are produced quite quickly. In a technical sense, polymerization requires accelerators, since only under their influence will the curing agent fulfill its initiating function rapidly enough. This fact is exploited in adhesive production and application. One the one hand, the methacrylates (monomers in powder form) are mixed with a suitable accelerator to make a chemically stable liquid (component A), on the other hand, a suitable accelerator is mixed with the monomers to make the liquid component B. That way, components A and B can be applied to both surfaces of the plastics to be joined in preprocessing. The polymerization reaction then begins after contact. These are the so-called A/B systems. Of course the A and B components can also be mixed immediately prior to joining and then applied to the adhesion surfaces. Joining must then be done without delay (corresponding to the processing of 2C systems). When the curing agent is dissolved in a solvent and applied directly to one joining surface, a reactive layer develops after the solvent has evaporated. After application of component B and joining, the polymerization reaction begins in the monomer. The adhesive is processed like a single-component system. No specific mixing processes are required, so it is called a "no mix" system. The curing agents and accelerators used in the past were by no means nontoxic, so new systems are now being developed. The adhesion gap for A/B systems is limited to about 0.4 mm, so that maximum gaps of 0.8 mm can be filled. The setting strength is reached after 2–5 min, final strength after 24 h. Since peroxides (preferably cyclohexanone and benzoyl peroxide) are used with these adhesives, there is a constant hazard potential. At excessively high temperatures conditions develop under which spontaneous combustion cannot be prevented. Also, direct contact with peroxides is harmful to health because of the highly reactive nature of these substances. The adhesives are, however, harmless when radical polymerization is completed. The uncrosslinked residues are special wastes, the crosslinked residues are household wastes.

More recent viscoelastic 2C acrylate adhesives often adhere to low-energy surfaces as well, making them suitable for adhesion to polyolefins without pretreatment (3 M Scotch-Weld DP 8005). The 2C acrylate adhesives are often supplied in double cartridges (side-by-side cartridges), whereby the flow-mix principle is used. Users process the adhesive like a 1C system. These acrylate adhesives are transparent and UV-stable, making them suitable for bonding glass. They can also be painted over.

3.8 Cyanacrylates

The methyl and ethyl ester of the α-cyanacrylates and modified variants are known as so-called "rapid adhesives." The term makes it clear that the adhesives react rapidly, so that the adhesion process can be readily integrated into existing production processes. At the same time, these are solvent-free adhesives that adhere to practically all materials. In the liquid state, these adhesives are low molecular substances that polymerize rapidly in the presence of OH ions. Polymerization is suppressed by certain additives in the liquid state. Initiation of polymerization requires only a very small amount of OH ions, so that the moisture on the substrate surface suffices to start the reaction.

Uniform adhesive strength requires constant air moisture levels between 40 and 80%. The reaction is delayed or even suppressed entirely on acidic surfaces.

Cyanacrylates can only react completely in thin layers. The structural components must therefore be joined with an exact fit and uniform adhesion layer thickness. The viscosity levels of the adhesives are between 4 and 20.000 mPa s. The highly fluid adhesives are suitable for production of adhesion layers of 0.02 mm, the more viscous fill gaps up to 0.3 mm. Adhesive strength drops as the gap width increases, since filling the gap requires modification of the adhesive.

Earlier disadvantages of adhesives such as brittleness, poor water resistance, blooming around the applied adhesive, or unpleasant odors have now been remedied to a considerable degree.

Since in the final state these are thermoplastic adhesives, the utilization temperature of the adhesive bonds is limited to approx. 80°C. Some adhesive types are heat-stable up to 130°C, although the "adhesive strength" at this temperature is greatly reduced since in this case the inherent strength of the cyanacrylate determines the stability of the plastic bond.

Typical properties of cyanacrylate adhesives:

- Rapid reaction, resulting in short process times, 1–15 s
- Reaction rate can be adapted to production conditions
- Adheres very well to PVC-U, ABS, SBR, SAN, EPDM, PET, PBT

Primers are used to increase adhesion of cyanacrylate adhesives to plastics that present adhesive difficulties (e.g., PE, PP, POM, thermoplastic elastomers (TPE), SI). These primers, dissolved in a rapidly evaporating solvent (frequently heptane), are applied in a thin layer and form, after an evaporation time of 20–60 s, an effectively adhesive layer on the plastics. Since they react with the adhesive at the same time, the results are high-strength adhesive bonds. In tensile strength tests with PE and PP, adhesive strengths of up to 8 MPa have been achieved. No special surface pretreatment is necessary. The primers are fluorescent, making it easy to check for full coverage of the adhesion surfaces and joints. The primed surfaces can also be put into intermediate storage for up to 2 days without any significant loss of strength.

Pretreatment methods such as flaming, corona treatment, or ND plasma treatment are not useful, or even disadvantageous, with cyanacrylate adhesives due to the formation of acidic cleavage products or components on the surface.

Pneumatically powered devices fitted with a wide range of dosing needles are available for application of even the tiniest amounts of adhesive, Fig. 8. This means a high level of consistency in the adhesive amounts and surface areas – an important precondition for uniformly reproducible adhesive strength levels. Also, loss and waste of adhesive is minimized in such applications, so that very little waste disposal is required. Boiling in alkaline solutions completely depolymerizes and dissolves the adhesive. This facilitates reprocessing or dismantling of adhesively joined structural components.

Fig. 8 Dosing unit for cyanacrylates

3.9 Dimethacrylates (Anaerobic Adhesives)

Dimethacrylates are solvent-free, single-component adhesives with special properties. Since the transition from liquid to solid state in these adhesives is only possible in the absence of oxygen, i.e., under "anaerobic" conditions (anaerobes are bacteria that thrive in the absence of oxygen), they are called anaerobic adhesives. Polymerization cannot take place in the presence of oxygen, i.e., as long as an oxygen atmosphere is present above the adhesive it remains liquid. Curing requires not only the absence of oxygen, but also the presence of metal ions, in particular Fe or Cu ions. The anaerobic adhesives are therefore used with plastics in combination with activators, here also designated as primers. Since some plastics contain residual amounts of metal ions from catalysts and stabilizers, curing conditions differ from plastic to plastic. In plastic–metal bonds, the curing rate may also vary because of greater reactivity on the metal side. Closed oxide layers on metals also influence the curing process. Oxides act as passive layers, so that shorter curing times results from their removal (grinding, sanding, sandblasting). Photoactivated anaerobic adhesives make use of a capacity for releasing metal ions in response to light irradiation, activating the crosslinking reaction in this way.

This anaerobic reaction mechanism has been put to use in particular as a screw compound and to achieve a sealing effect in narrow gaps. The adhesive can be applied in thin layers without the curing reaction being initiated immediately. The curing process does not begin until the bolting and assembly procedures are completed. The varying tolerances of different screws determine the "adhesive gap" in each case, so that excess adhesive can be removed before curing commences. In the same way, uneven surfaces and roughness variations are smoothed out on seals. However, there's a connection between viscosity and complete gap filling, i.e., the viscosity or adhesive must be selected to fit the specific application.

The available viscosities are between 100 and 7.000 mPa s. The low-viscosity adhesives are used mainly to fill and seal narrow gaps. The high-viscosity types are very effective fillers and are therefore used to fill and seal larger gaps. The degree of roughness of a metal surface can vary between 5 and 40 μm. On the other hand, the achievable adhesive strength levels drop as gap widths increase and are at 0.25 mm only 20% as high as at 0.05 mm.

In addition to the screw sealant function, plastic seals can also be attached quickly and reliably. With a combination of photocured and anaerobically cured adhesives, rapid fixation and reliable sealing can be achieved.

Since the dimethacrylate adhesives are thermoplastics, they “soften” as the temperature rises. This effect is made use of to dismantle screw compounds and seals, whose connections are insoluble at room temperature but soluble at higher temperatures.

Anaerobic adhesives are heat-stable up to about 200°C and show no loss of strength under a continuous heat load of up to 130°C. The temperature range for use of these adhesives is therefore above that of most other plastics.

The reaction rate of anaerobic adhesives can be increased by heating, making it possible to adapt the adhesion process to other production processes. At temperatures under 10°C the curing reaction (nearly) stops.

These adhesives possess no specific hazard potential and are a good example of an unproblematic adhesive application.

3.10 Photocuring and UV-Curing Systems

When special acrylates, epoxies or silicone photoinitiators are added, these adhesives are cured spontaneously by lightwaves or UV radiation. The crosslinking reaction is initiated at certain wavelengths only on the basis of the photoinitiators selected. It must be noted, however, that the curing rate is very high at the moment of “exposure,” so that technical cycle times of 0.3–10 s are feasible.

These solvent-free, so-called PI, adhesives are used to join PC, PMMA, PET, PS, PVC, and glass, whereby at least one component must be transparent, so that the composites usually comprise plastic–plastic, glass–plastic and plastic–metal combinations (optics industry, microelectronics). In exceptional cases (fixation of structural components on nontransparent carriers), it is also possible to cure a surrounding strip of adhesive directly.

The wavelengths at which the photoinitiators are activated are between 380 nm (UVA radiation) and 700 nm (visible light). A working wavelength in the 500 nm range is called blue light. Light sources that emit a specific wavelength spectrum, for example UV lamps in connection with UV lightwave conductors, are used for curing. By means of flexible glass fiber cables, the radiation can also be transmitted directly to the adhesive joint, making automated production possible. In the so-called blue light tunnel, adhesive activation can be done discontinuously (batch operation) or continuously (use of conveyor belts).

Since the adhesives only crosslink at specific wavelengths, the parts to be joined can be premounted and fixed with a high degree of positional accuracy under normal workplace conditions. Quality control can also be realized (proof of adhesive application, positional correction) without affecting the adhesion of the bond.

Use of these adhesives not only requires that one part be transparent: The components must allow the radiation to pass through them and to get to the photoinitiators with a sufficient level of intensity. Since the transmission characteristics of the different plastics are wavelength-dependent, this influential factor must be taken into consideration when selecting the adhesive. The interdependence of the factors transmission, adhesive selection, and plastic type becomes most readily apparent when the plastics contain photostabilizers or UV blockers. These substances extend the curing time by a considerable margin since the task of a photostabilizer is to prevent light from destabilizing the plastic material, in particular to ward off the effects of UV radiation. The exposure time for photostabilized PVC must be considerably longer than for unstabilized PVC to achieve the same adhesive strength. Adhesive strength not only depends on the sensitivity of the initiator and radiolucency of the components, but also on the intensity of the curing light and the power density brought to bear in the adhesive joint in terms of the adhesive volume present there. Therefore, the distance between the light source and the adhesive joint also influences the curing process. The distances between the light sources are approx. 80 mm, the light intensity is 30–100 mW cm^{-2}. The adhesives can be used to seal gap widths up to about 0.5 mm, especially in glass–plastic combinations.

The photoinitiators and the types of the initial chemical products determine the course of the reaction in the photocuring adhesives. A radical reaction requires lightwaves with lengths between 315 and 500 nm, whereby the reaction is stopped the instant the light source is switched off (for plastics polyurethane-modified acrylates, in particular polyetherurethane acrylates (BASF), photobond adhesives). This mechanism can be technically exploited. It must be remembered, however, that in radical, very rapid polymerization processes sticky layers can form with oxygen on the surface of the adhesive that are in some cases undesirable. In the cationic reaction, lightwaves with wavelengths of 400–500 nm are required (for plastics, photoactivation of *Katiobond* adhesives on EP basis). As soon as the cationic reaction has been initiated after photoexposure, i.e., as soon as the polymerization process has been activated, complete curing ensues. The reactivity of the initiators and the primary substances determine whether the final strength of the bond is reached after a few minutes or after 24 h. Cationic curing has the advantage that the reaction rate can be accelerated or continued by means of heat. Cationically reactive adhesives can also be thoroughly cured by means of a heat treatment in so-called shadow zones, i.e., areas not reached by the lightwaves. The initiation of the curing reaction, and thus the origin of initial adhesion strength as required in the technical process, is realized by photoactivation. The fixing times of the adhesive bonds can be reduced by a considerable margin. The final strength will result from a more or less intensive heat treatment.

The curing times of photocuring adhesives are between 1 s and 15 min. For this reason, these adhesives are particularly attractive for large series production (e.g., production of chips). These adhesives must also possess good capillary qualities to achieve rapid distribution into the, usually narrow, adhesion gaps in all rapid process steps. The viscosities are between 70 mPa s and 30 Pa s.

The UV-curing polyacrylates are particularly variable in terms of flexibility, viscosity adjustment (microdosing in the μg range), flow behavior (thixotropy), and adhesion. Flexibility is particularly important in hard–soft combinations such as plastic–metal and glass–plastic in order to compensate for expansion due to temperature variations. UV-curing adhesives are also used for cladding applications in composites.

3.11 Postpolymerizing Adhesives

Postpolymerizing hotmelt adhesives, a combination of reactive and nonreactive systems, represent an important development in the adhesives sector. They are processed like hotmelt adhesives, after which a postreaction sets in without any further technical measures, involving in particular the crosslinking of the existing thermoplastic structure. The postreacting hotmelt adhesives, also known as reactive hotmelt (RHM) adhesives, include mainly polyurethanes, PUR/EVA copolymers, silane-modified polyoxypropylenes and silanized, amorphous poly-α-olefins. Reactive hotmelt adhesives based on bismaleimides are special products that are processed like hotmelt adhesives but behave like duromeric polymers after crosslinking. Volatile organic compounds (VOC) measurements with these adhesives have demonstrated that no significant outgassing volumes occur. Since these adhesives contain no solvents, only small amounts of intermediate products are detected. The butylhydroxytoluene detected is an antioxidant that is added to many plastics. More problematical is the detection of 1.4-dioxane derivatives resulting from secondary reactions of propyl glycols and ethyl glycols. These dioxane compounds must be classified as carcinogenic on a precautionary basis.

Reactive hotmelt adhesives in the initial state are meltable prepolymers with isocyanate groups. The crosslinking agent diphenylmethane diisocyanate, MDI, determines the toxicity of the adhesives. With the polyurethanes as well, air moisture initiates the crosslinking process. This raises the inherent (structural) strength of the material, improving the mechanical and thermal stability of these adhesives as compared to the initial state. The postpolymerization process ceases after about 2–7 days, depending on the reactivity of the polyurethanes, Fig. 9. There are thus two different strength levels: a technically necessary strength built up rapidly at the beginning, followed by later development of the strength level required for practical utilization.

The reactive hotmelt adhesives retain a high level of flexibility and dynamic load-bearing capacities even after crosslinking and are used to join plastics to one another as well as to wood (furniture industry), glass (construction industry), aluminum (sandwich elements), and painted surfaces. Typical applications include window casement sheathing, foil laminations, clip fasteners, bookbinding, textile

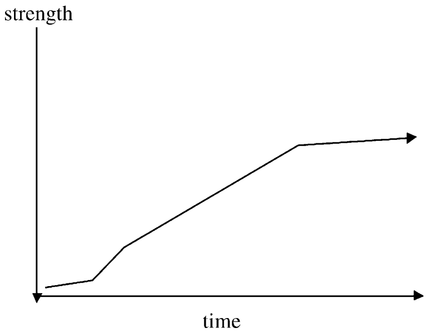


Fig. 9 Strength increase in postpolymerizing hotmelt adhesives

adhesive applications, and paneling in motor vehicles. The different materials that can be joined include PP, PVC, ABS, leather, wood, and aluminum. Since the melt temperatures are between 80 and 160°C, thermally sensitive materials such as very thin films can also be adhesively joined. The precondition that always applies is accessibility to moisture.

Since wood, leather, and textiles always continue to "supply" sufficient moisture, these materials are particularly well-suited to adhesive joining with these adhesives. With impermeable adhesives, the moisture can only diffuse through the adhesive film, so that the postpolymerization process is much slower; exceptions to this include, for example, polyamides that contain moisture.

1 day	40% Final strength 1–3 MPa
4 days	90% Final strength
7 days	100% Final strength 5–10 MPa

It must also be kept in mind that undesirable moisture diffusion, for example during storage, will also initiate postpolymerization, significantly shortening the stability period of the adhesives.

The application temperatures are normally around 120°C. As the temperature rises, working viscosity levels drop, as does the thermal stress load and the rate of reaction with moisture. Processing requires special equipment to ensure gradual and gentle heating and melting as well as exclusion of air moisture from contact with the adhesive prior to application (tank farm storage under dry nitrogen gas).

RHM adhesives have the following advantages over the standard hotmelt adhesives:

- Greater heat resistance
- Greater solvent resistance
- Less sensitive to hydrolysis

3.12 Nonreactive Adhesives

Nonreactive adhesives are already in their final chemical state at the moment of adhesive application and therefore do not require any special dosing or mixing processes. There is also no reaction time to achieve maximum adhesive strength. The adhesive strength is derived solely from physical processes such as the evaporation of solvents and the cooling of melted adhesives. The parameters by which the adhesive process and adhesive strength are influenced therefore differ from those that apply to the reactive adhesives. On the other hand, many nonreactive adhesives are modified to enter into chemical interactions with plastic surfaces after application. Chemical interaction with metals is less frequent.

3.13 Solvent and Diffusion Adhesives (Adhesive Varnishes, Contact Adhesives)

Although solvent applications are becoming less frequent for reasons of environmental protection and the high cost of workplace safety, there are a number of applications in which pure solvents and solutions of plastics have proven to be the best adhesives for plastics. The basic principle of solvent and diffusion adhesives is the ready solubility and/or swelling of plastics in response to the effects of organic solvents. Both processes, dissolution and swelling, depend on both the plastic and the solvent used, so that there are no "universal adhesives." Plastics with polar groups and low crystallinity are readily soluble. This makes them suitable for diffusion adhesion and they are frequently classified as readily bondable (PS, PMMA, PC, PVC). Many amorphous plastics show very ready solubility, but also a tendency for stress cracking.

Diffusion and adhesion bonding are based on different adhesion mechanisms related to solubility.

The solubility of organic solvents proves useful in a number of ways: It is made use of in production of plastic solutions as well as for direct bonding without any other adhesive film in the adhesive joint. Both processes are also known as "cold or solvent bonding or welding", although these terms are not, strictly speaking, technically accurate.

When pure solvents are used, the "adhesive process" involves the rapid dissolution or partial dissolution of layers close to the surface, which are then mixed when the parts are joined by means of light pressure. In the segments of the bonding joint in solution the levels of molecular mobility in the polymers are raised, and this circumstance already makes an improved "intermolecular mixture" possible.

For PSU and PESU, use of *N*-methyl-pyrrolidone, dimethylformamide, and dichloromethane is recommended (BASF publication).

Another form of adhesive bonding is completely to dissolve a certain amount of the plastic to be bonded, or a very similar plastic, to produce a solvent–solid mixture with a molecularly dispersed character. This mixture may consist of several solvents, plastics, and plasticizers and is also known as an adhesive varnish. Following application of the adhesive, most of the solvent evaporates and only a small amount diffuses into the plastic. The surfaces are joined after the evaporation time. The residual solvent either evaporates later or migrates into the plastics. The adhesive layer thickness is the sum of the wet film thickness and the solid component (mainly the solute polymer, sometimes an added filler as well) in the solvent. The dry film thickness remains after the solvent has evaporated.

The adhesives that are also known as contact adhesives contain, besides the solvents, additional substances (usually rubber-like, sticky primary substances such as natural latex, nitrile rubber, copolymer of BR and 20–40% acrylonitrile, polychloroprene). The contact adhesives are applied to both surfaces. After the solvents have evaporated, the two parts are joined under pressure. Before joining, the adhesive surfaces are in some cases sticky, very similar to PSAs. Significant factors influencing the technical adhesive joining procedure and adhesive strength include the minimum drying time (minimum evaporation or ventilation time and time until the adhesive surfaces are joined, open waiting time), contact bonding time (required joining time under sufficient contact pressure of approx. 0.6 MPa) and the "wet tack" (stickiness after evaporation of most of the solvents, but leaving some residue to ensure sufficient mixing of the polymer molecules upon adhesive contact). With all contact adhesives there is a certain point in time at which maximum adhesive strength can be achieved. This point in time must be determined experimentally, whereby process tolerance is a further important parameter. Within certain limits, contact adhesives can be reactivated by spraying them with the solvent. The adhesives can also be used in spray form, ensuring efficient processing even in small series production. Since the solvents used are characterized by low vapor pressures, their evaporation rates are high. The TLVs are quickly reached when spraying in closed rooms. For this reason, the technique is now mainly used under construction site conditions only.

Contact adhesives can also be processed in the form of aqueous dispersions, whereby the longer time required for evaporation of the water must be taken into account. These contact adhesives are also more sensitive to moisture. Typical examples of contact adhesives are solutions of polychloroprene (CR) (e.g., Baypren from Bayer AG, Neoprene from DuPont). The solvents are xylene, benzine, cyclohexanone, ethyl acetate, or methylene chloride. CR is characterized by a pronounced crystallization behavior with a crystallite melting temperature of 53°C. The crystallinity is controlled in accordance with the specific formula in each case (adhesive contains Zn and Mg oxides that result in partial crosslinkage of chlorine to carbon with double bonds). The adhesive strength and heat resistance increase with the degree of crystallinity, UV stability and flexibility are very high.

The range of contact adhesives has been expanded considerably in recent years, since TPE such as SIS, SEBS, or SEB are also suitable for these applications in combinations with adhesive resins.

Contact adhesives are used to bond polyolefins and so-called low-energy materials both with one another and with painted metals, without any special pretreatment.

The paintability of diffusion and contact adhesives depends on the solvent, the concentration, and the temperature. High solvent concentrations render the contact adhesives readily sprayable, which is particularly important for large surfaces. The sprayability of CR is only ensured at relatively low adhesive content levels of approx. 18%, since the viscosity rises very quickly as the solvent percentage is reduced. The dry film thickness is therefore very low compared to SBS contact adhesives. Since the emission levels (and the attendant disposal costs) can be reduced by raising the concentration of solids, high solid (60%) and super high solid adhesives (80%) were developed. The processing viscosity of these materials is between 300 and 15.000 mPa s.

The dissolution and/or swelling of the molecular structure of the surface layers caused by contact and diffusion adhesives result in the following disadvantages:

- Stress cracking
- Changes in surface optics
- Increased susceptibility to stress cracking

With some diffusion adhesives, solvent residues can still be found in the adhesive joints after several months.

With foams in particular, it must be remembered that solvents quickly dissolve the cell walls so that solvents used in massive structural components are unsuitable for foams. Aromatic hydrocarbons, esters, ketones, and amines can easily destroy polystyrene foams and should not be used as adhesives with these materials.

Typical organic solvents for diffusion adhesives are methylene chloride (for PC, ABS, PMMA), xylene, cyclohexanone (ABS), tetrahydrofurane (THF adhesive for PVC-U, ABS, SAN, SB), ethyl and butyl acetate (ABS), alcoholic-aqueous solution of resorcin and phenol (for PA 6, PA 6.6 and PA 12), DMF, higher primary alcohols, *N*-methyl-pyrrolidone (for PA 11), methylethyl ketone (for CA, CAB, CP, CN, ABS, SAN, SB, PMMA), xylene, toluene for PS. It is remarkable that so much of these solvents is used despite the known high hazard potential.

A typical mixture for a solvent adhesive application comprises acetone, tetrahydrofurane, and alcohols (Cellpack). Agrifix 108 (Röhm, Darmstadt) is a mixture of PC with methylene chloride that is used for adhesive bonding of PC. The contact pressure after the adhesive is applied should be 0.01 MPa. The viscosity of the adhesives can be regulated by addition of a certain amount of PC. Other adhesives are Acrifix 116–118 for PMMA, PS, SBC, ABS PVC-U, CAB, and PC.

Because of their high solvent content levels, most adhesives are not joint-filling, which must be taken into consideration in the structural design. The swelling, i.e., solvent uptake, also releases internal tensions and can lead to warpage in stiff plastics in particular.

The best-known applications of adhesives containing solvents include bonding of PVC tube sections, shoe soles, rubber components, sheathing and paneling with PVC-U foils and PVC-P foils, bonding of “artificial leather,” EPDM profiles on painted surfaces or adhesive bonding of large foam surfaces.

Efforts are also being made to develop and use aqueous dispersed contact adhesives. The main types suitable for use as contact adhesives are the latex dispersions. Tivotakt 2500/61 (Tivoli Hamburg) is a “dispersion contact adhesive” based on E/VA for foams with higher wet adhesion and no solvents. In this product, the increasing stickiness results from the reduction of the water content of the E/VA polymer in the sense of a contact adhesive. Genuine alternatives include mixtures of CR with vinyl acrylate copolymers: The crystallized CR is dispersed in water. As increasing amounts of water evaporate and the film begins to form, recrystallization occurs, i.e., the CR is briefly in an amorphous, sticky (or “tacky”) state. Parallel to this, vinyl acrylates develop high levels of adhesiveness to many plastics and materials that are difficult to bond. The decisive task is to develop formulae that can compete with the CR contact adhesives that contain solvents, especially the 2C systems. 3 M Fastbond is a contact adhesive with an integrated polychloroprene-based activator, which is at the same time a dispersion adhesive and can be spray-applied to foams. The adhesive seams remain elastic and soft due to CR flexibility and a high degree of thermal stability of the CR bond is ensured.

3.14 Dispersion Adhesives

It is normally impossible to disperse plastics in powder form homogeneously in water. On the other hand, the proper chemical modification of plastic particles between 0.1 and 5 μm in size produces stable heterogeneous mixtures with the appearance of milky liquids. Because of the size of the particles, the polymer molecules are distributed as in a dispersion and surrounded by an envelope of water. Decisive for the quality of these adhesive dispersions is the requirement that the particles not coagulate, since otherwise a uniform closed film of sufficient adhesive strength will not be able to form after the water has evaporated. Factors contributing to the stability of the dispersions include the integration of sulfonate groups and addition of surface-active emulsifiers, see Fig. 6. When rubber-like polymers are dispersed, the resulting dispersions are often called lattices because of the similarity with natural latex.

This transformation of nondispersible plastics into dispersion adhesives is carried out with the following polymers:

- Polyvinyl acetate and polyvinyl acetate copolymers (EVA, PVAC for low-cost adhesive bonding of plastics to wood, paper, leather, and metals)
- Polyurethane (suitable for high-strength bonding), ionothanes as adhesion promoters
- Rubber-like polymers (made of polychloroprene, polybutadiene copolymers, SIS, SBS for adhesive bonding of elastomers and as substitutes for solvent-based adhesives)
- Polyacrylates and polyacrylate copolymers (suitable for mechanically and thermally resistant adhesive bonds, no plasticizer migration)
- Fluoropolymers (suitable for very high thermal load levels)

The percentage of solids in the dispersion adhesives is 35–55%, in some cases as much as 70%, the rest is water, which after the adhesive application must either be completely evaporated (ventilation time) or diffuse into the joined parts (wood, textiles, concrete, foams, leather). The film formation temperature in types containing plasticizers and flexibilizing additives is lower than in types that are free of plasticizers. Additives, so-called high boilers (ethyl glycol, ethyl glycol acetate, ethylhexanol), are used to bring the film formation temperature down.

Frequently, differences in substrate absorbency form the reason for variations in adhesive strength in bonds between PVC films and wood, plastic foams, or textiles. To speed up evaporation of the water from nonabsorbent plastics, continuous feed ovens can be used or water binding substances such as ettringite can be added just before application. Coarsely dispersed adhesives should be used on highly absorbent substrates, since very small particles tend to migrate into the substrate.

Acrylate dispersions are among the best performing aqueous adhesives, since they require no plasticizers to render them flexible and allow no plasticizer migration from the plastic materials (impermeable boundary). These dispersions are therefore always used in products in which hazards to humans must be excluded, for example in wound bandages.

Polyvinyl acetate dispersions in the form of homopolymers and copolymers are among the cheapest and most important dispersion adhesives. Since these materials are readily compatible with pigments, fillers and plasticizers, many different types of adhesives can meet the specifications. Dilutions with water and intermixing can be easily realized. Typical thickening agents include polyvinyl alcohol, casein, starch, gelatins, and animal glues. These additives influence the gloss and water stability of the adhesives.

3.15 Hotmelt Adhesives

Hotmelt adhesives are thermoplastics that are processed free of solvents in the melted state and are therefore known as hotmelts. Since the adhesives are 100% solids, no volatile components can be released. No incineration and/or ventilation systems are required to "dispose of" the solvents. These adhesives are used to fill larger gaps and therefore often function as both adhesives and sealants. Foamed hotmelt adhesives comprise a special category: They are capable of filling large gaps with very little material while still bonding the substrates.

The process time is determined by the technical parameters heatup, application, and cooling: It is very short compared to the process times of reactive adhesives. Processing is done with so-called sticks, spreadable powders, extrusions, nets, or films. Hotmelt adhesives in the form of films in particular are among the heat-activated or heat seal adhesives. In film and textile composites the term used is laminate adhesives.

In hotmelt adhesive guns, the adhesive granulates or sticks are melted, and then transported in liquid form through heated tubes for application. Hotmelt adhesives are applied in dot patterns, in the form of beads, by spraying or by means of rollers in the transfer method. The adhesive is applied continuously in timed cycles, resulting in highly variable adhesive patterns and variable adhesive layer thicknesses. In laminating systems, both liquid hotmelt adhesives and adhesive films can be processed.

A typical cycle for hotmelt adhesives is Melting → Transport of melt to application location → (possibly distribution) → Covering of the structural components to be joined → Cooling. The relationship between viscosity and temperature is decisive at every single process step, so that these relationships should be familiarized for all hotmelt adhesives.

A special form of application results when gases are absorbed by the molten mass (enter into solution) or are stirred into the melt (mechanical distribution). The material expands and foams after exiting from the nozzle. The densities are reduced by about 100% compared to the compact adhesives. This type of adhesive application

- Reduces adhesive consumption because of improved flow behavior
- Raises the level of heat insulation and prolongs the “open time” before joining is necessary
- Reduces setting time by spontaneously illuminating the gas bubbles in joints under pressure
- Fills gaps better than sealant adhesives
- Results in more stable large beads
- Improves the “wettability” of porous materials and textiles
- Makes for more stable adhesive layers on upright walls

Hotmelt adhesives are suitable for adhesive joining of clips, lamination of films, leather and textiles and bonding of films, foams, textiles, and wood. Resistance to hot water and steam is a problem that arises most particularly in the field of textile bonding. This problem was solved using hotmelt adhesives based on copolyamides.

Polyamide and polyester-based adhesives: These are the most heat-resistant of all hotmelt adhesives. The melting temperatures are between 240 and 280°C, which may even lead to problems with sensitive and thin-walled structural components. By means of modifications, the melting ranges can be reduced to 80–100°C at the price of some degree of curing capacity, but still retaining high levels of flexibility. Using copolyesters, PUR foams can be bonded directly to polyester textiles without flame lamination (whereby the fogging effect of the polyetherurethane foams is intensified).

The primary components used to make polyamide-based hotmelt adhesives are copolyamides with PA 12 and so-called polyamide resins.

Ethylene vinyl acetate copolymers: Copolymers made from ethylene and vinyl acetate (E/VA) are among the most important hotmelt adhesives. The vinyl acetate content of the copolymer varies between 10 and 50%. The density increases in proportion to the VAC content. Other possible components include resins, waxes, fillers, plasticizers, and antioxidants. The content level of vinyl acetate in the copolymer, as well as the additives, determine the processing temperature, adhesion, crystallinity, and flexibility of the bond. As the VAC content increases, crystallinity and strength are reduced; at the same time, flexibility and adhesion are enhanced. Strength, however, depends to a considerable degree on the temperature (yield stress at 23°C 5 MPa, and at 0°C 35 MPa).

Polyolefin-based adhesives: PE-LLD (melting temperature 107°C), LDPE (melting temperature 128°C), PP (melting temperature 154°C), polybutene, poly-α-olefins (APAO, melting range depending on formula 80–105°C) are typical hotmelt adhesives. They are amorphous, cooled gradually, and reach an initial level of adhesion quickly. The APAOs contain additives with no double bonds such as terpenes or hydrogenated, colophonic and hydrocarbon resins. Additives do not increase the adhesiveness of polyolefins. Other adhesion-enhancing components include PIB, SIS or SEBS rubbers and oils, which also influence the processing viscosity.

The polyolefinic hotmelt adhesives are characterized by aging stability, i.e., the laws of adhesion and flexibility and the appearance of yellowing are not as pronounced as in the TPEs.

Thermoplastic elastomers (TPE): Styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) block copolymers represent primary materials for other hotmelt adhesives. They are characterized by long open times, high elasticity levels, good spring qualities and a lasting stickiness, so that precoated surfaces always retain some of the qualities of PSAs. The melting temperatures of these adhesives are particularly low at about 65°C, so that they can be used for thermally sensitive materials (foams, fleeces, thin films).

3.16 Pressure-Sensitive Adhesives

These adhesives form a special class of adhesives, in which the adhesive mechanism is derived mainly from the formulation of the components. PSAs are highly viscous liquids that contain, in addition to a polymeric skeleton, special tackifying agents that gives them their adhesive character. The tackifying agents are what cause contact adhesives to stick immediately when pressed onto a plastic surface. This immediate adhesion is called tack.

The polymeric skeleton materials used are:

- Pure acrylates
- Modified acrylates
- Polyesters
- Polyurethanes
- Rubbers

These substances determine the heat and moisture resistance of the adhesives, but are also responsible for the effectiveness of the tackifying agents. Pure acrylates are among the best PSAs.

Several different properties are united in the PSAs: They remain permanently adherent, can in some cases be used repeatedly, and stick when pressed briefly against a surface. The PSAs, are "highly viscous liquids" usually applied to carrying materials such as paper, textiles, metal strips, or plastic films. To make transfer strips, the PSAs are applied to siliconized paper, from which they are transferred when needed to a component by means of pressure. Then this component can be adhesively joined to another.

The first PSAs consisted of rubber systems. Later, pure acrylates and acrylate copolymers, as well as polyurethane systems, were modified so as to meet higher specifications. The latest PSAs are made of polyolefinic adhesives.

Rubber systems do stick to many plastics well, but they are relatively moisture-sensitive. There's always a risk that they may lose their adhesive strength at high humidity levels. At temperatures above about 40°C, they turn very soft and lose their inherent strength. Pure acrylates and modified acrylates are primary materials that provide PSAs with greater moisture resistance and thermal stability. Pure acrylates above all remain sufficiently adhesive up to about 150 or for short periods 200°C. Adhesive tapes of this kind are used for masking purposes in powder-coating techniques.

Besides consumer products, another important field of application for PSAs is that of plastic adhesive labels. The PSAs must adhere very efficiently to the plastic carrying material and at the same time adhere well to a wide variety of plastic packaging types (e.g., bottles, containers for chemicals).

PSAs (readily soluble rubber systems) are also available in spray forms, making it possible to cover large areas with an adhesive film and to adapt the film thickness to the requirements at hand, whereby however large amounts of solvent evaporate.

3.17 Heat-Activated Adhesives

A characteristic of all thermoplastics is tolerance of multiple melting. At the same time, many of these plastics in the molten state adhere well to many different surfaces. The adhesion can be additionally enhanced by means of suitable additives and/or chemical modification of the polymeric structure. For this reason, many thermoplastics are also heat-activated adhesives. Because of the high dielectric constants, hotmelt adhesives can be heated by employing the principle of HF welding equipment. The hotmelt adhesive films are then used as "welding materials." Since the composite pairings (textiles, foams, fleeces, massive structural components) are not melted themselves, this is more of a sealing procedure in which the sealant is introduced either internally or externally, for which reason these adhesives are also referred to as hot seal adhesives. In such cases, the adhesive films act as barriers to gases and liquids, assuming they are thick enough.

The heat-activated films are also used for back injection with polyurethanes, PET, copolyamides, TPE and polyolefins. The films exercise a barrier function for the flowable injection molding material. With composite films, the results are plastic composites with external layers that are visually attractive (color, gloss, embossing), highly stable mechanically and can be produced in a single process. Another variant is represented by multilayered adhesive composite films with an inside carrier film that will lend the resulting composite a predefined strength and/or flexibility.

There are three typical differentiating characteristics for heat-activated adhesives:

- Chemical structure and degree of modification
- Method of application (double dot coating, hotmelt print, film or extrusion lamination)
- Type of activation (hot air, IR radiation)

The typical melting temperatures are between 60 and 200°C, so that temperature-sensitive products can be adhesively joined, resulting in bonds that can withstand high thermal load levels.

3.18 Natural Product Adhesives

Vegetable and animal biopolymers that occur in nature such as protein, glutin, casein, cellulose, natural rubber lattices, and starch provide the primary materials for the “natural” adhesives, also known as glues and pastes. Industrial processing does require some additives, so that only a small number of these adhesives are really pure natural products. At any rate, these adhesives are quite important in the fields of consumer products and foodstuffs, especially since these applications generally do not require maximum adhesive strengths. Glues and pastes also include aqueous polyvinyl alcohol and polyvinyl pyrrolidone, urea-formaldehyde, phenol and resorcin solutions still used in special applications but increasingly being replaced by newer adhesives.

It can be expected in the future that the way these adhesives are produced in nature will become a serious object of study, the aim being to improve the production strategies used for known adhesives if possible. Of course there is also the possibility that genetic manipulations will result in natural adhesives with greatly improved properties.

4 Processes in Joining Technology

The process steps to ensure high-quality, reliable adhesive bonds are:

- Preparation or pretreatment of the surfaces to be joined
- Adhesive application
- Structural component fixation (with longer curing or setting times)
- Curing or setting
- Control of process and adhesive connection

This procedure applies in principle to all materials and material combinations, whereby the priorities shift depending on the specific materials and/or adhesives used.

Pretreatment is particularly important for structural adhesive joints such as those used in aircraft and motor vehicle construction. Aluminum adhesive surfaces are subjected to chromic acid treatment and an anodizing process, major factors in the overall joining costs. The disposal of used pickling baths is particularly demanding and expensive, especially in view of the CrVI ions resulting from the pickling process.

The polyolefins (PO) have come to the fore in the adhesive joining of plastics over the past 20 years. This class of plastics has reduced the preeminence of polyvinyl chloride (PVC). Adhesive joining of PVC involved few problems due to the polar structure of the material and its ready solubility, so that little was required by way of pretreatment. In contrast to this, the polyolefins, nonpolar plastics, can apparently not be adhesively joined at all without pretreatment. This was considered impossible as late as the early 1970s. Now, a number of pretreatment methods have been developed that activate polyolefin surfaces reliably under industrial conditions, making adhesive joining possible. Pretreatment plays an important role with all plastics that present adhesive joining difficulties and is often a weightier factor regarding the stability and endurance of an adhesive bond than the particular adhesive used.

On the other hand, the most recent developments have resulted in adhesives capable of adhesive joining of PE, PP, copolymers and PTFE without pretreatment.

In pretreatment of glass, the different levels of solubility of ions from the crystalline structure must be taken into account, so that pretreatment methods may vary from one glass type to another.

Up until a few years ago, many plastic types were cleaned with solvents before adhesive joining. The solvents were selected specifically for the particular plastics so as to avoid swelling and stress cracking. Organic solvents were even used in pretreatment of metals and glass types. This pretreatment, also known as fine cleaning or purification, sufficed in many applications to ensure high adhesive strength levels. However, it must also be mentioned that fluorinated chlorinated hydrocarbons (FCHCs), and later chlorinated hydrocarbons (CHCs) or pure hydrocarbons (methylethyl ketone, isopropanol, methanol, ethanol, acetone, or benzine) were used for this purpose. The hazardous potential of CHCs makes it necessary to carry out fine cleaning in closed purifying units only. This equipment must demonstrably prevent CHCs from escaping and all contaminated purification baths must be safely and reliably disposable.

5 Legal Regulations

The hazardous nature of some of these chemicals, their cross-border transport and the legal regulations required for product liability have resulted in the passing of regulations, directives, and laws aimed at facilitating accurate assessments of the risks and minimizing the potential hazards. Some of the regulations cover suitable methods of detection designed to render the effects of various components in adhesives or structural components apparent and assessable. The most important regulations include:

- Directive 93/67/EEC: Risk Assessment of Hazardous Substances
- Recommendation 1999/721/EC A Risk Assessment of Ethoxy Compounds
- Directive 1999/13/EC: Limitation of the Emissions of Volatile Organic Solvents in Terms of VOC Emissions
- Directive 2002/45/EC, issued by the European Parliament, dealing with limitations on work with chloroparaffins
- DIN 75201: Fogging Behavior
- VDA Guideline 270: Odor Behavior
- VDA 232-101
- VDA 276 and 278

All organic materials are characterized by a certain degree of volatility, which is particularly pronounced in organic substances with a low molar mass and low vapor pressure. Since many adhesives, after curing or setting, consist not only of the macromolecular bonding agents, but also contain low molecular "residues" of the primary components and other ingredients, there is always a risk of emission of such substances. Their volatility is measured in terms of the VOC level, or as HC emissions, since the emissions involved are hydrocarbons. The emissions are noticed as typical odors. When the volatile substances are redeposited, resulting in a new layer, this is termed fogging. The fogging effect appears as a slightly murky, smeary layer on transparent surfaces. The best-known example is the "fogging" on the inside of the windshield in new cars, especially when the heating system is used intensively or the interior is heated up by the sun. The fogging effect diminishes sharply after a while, but it never completely disappears if the adhesives and plastics in the car interior include components that migrate very slowly to the surface. According to DIN 75201, the VOC value is measured as the loss of mass of, for example, an adhesive, also at higher temperatures, or as a change in the transmission or reflection of radiation through a glass plate with a defined initial reflection level. The VOC value covers all volatile components, the FOG value all components that are deposited on a glass plate so as to form a film. The following values can be expected with aliphatic PUR:

Fogging gravimetry (mg)	<2	DIN 75201 (120°C)
Fogging reflection (%)	>90	DIN 75201
Emission VOC (ppm)	<100	PB VWL 709
FOG (ppm)		50–70

The components in adhesives and pretreatment chemicals are characterized and differentiated in terms of their volatility, Table 2.

In addition to the special regulations designed to prevent emissions and fogging effects, European chemical legislation will in future also follow and control

Table 2 Volatility of HC components

Very volatile organic compounds (VVOC)	Volatile organic compounds (VOC)	Semivolatile organic compounds (SVOC)
Solvents in diffusion adhesives, organic purification agents, primers, blowing agents ⟵ ⟶	Solvents, residual monomers, additives, photoinitiators, curing agents Odor nuisance	Plasticizers, bactericidal agents, curing agents
Boiling range: up to 100°C	50–260	260–500

developments in the field of adhesive engineering (adhesives, pretreatment chemicals, disposal of operating supplies). The so-called "EU Whitebook" – Strategy for a Future Chemicals Policy demands that both the supplier and user (in this case adhesives developer) report the hazard potential of every single raw material, and above all for every mixture of raw materials. The principle of "shared product responsibility" applies, i.e., each producer bears responsibility for safe use of his product within the production chain and may not avoid responsibility by means of reference to declarations of harmlessness issued by his suppliers. For small companies, this can mean major investments, both internal and external, for instance to market a new adhesive product. Since market acceptance of new adhesives or chemical mixtures is far from certain at market introduction, losses may be incurred that exceed the capacity of medium-sized businesses. This means much greater product development risks, so that some creative ideas for product developments will go by the wayside. In view of the laxer regulations governing use of chemicals in other industrial zones, it becomes apparent that development of new adhesives in the near future can be expected above all from threshold countries.

Even assuming that businesses in the small and medium-sized sector do manage to pay the costs of certification of harmlessness and the hazard potential descriptions, the result will be large numbers of duplicate tests, since every supplier bears responsibility for the raw materials, intermediate products and end products he uses or produces and must answer to the product liability laws.

In the automotive industry in particular, the emissions of all materials used are assessed with particular acuity. Fuel and nonfuel emissions are differentiated. In the US and (in the future) in Europe as well, there is a call for "zero rate" fuel emissions. The nonfuel emissions come from the plastics, lubricants and cleaning agents, as well as from the adhesives and sealants in which they are enclosed. Their effects include the typical "new smell" and fogging effects in new cars. The "invisible" dermatological effects of these emissions are not yet taken into account and are not objects of scientific studies, since it is assumed that the minimum concentrations involved do not cause damage, for example to the skin. The nonfuel emissions account for only 15% of all emissions and are reduced by 90% within 1 year in a middle-class car. The Californian law CARB – 1999 can be used as a guideline for further legislative controls. This law prescribes a limit of 2 g d^{-1} for hydrocarbon emission (HC emissions) for a one-year-old car. With the amended law CARB 2002, this limit will in future be reduced to 0.35 g d^{-1} for electric vehicles and

0.5 g d^{-1} for other vehicles, so that even minimum emissions become significant factors. Within this framework, emissions from adhesives – even at the very lowest levels – will be focused on more and more. Beginning in 2008, practically all motor vehicles will be required to comply with the reduced emissions limit of 0.35 g d^{-1}. European and Japanese carmakers will have to meet these legal requirements, so the necessary development work and studies are now ongoing.

For electric vehicles, "zero emissions" will come into force in the coming years for fuel emissions and 0.35 g d^{-1} for nonfuel emissions. These so-called zero-emissions vehicles will be marketed accordingly: "Zero emissions" will become a watchword in both sales and purchasing practice.

Highly sophisticated testing and measuring methods are used by the automotive industry to measure the fogging levels and HC emissions (CARB Diurnal Test, Summer Test acc. to VDA 276, Thermodesorption acc. to VDA 278). For adhesive technology, the Summer Test, Fig. 10, provides information on the course and intensity of emissions. The adhesively bonded parts are stored in a chamber for 5 h at 65°C and an air circulation rate of 400 l h^{-1}. Then the HC components are bound adsorptively and the amount/m^3 of air is measured. Specific adsorption of individual substances that are particularly problematical in terms of environmental contamination can provide a basis for measures targeted to reduce these emissions.

Thermodesorption, Fig. 11, is a "quick test" method for small samples involving phased heatup to 120°C within 1 h. The volatile components, at different temperatures, are collected in a cryogenic (cold) trap, then identified using gas chromatography and mass spectroscopy. The high-tech measurement methods employed in this procedure make it relatively expensive and suitable only for basic studies.

Outgassing analyses of adhesives containing solvents detect mainly ethyl acetate, 2-butanone, ethyl benzole, xylene, and propylene glycol, Fig. 12, in particular MDI and TDI in the PUR adhesives and adhesives crosslinked with isocyanates. In view of the fact that the TLVs differ in some cases by a factor of one thousand (xylene TLV 440 mg m^{-3}, MDI TLV 0.05 mg m^{-3}), the risks involved in use of PUR adhesives must be classified as more significant.

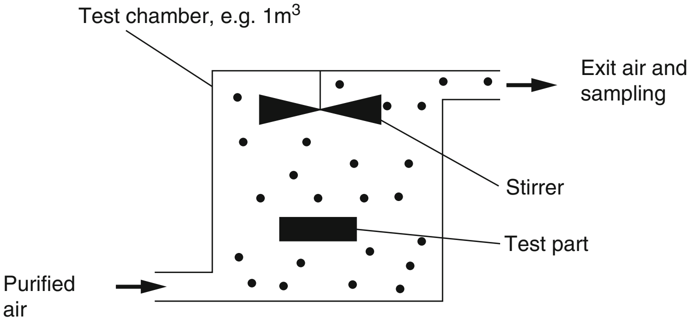
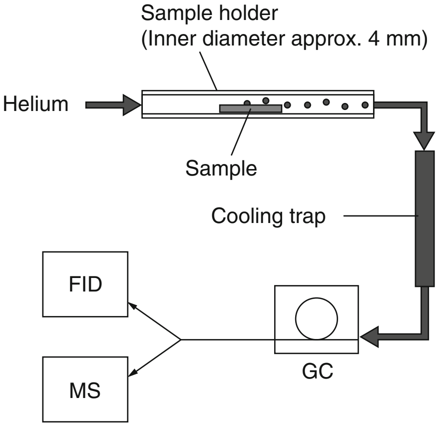


Fig. 10 Summer Test acc. to VDA 256 for detection of HC emissions

Fig. 11 Thermodesorption equipment. *GC*: Gas chromatograph; *MS*: Mass spectrometer; *FID*: Flame ionization detector



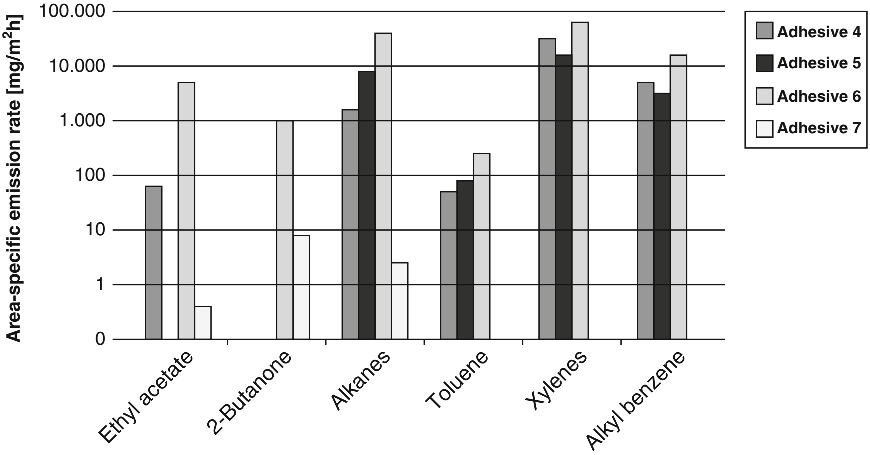


Fig. 12 Outgassing rates of different PUR adhesives. *Source:* IFAM Bremen

Preferred adhesives in the automotive industry:

- 2C PUR
- 1C PUR
- PUR with solvents
- Reactive hotmelt adhesives
- Adhesive tapes
- Butyl rubber as a sealant adhesive

All of these adhesives contain additives or form volatile reaction products. PSAs also contain adhesive resins with sufficient levels of volatility.

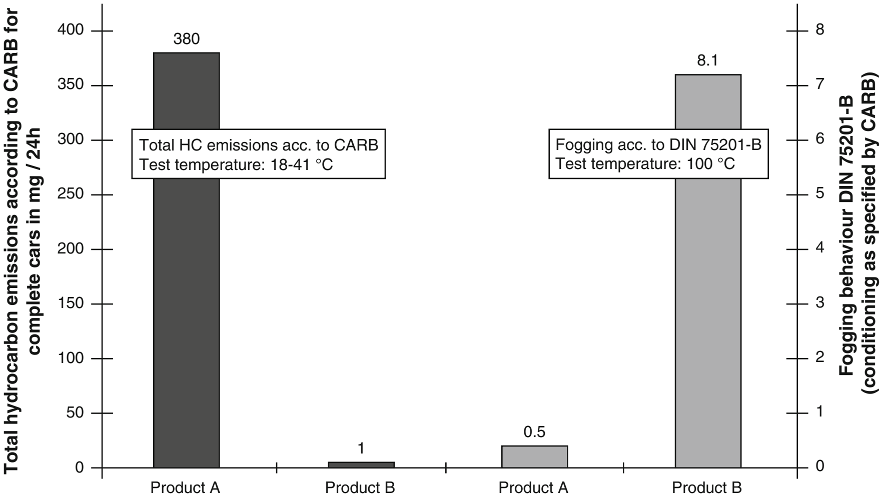


Fig. 13 Emissions from different PUR disk adhesives. *Source:* Frank, U: Development of emission-optimized automotive structural components with PUR, BMW AG (in German), Munich

The phenol-formaldehyde resins used in the past are now no longer used, since formation of even the tiniest amounts of formaldehyde is no longer considered acceptable.

HC emissions from adhesives can vary within a wide range, Fig. 13.

6 Targeted Development and Risk Minimization

In view of current world population growth figures and the increasing standard of living in the so-called threshold countries, as well as in the near future in so-called Third World countries, a disproportionate increase in the production and supply of the various types of materials and fuels would be appropriate. Carried to its logical conclusion, this chain of logic would lead to irreparable "exploitation" of the remaining natural resources. Therefore, at least the industrialized countries are obligated to go easy on the available resources. Recycling, including new laws regulating packaging and automobile disposal, is one approach. Both old and new products must now be much more closely scrutinized to determine whether their "disposal" is feasible in a manner that does justice to the principle of resource preservation. While reutilization of the materials is the ideal solution, thermal "disposal" as a fuel can also be considered if other fuels are conserved in the process. At any rate, the most reliable and safest form of resource preservation is to reduce the volume of material used in the first place, without affecting structural component functionality.

Recent years have seen a number of developments aimed at material savings in the packaging sector, for example in packaging of hotmelts. Hotmelts used to be packaged in bags or cans with siliconized layers. It was often not possible to actually utilize more than 95% of the content of these packages in the melting units. The residual adhesive was then disposed of together with the packaging material, at best incinerated with paper packaging and at worst deposited in waste dumps. The most recently developed packaging films are made of materials that can be processed as hotmelts themselves. These materials are included in the hotmelt mass and produce readily processable hotmelts. Even though this solution cannot be extended to all hotmelt applications, the example does demonstrate how demands to eliminate avoidable packaging wastes can be met.

In the packaging industry, recent years have witnessed a shift, encouraged by public discussion, to the practice of doing without outer packaging wherever feasible and selling products directly in original packaging or dispensers. To realize this, the dispensers (e.g., toothpaste, cleaning agents, food products in paste and liquid form, spray bottles) had to be fixed inside the cartons so as to ensure both reliable shipping and ready removal from sales shelves. The solution was provided by PSAs with defined adhesive strength. These PSAs made it possible to do without many different types of outer packaging.

In labeling as well, efforts to develop ecologically compatible solutions are ongoing. Because of increasing global distribution of food products and stringent requirements regarding product information, packaging is now covered with labels to a much greater extent, i.e., absolute demand for labeling material has increased. At the same time, more and more plastic packaging material is being used, resulting in changing specifications for the labels. Figure 14 illustrates the labeling procedure.

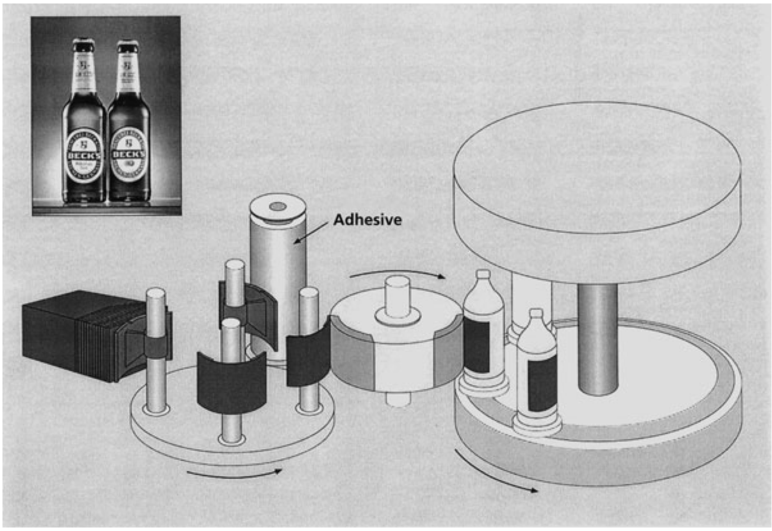


Fig. 14 Labeling of bottles with labels attached with natural adhesives that are removable by washing

The labels in use years ago were mainly made of paper and were attached using natural adhesives or synthetic adhesives containing solvents. Presently, the demand for plastic labels, in particular PP labels, is on the increase. This application represents a considerable challenge to the adhesives industry, since reliable bonding has proven impossible with the standard natural adhesives (especially in rounded packages, the tendency of the labels to roll up led to their detachment). For this reason, synthetic adhesives were later replaced by dispersion adhesives and, today, by UV-crosslinking PSAs. This has solved the problems presented by solvent disposal and the necessity of constant machine cleaning to remove adhesive deposits. Hydrophobic hotmelt adhesives are used for so-called allround labels of single-use packages.

The casein adhesives developed for paper labels have proven to be readily soluble when the glass bottles are washed at defined pH levels. This has shortened the washing procedure and the labels have been able to comply with all further specifications.

As has been mentioned repeatedly, the packaging industry is the single largest consumer of adhesives. Therefore, developments in the packaging sector are reflected to a significant degree in the adhesives industry. In the other direction, adhesives the production and processing of which bear out a pronounced ecological orientation also show significant effects on the market as a whole.

The concept of recycling is currently being applied as a matter of course to development of (many) new products. Among the first materials that were recycled were paper and cardboard. At first, cellulose products made with recycled material definitely “looked the part.” Later developments have improved processing methods to the point where product quality differences are now hardly noticed. An essential factor in this development was adhesives that did not interfere with the recycling process and reprocessing of the used and recycled cellulose material. The adhesives were modified so that they could be removed with great accuracy, leaving only the cellulose to be reprocessed. Because of the sheer volume of the adhesive market, manufacturers were “forced” to develop new adhesives if they were to maintain their market positions.

Any discussion about recycling of materials and difficulties with dismantling of adhesively joined structural components must take into account the fact that costs for pure-material separation increase exponentially with the degree of purity demanded. For this reason, it makes more sense to recycle mixed plastic components (with the exception of plastics containing halogens) as fuels. From the ecological point of view, metal–plastic shredder fractions in particular should preferably be reutilized as blast-furnace charges, since the plastics are ideal hydrogen donors and can therefore substitute for other hydrocarbon-based fuels.

How long terminal waste dumping (“throwaway mentality”) will be deemed acceptable at all is a question for the future. It can be assumed that society will adopt a new point of view. In other words, “replacement parts” will begin to find a market wherever their use makes good ecological sense. Of course, the lower costs are another incentive for use of replacement parts. In the area of replacement car parts in particular, there is a clear-cut opportunity to get away from the throwaway mentality. Adhesive engineering has made new applications possible in this field. New repair technologies include adhesives for repair of minor body damage so that slightly damaged parts will no longer have to be replaced entirely and disposed of as waste. The basic technology involved has been around for years. What is new now is the level of market acceptance for such repair sets, so that new products have recently been developed to fill the demand.

The concept of recycling is most readily implemented if different structural components can be made out of the same material (Al, plastics), i.e., in one-material systems. Recently, polyolefins have appeared to fit the bill particularly well in this respect, i.e., the many potential forms of polyolefins have made possible adaptations for a wide variety of structural requirements. As an adjunct to these developments, polyolefin melt adhesives have been developed for bonding polyolefin parts to one another. Where this is feasible, total dismantling is no longer necessary and the parts can be reprocessed without any essential loss of properties.

In addition to the research being done on development of new adhesive formulae, training programs and corresponding DVS guidelines have been available to employees in the field of adhesive technology for about 10 years now. This educational program (regulated by legislation) was developed in response to increasing demands made on adhesive technicians and engineers. Not only are there more applications to be mastered: The range of adhesives, the complexity of the processes, and the quality requirements have all increased as well. The variety of chemicals used in this area has also grown, so that the training program content must be geared toward a more environmentally oriented handling of adhesives. The instructions for use and disposal in the Safety Data Sheets can only be applied and complied with if the persons involved are given the opportunity to gain sufficient knowledge of potential hazards.

The most important ecological precept, that of waste avoidance, is particularly important when it comes to adhesives because of the many potential toxic hazards involved. The chances of adhesive technology are therefore to be seen in the use of starting materials without inherent potential hazards and in waste avoidance. The high expenditures required for disposal of residual adhesives and other wastes are cited by many potential users as a hindrance to use of adhesive technology (source: IFAM Bremen). A further difficulty arises due to the general absence of on-site solutions within the companies, particularly in view of the relatively small volumes and wide variety of types of adhesive materials involved. In the many different product descriptions with their listings of different substances, simplified descriptions of the hazard potential must be aimed for, for example using risk classes. This would provide users with a quick overview of the applications regarding the necessary workplace and disposal measures. Detailed descriptions of substances tend to have a discouraging effect when it comes to use of adhesives.

The volume of wastes produced is often not a matter of the type of adhesive used, but is rather a question of the application technique used. Therefore, developments in process engineering must be followed and applied along with the new adhesives. Market acceptance of adhesive technology will rise when adhesives suppliers become system suppliers, i.e., when they can supply both a selection of adhesives and the equipment needed to process and apply each particular type (mixing, dosing, application). The transition from 2C adhesives to 1C adhesives is always an important initial step in reduction of potential hazards and environmental contamination.

Provision of information concerning consultants and disposal locations to accompany the sale of adhesives would be an important step toward raising the acceptance of these products. For its part, the adhesives industry should demonstrate good will by providing such information generously.

Microstructured Polymer Surfaces with Complex Optical Functions for Solar Applications

Benedikt Bläsi, Andreas Gombert, and Michael Niggemann

Abstract In solar applications microstructured polymer surfaces can be used as optically functional devices. Examples are antireflective surfaces, daylighting, sun protection systems, concentrator photovoltaic modules and light trapping structures in organic solar cells. The examples and the principles of function of the respective microstructures are described in detail. The suitability of different manufacturing methods is discussed. Two of them, ultraprecision machining and interference lithography are described. For the latter experimental results are shown. Finally, the opportunities and the risks of the shown approaches are discussed.

Keywords Interference lithography, Microstructures, Optically functional surfaces, Replication, Solar applications

Contents

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Abbreviations

AR	Antireflective
CPC	Compound parabolic concentrator
CPV	Concentrator photovoltaics
P3HT	Poly-3(hexyl-thiophene)
PC	Poly(carbonate)
PCBM	[6,6]-Phenyl-C_{61}-butyric acid methylester
PEDOT	Poly(3,4-ethylenedioxythiophene)
PET	Poly(ethylene terephthalate)
PMMA	Poly(methyl methacrylate)
PSS	Poly(styrene sulfonate)
PV	Photovoltaic(s)
SEM	Scanning electron microscope
1D	One dimensional
2D	Two dimensional

1 Introduction

By modifying the surface texture of a product many of its properties can be transformed such as friction, adhesion, wetting, and optics. With engineered microstructured surfaces one can obtain optical properties which were to date related to optical thin films or bulky optical components. It is possible to make surfaces antireflective or retro-reflective, to steer light and to trap it. The mentioned optical properties are required on large areas particularly in solar energy systems. The major advantage of surface-relief structures with the mentioned optical properties is the possibility of mass production by relatively low-cost replication processes. Complex optical functions are transferred to high volume products by embossing, molding, or casting. From the materials point of view, polymers are especially suitable because all the replication processes are very well established.

In order to study the optical properties of microstructures it is helpful to consider periodic structures (Fig. 1). Periodic surface-relief structures are called diffraction gratings in an optical context. By regularly repeating a surface-relief in one or two directions one-dimensional (1D) or two-dimensional (2D) surface-relief gratings are formed. The spacing between the repeated structures is called period Λ. Because of the periodic structure the incident radiation is diffracted into diffraction orders

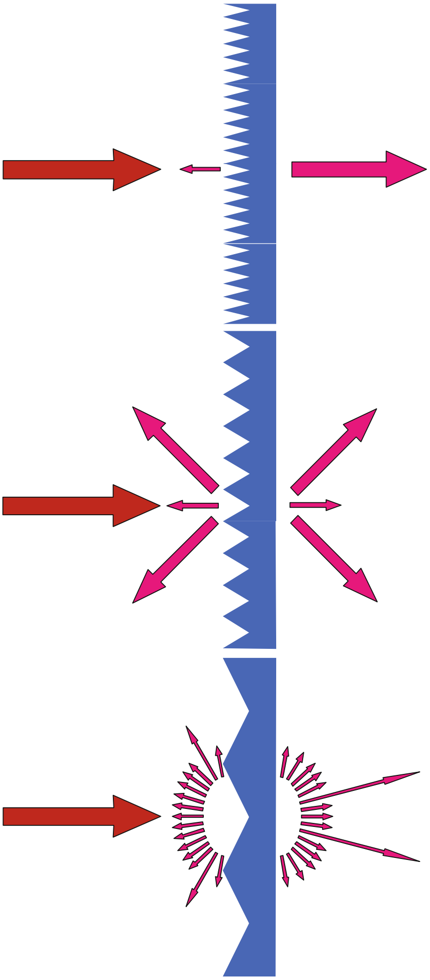


Fig. 1 The period-to-wavelength ratio defines the optical properties of a diffraction grating; (a) $\Lambda \ll \lambda$, (**b**) $\Lambda \approx \lambda$, (**c**) $\Lambda \gg \lambda$

with discrete propagation directions. The diffraction efficiency for a specific order indicates how much of the incident energy is transported in this diffraction order.

The optical properties of the microstructured surface depend very much on the relation between the wavelength λ of the radiation which is incident on the structure and the period Λ. If $\Lambda \ll \lambda$ then the microstructure leads to a modification of reflection and transmission at the air-to-material boundary but not to a modification of the propagation direction of the radiation (Fig. 1a). Only the zero-order diffracted wave is propagating and the wavelength dependence of the optical properties is small in this case. The optical properties of the microstructure can be modeled by regarding the structured region as a homogeneous effective medium. The effective refractive index of this effective medium depends on the refractive indices of the two media in the structured region and on the volume fractions of each of the media.

Such subwavelength gratings can be used for antireflective surfaces or for polarization-sensitive devices.

If $\Lambda \approx \lambda$ then resonance effects dominate and the result is a strong wavelength dependence of the optical properties. It is possible to achieve high diffraction efficiencies in a specific diffraction order just due to the fact that only few diffracted orders propagate. The optical properties of such gratings have in general to be modeled by using rigorous diffraction theory, i.e., by solving Maxwell equations numerically [1]. Gratings in the resonance region have mainly been used for spectral filtering, e.g., in spectrometers. More generally, periodic structures in the resonance region are called photonic crystals and show pronounced angle and wavelength selective optical properties [2, 3]. In solar energy systems, they can be used for spectral filtering or light trapping [4–6].

If $\Lambda \gg \lambda$ then many diffracted orders propagate. The distribution of the diffraction efficiencies depends very much on the structure profile. For very large ratios Λ/λ, the optical properties of the surface-relief grating can be derived by means of geometrical optics because this is an approximation which holds for $\lambda \rightarrow 0$. The grating then represents an array of prisms, lenses, etc. which can be modeled by using ray-tracing methods. For ratios Λ/λ up to 100, the ray tracing method is not sufficiently accurate in many cases. Then, extended scalar approaches or rigorous diffraction theory has to be applied. Surface-relief gratings with a large ratio Λ/λ are particularly suited for light-redirecting elements.

The above-mentioned considerations can also be applied to nonperiodic structures. The Fourier analysis of a nonperiodic structure gives us a distribution of spatial frequencies which are just the inverse of the period Λ. If this distribution has a broad bandwidth then all the mentioned optical effects from effective media over resonance to refraction can occur simultaneously. Unfortunately, the modeling of nonperiodic structures would in most cases also require a rigorous approach which is not possible in general. The solution there is based on the application of scalar diffraction theories which neglect polarization effects and therefore are not suitable for steep profiles or large scattering angles.

2 Solar Applications

Almost every system which converts solar energy is protected from environmental impact by a sheet of transparent material. Examples are covers of solar thermal collectors or photovoltaic (PV) systems or double-glazing used for windows. A modification of the optical properties of this transparent component offers the opportunity to optimize the efficiency of the solar energy system. Surface-relief structures are an elegant possibility to modify the optical properties of this transparent component. Research work concerning surface-relief structures on glazings or transparent covers has been done on several applications: antireflective (AR) surfaces, daylighting, sun protection systems, concentrator systems, and light-trapping devices.

2.1 *Reduction of Reflection Losses*

At the transparent cover of solar energy systems a part of the incident solar radiation is lost by reflection. For a material with a refractive index of 1.5 the losses per surface due to reflection range from 4% at normal incidence to 9% at an angle of incidence of 60°. Depending on the solar system, there are up to six air-to-material interfaces at which reflection may occur. Therefore, many approaches have been made in the past to reduce these losses by a suitable modification of the surface. Most were made on glass which is still the standard material for transparent covers of solar devices, only a few took polymer materials into consideration [7–9]. The major difficulty is given by the range of wavelengths of the solar spectrum which is extended from 0.3 to 2.5 μm. For such a broad spectral range classical interference coatings are not suitable because they reduce reflectance only over a spectral range of one octave. When a classical interference coating designed for visible wavelengths is used for the solar spectrum the net reduction of the average reflectance in the solar spectral range is almost zero. The reduction of reflectance in the visible is compensated by an increased reflectance in the near infrared.

Ideally, the surface of the transparent cover should have a gradient of the index of refraction ranging from 1.0 for air to the index of refraction of the cover material. For the required very small indices of refraction no materials exist in nature. Such small indices of refraction can only be made by effective media in which the cover material is mixed with air on a subwavelength scale as described in Sect. 1. Subwavelength surface-relief structures with a continuous profile as shown in Fig. 2 form an effective refractive index gradient and are therefore well suited for broadband AR surfaces. This type of AR surface-relief grating is called a "moth-eye" structure according to the example found in nature on the cornea of

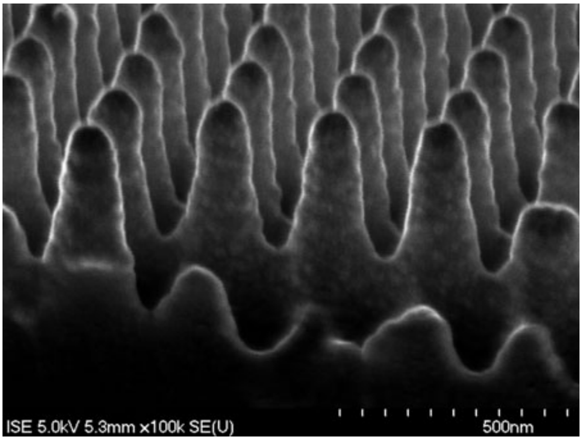


Fig. 2 SEM picture of an artificial "moth-eye" structure originated in photoresist

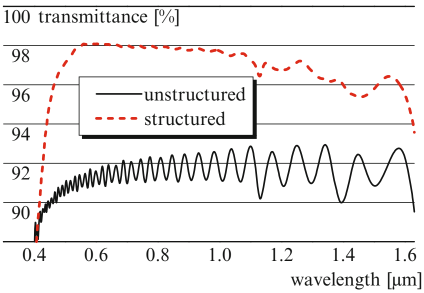


Fig. 3 Transmittance spectra of a microstructured and an unstructured PET film with a thickness of 125 µm. The interference modulation of the unstructured film is due to the mismatch of the refractive indices of the PET film and the acrylic coatings

night-flying moths [10]. The quality of the microstructured AR surface depends on the period and the depth of the structure. The period should be as small as possible, the depth as large as possible. For solar applications, the depth-to-period ratio should be in the range of 10 but is limited for technological reasons to approximately one. This makes an optimization of the subwavelength structures for the specific applications necessary. The typical periods and depths for such gratings range from 200 to 350 nm. The highest values for the average solar transmittance of a microstructured poly(ethylene terephthalate) (PET) film for example were 97% instead of 91% for the unstructured film (Fig. 3). Each of the surfaces of both film samples was first coated with an ultraviolet (UV) curable acrylic lacquer. For replication of the microstructure the acrylic coating was then UV cured while being in contact with the microstructured mold (see also Sect. 3.2). For the flat reference sample a flat mold was used. The AR gratings on both surfaces of the structured film were crossed gratings with periods of 300 nm and a depth of approximately 330 nm. In the near infrared the AR effect is reduced because the mentioned structure depth is not sufficient to produce a good AR effect at wavelengths longer than 1 µm.

2.2 Daylighting

An increased use of daylight in buildings could save energy and provide better visual comfort. The major problem is that the light is too bright near the window and too dark deep in the rooms in most cases. In the past, different components were developed which allow the light to penetrate deeper in the building by steering it towards the ceiling from which it was then reflected and further distributed. By doing so, the irradiance is reduced close to the window and increased several meters away.

Generally, all optical components which modify the light path through a window should be light-weight, use a small amount of material, and have a homogeneous appearance for static, economic, environmental, and aesthetic reasons. Therefore, microstructured polymer films have been taken into consideration. Two approaches

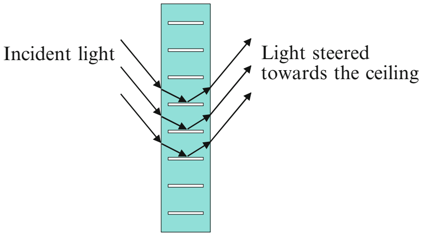


Fig. 4 Sketch of a daylighting device based on total internal reflection

exist to fulfill the described task by using polymer films or sheets containing regular microstructures. The first approach is based on total internal reflection on air slits in polymers [11–13]. The air slits can be made by laser cutting [11]. In more recent developments, two sheets of microstructured polymer are glued together in order to form a 1D grating of only a few micron wide air slits in an optically homogeneous sheet of polymer [12, 13]. This sheet of polymer is then laminated onto one surface of a double-glazed window for example. The incident light is steered towards the ceiling of the room by total internal reflection (Fig. 4). Because of the fact that the light must be deflected in only one direction, a 1D grating structure is sufficient. The length-to-spacing ratio of the air slits has to be optimized in order to achieve maximum deflection efficiency. If the spacing is too large for a given width and a given angle of incidence some of the light is not deflected. If the spacing is too small for a given width and a given angle of incidence, light rays can be reflected at the lower and at the upper air slit. This would also result in no deflection from the original path of the light. As the angles of incidence vary with the path of the sun, the deflection efficiency of the light-steering device also varies.

The daylight steering approach based on diffraction makes use of 1D surface-relief gratings in the resonance case. The periods of these surface-relief gratings are such that only the zero-order diffracted wave and the first-order diffracted waves propagate outside the material for visible light, e.g., in the range from 400 to 1,000 nm. By adjusting the grating profile it is possible to achieve a very high diffraction efficiency for the first-order diffracted wave [14] making the grating a suitable light-steering device.

Of course, in the case of a diffraction grating the deflection angle depends strongly on the wavelength. The visible spectrum contains wavelengths from 380 to 780 nm. Using one single period for the grating would result in a clearly visible separation of the colors as each of the spectral intervals is deflected in a different direction. Therefore, the approach is to use segmented microstructured polymer films in which each of the segments covers a grating with a slightly different period. Thus, at a sufficiently large distance from the polymer film the light coming from different segments with different colors is mixed up in order to result in white light again.

This approach has the advantage that very small structures and thin polymer films can be used. The disadvantage is that the required grating profile has a very high aspect ratio which is difficult to achieve technologically on large areas.

2.3 Sun Protection Systems

Over-heating of buildings due to irradiation by direct sunlight is a severe problem especially for modern office buildings. The architectural trend to increase the glazed area of façades makes an efficient sun protection necessary. Classically, sun protection consists of venetian blinds made out of metallic lamellae. Their disadvantage is that they reduce in general also the level of daylight in the building when they are closed. In order to overcome this problem a sun protection would be ideal which transmits the diffuse daylight and reflects the direct sunlight. One can come quite close to this ideal by making use of the fact that direct sunlight irradiates the façade from very distinct angles of incidence whereas the diffuse daylight is incident from a much wider range of angles of incidence.

The task is to realize angle selective reflectors which have a high reflectance for angles of incidence under which direct sunlight irradiates the façade and a high transmittance for all other angles of incidence. This can be fulfilled by prismatic microstructures. As in the case of the daylighting structures 1D gratings are used. They can be applied on lamellae of a venetian blind which are made out of a transparent material or in a double glazing (Fig. 5). The venetian blind system with the translucent lamellae can be adjusted actively to the height of the sun by rotating the lamellae slightly [15]. The double-glazed system in which the prism film is laminated onto one of the glass panes is designed to reflect the direct sunlight in summertime and to transmit it in wintertime. The design parameters are the prism profile and the refractive index of the material. With the design parameters different locations concerning the altitude can be taken into account and the gradient of the angle-dependent transmission curve can be influenced. Additionally, the shown surface-relief profile contains coplanar segments in order to enable one to look through. A clear view is not possible with such a system because the prisms will produce secondary images but at least some perception of the environment will be possible.

Another structure type suitable as an angle-selective reflector is the so-called compound parabolic concentrator (CPC) [16]. Light from a defined range of angles of incidence is reflected by total internal reflection on the parabolic walls of the CPC and concentrated at the exit of the CPC. If this exit is covered by a mirror then

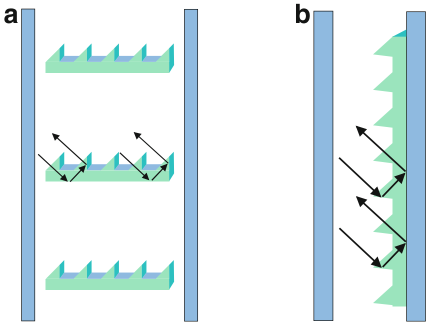


Fig. 5 Sketch of two different prismatic sun protection systems; (**a**) venetian blind with lamellae which are translucent for most angles of incidence, (**b**) double-glazed seasonal sun protection system. The solar radiation is incident from the upper left corner

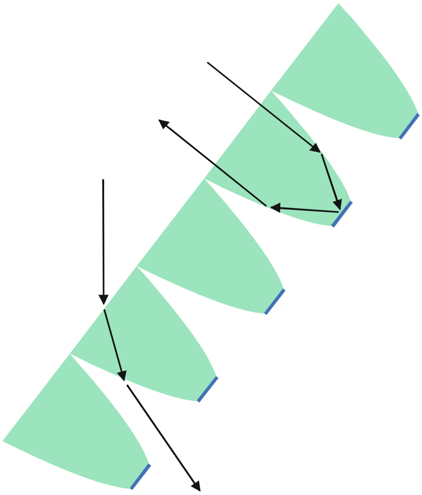


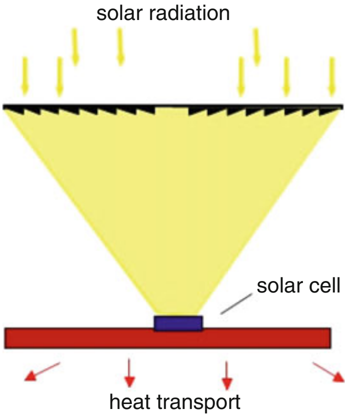
Fig. 6 Sketch of a CPC array showing the principle of operation. The upper rays describe the reflection case, the lower rays the transmittance case

most of the light is reflected and a small amount is absorbed. For larger angles of incidence, the critical angle at the parabolic wall is not reached and the light is transmitted (Fig. 6). The design parameters are again the surface-relief profile and the refractive index of the material. The advantage of CPCs compared to prisms is the greater freedom to tailor the range of angles of incidence under which the light is blocked. The disadvantage is that a further production process is needed for applying the mirrors at the exits of the CPCs. Symmetric CPCs reflect light for angles of incidence which are symmetric to normal incidence. Therefore, they are mainly suited for sun protection systems which are integrated in roofs which is indicated by the oblique orientation of the CPC array in Fig. 6.

2.4 Concentrator Photovoltaics

One of the most important optimization goals in photovoltaics is cost reduction in order to achieve levelized cost of electricity which does not require guaranteed feed in tariffs to be economically viable. In concentrator photovoltaics (CPV), the solar radiation is concentrated onto the solar cell be means of an optical concentrator. The cost reduction is achieved due to the replacement of expensive PV cell material by lower cost optical systems covering the receiver aperture. This approach is especially interesting since very highly efficient multijunction III–V concentrator solar cells became available. There are many approaches for solar concentrators dependent on the optical principles behind them and on the two principle classes, imaging and nonimaging. This classification is made by Leutz and Suzuki in [17] and gives a very good overview. The optical principles are reflection, refraction, dispersion/diffraction, and fluorescence. In many solar concentrators, polymers as optical materials play an important role.

Fig. 7 Sketch of the main components of a CPV system. A Fresnel lens concentrates the solar radiation onto the solar cell which is mounted on a heat dissipater



Probably, the most used optical concentrator in CPV is a Fresnel lens. This type of lens was originally developed by Augustin-Jean Fresnel for lighthouses in 1822. His basic idea was to reduce the thickness of a plano-convex lens by slicing the curved surface in concentric annular sections. Of course, the impact of the discontinuities between the sections, the so-called draft facet, should be kept as small as possible as these do not contribute to the imaging power of the Fresnel lens. With this sectioning, rather thin lenses can be made which makes this type of lens especially suitable for solar applications where optical concentrators, e.g., lens arrays, must cover large areas. In Fig. 7, the major components of a Fresnel lens-based CPV system are sketched. Fresnel lenses cannot fulfill perfectly all the requirements on solar concentrators for PV, e.g., high optical efficiency and concentration, uniform illumination, suitability for low-cost mass production, insensitivity to tracking and manufacturing errors and to atmospheric variations of the incident direct solar radiation, suitability to be arranged in modules, durability, low weight, and low aspect ratio (height/width) in order to be able to produce flat modules. Nevertheless, Fresnel lens arrays seem to be one of the best possible solutions.

Currently, there are many research institutes and companies around the world working on the market introduction of CPV. The experimental set-ups of the last 30 years are now replaced by small- and medium-scale PV power plants as shown e.g., in Fig. 8. High peak efficiencies of 27–29% at a concentration of approximately 500 have already been measured for modules with flat or dome-shaped Fresnel lenses as the primary concentrator and III–V multijunction solar cells [18, 19]. Most Fresnel lenses have a pitch in the order of magnitude of 1 mm or even below. The small pitch and the need to keep the negative impact of the draft facets small require very precise mass production techniques for which polymers such as PMMA are often chosen. Another approach is to cast the Fresnel lens arrays into a rubber silicone on a glass surface. This so-called SOG (silicone-on-glass) technology has the advantage that the very scratch resistant and durable material glass protects not only the Fresnel lens but also the complete CPV module.

Fig. 8 CPV power plant built by Concentrix Solar GmbH in Puertollano, Spain, at the installation of the ISFOC Institute

2.5 Light Trapping in Organic Solar Cells

Organic solar cells have become a very attractive research topic, as they have the potential to be produced at low cost and are expected to give rise to new applications due to their mechanical flexibility and low weight. Device efficiency has been doubled during the last four years, reaching values above 5% [20]. Together with the reported long-term stability, the goal of commercialization of the first organic solar cell products is within reach. A promising concept of an organic solar cell is the so-called bulk heterojunction solar cell [21]. The photoactive layer comprises of an intimate mixture of two organic semiconductors with a phase separation in the order of nanometers. The most widely investigated organic semiconductors for organic solar cells processed from solution are the conjugated polymers poly-3 (hexyl-thiophene) (P3HT) serving as the electron donor component and [6,6]-phenyl-C_{61}-butyric acid methylester (PCBM, a C_{60}-derivative) as the electron acceptor [22].

A large optimization potential for increasing the solar power conversion efficiency of organic solar cells is seen in the proper tailoring of the energy levels of the organic semiconductor with respect to an efficient photon harvesting under solar illumination and a minimization of the energy loss during the charge carrier transfer between donor and acceptor [23]. An organic solar cell typically consists of a photoactive layer sandwiched between a transparent front and a highly reflective back electrode. The light absorption strongly depends on the layer structure. Although the extinction coefficients of organic semiconductors can be more than a magnitude higher than in indirect inorganic semiconductors, the charge carrier mobilities below 10^{-3} cm^2 $(\mathrm{Vs})^{-1}$ in the photoactive composite result in a transport limitation of these devices. The general goal of light trapping is to optimize the light absorption and charge carrier extraction simultaneously in order to reach higher power conversion efficiencies. Therefore, light trapping can only be beneficial if the power conversion efficiency of a solar cell is significantly limited by the extraction of charge carriers from the device. The extraction is primarily governed by the charge carrier mobilities and recombination. The planar solar cell architecture can be conceived as a 1D photonic device. Two-dimensional solar cell architectures in the micrometer scale present a promising approach to enhance the power conversion efficiency in organic solar cells.

Folded solar cell architectures: In order to benefit from the enhanced light absorption under the illumination at inclined incident angles, folded solar cell architectures have been developed for organic solar cells [24] (Fig. 9). An additional – and no less pronounced – light-trapping effect is due to multiple reflections and absorptions. Using substrates with a three-dimensional surface topography at the micrometer scale allows one to realize compact and flexible solar cells. Different

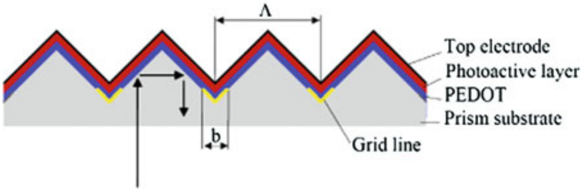


Fig. 9 Schematic cross section of an organic microprism solar cell. The transparent microstructured polymer substrate is made by microreplication. Metal grid lines are deposited in the valley of the structures. The transparent PEDOT:PSS anode, the photoactive layer, and the evaporated cathode follow the shape of the microstructure

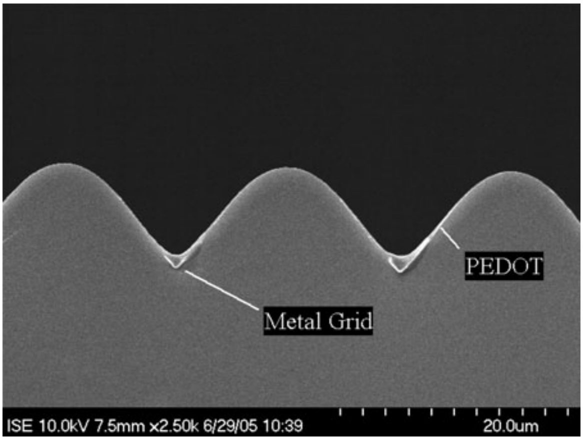


Fig. 10 Cross section of a microprism substrate with a structure period of 20 μm originated by interference lithography, carrying a microgrid and coated with the polymer anode (SEM image)

types of geometries from prismatic to parabolic and of different sizes from a few micrometers to several hundred micrometers can be generated by micromachining or interference lithography (Fig. 10). The cost-efficient substrate generation by microreplication is common to both approaches. Another advantage of the proposed solar cell architecture is the substitution of the ITO-electrode by a highly conductive polymer layer with a supporting metal grid located in the valley of the structure if microstructures are used.

3 Manufacturing Methods

In general, surface-relief structures can be manufactured by four types of processes: removing material (e.g., etching or cutting), material deposition (e.g., physical vapor deposition or galvanic processes), replication (e.g., injection molding), and material modification (e.g., laser texturing). Of course, in many cases processes of different types are combined. Because of their plasticity polymers are especially suited for replication processes. Therefore, for manufacturing microstructured polymer films only two major parts of the replication process will be considered in the following: the origination of the master structures and using them or replicas of them as tools for transferring the microstructures in subsequent high-volume replication processes into polymers.

3.1 Microstructure Origination

The origination of master microstructures on large areas is still not very well established. Within the field of mechanical, electrical, and optical microsystems origination techniques such as e-beam writing, laser writing, focused ion beam etching, photo or X-ray lithography are widely used and mature. Unfortunately, many of them are not suited to originate well-defined continuous surface-relief profiles and are especially not suited to originate the microstructures on large areas homogeneously.

One possibility would be to use a so-called recombination process, i.e., to originate the microstructure on small areas and then to enlarge the area by putting small-area replicas in a step-and-repeat process together in order to form a larger tool for further replication. This would make many of the mentioned origination techniques suitable for large-area applications. Recombination processes exist but the seams between recombined areas are often not tolerated for aesthetic reasons. Research on novel recombination techniques providing “invisible” seam widths are ongoing but these techniques are not commercially available so far.

As a result, none of the above-mentioned origination technologies is used for the origination of master structures for the applications mentioned in Sect. 2 to date. For these applications, ultraprecision machining and interference lithography are used as origination techniques for suitable homogeneous large-area master structures.

Ultraprecision machining is a technique where the classical machining techniques such as turning, drilling, milling, and cutting are performed by using ultraprecision machines, diamonds as tools, and metals as material [25]. The typical dimensions of microstructures that are made by ultraprecision machining are in the range of 10–500 μm. As the shape of the diamond in most cases is the shape of the microstructure, especially prism-like profiles can be made very precisely and with a low surface roughness. The origination of large-area master tools is very time consuming since it is a serial process, i.e., each single groove has to be originated after the other. Therefore, one rarely finds ultraprecision-machined master structures with periods below 100 μm on large areas.

Interference lithography makes use of the interference pattern which is formed when two or more coherent light waves are superposed. In a typical optical set-up, a laser is used as a source for UV radiation. The laser beam is split into two beams. Each of the beams is directed by mirrors towards a substrate coated with photoresist where the beams are superposed after being expanded. Two interfering beams produce a 1D grating with a sinusoidal intensity distribution. To this intensity pattern the UV-sensitive photoresist is exposed. After exposure the photoresist plate is developed where exposed or unexposed. Photoresist is removed depending on the type of photoresist. As the intensity profile is sinusoidal continuous microstructure profiles will result in general.

The advantage of this technique is that even submicron structures can be originated on large areas simultaneously. One might regard the restricted possibility to change the intensity profile of the interference pattern as a disadvantage. It is a severe restriction but by using the possibilities described in the following one can nevertheless originate a variety of structure profiles (Fig. 11). Firstly, one can change the grating period by adjusting the angle between the interfering beams. Secondly, double exposures with a rotation of the photoresist plate will result in 2D gratings. Thirdly, the use of asymmetric angles of incidence for the interfering beams results in asymmetric structure profiles. Fourthly, aperiodic surface-relief

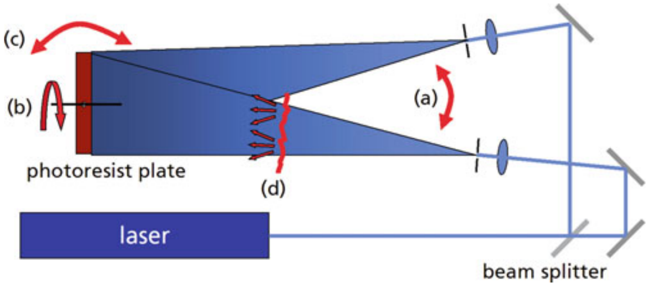


Fig. 11 Sketch of an interference lithography set-up. Also shown are the different possibilities to influence the resulting photoresist profiles: (**a**) change of angle between the interfering beams, (**b**) double exposures with intermediate rotation of the photoresist plate, (**c**) asymmetric angles of incidence, and (**d**) use of a diffusor

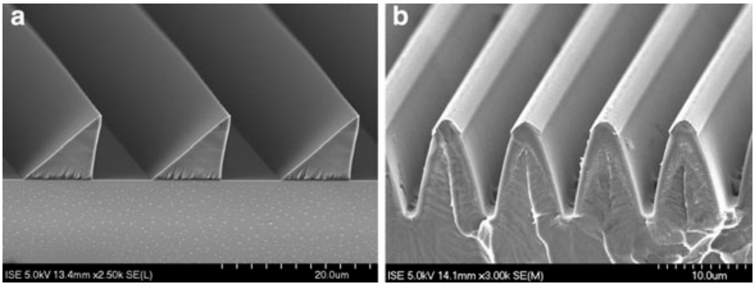


Fig. 12 SEM pictures of two microstructures which were originated by interference lithography: (**a**) prism array structure in photoresist, (**b**) replica of a CPC array in poly(methyl methacrylate) (PMMA) partly coated with metal

structures can be manufactured by inserting a diffuser in the optical set-up. And finally, all exposure techniques can be combined.

The major difficulty in applying these techniques for the origination of microstructures on large areas is to achieve very stable conditions during the recording of the interference pattern in photoresist which can take hours. When the process is sufficiently controlled also demanding profiles like prism and CPC structures for sun protection systems can be originated (Fig. 12). In the case of CPC structures interference lithography is ideally suited because almost perfect parabolic photoresist profiles result from the development process when diazonaphtochinone-based photoresist is used.

3.2 Replication

The master structures cannot be used as embossing tools directly in the case of photoresist and are not often used for cost reasons in the case of machined metal masters. The standard process chain includes therefore the replication of the master structures by electroforming into nickel. When photoresist master structures are used, a thin conducting layer is deposited by evaporation, sputtering or by the wet chemical reduction of silver firstly. Then, nickel is grown with a thickness in the range of 50 μm–3 mm by using nickel sulfamate solutions on top of the master structures. This first nickel replica is then separated from the original. After passivation, the first nickel replica is copied by electroforming again. By applying the process repeatedly, several generations of so-called nickel shims can be produced without too much loss in the structural details.

The daughter generations of the nickel shims are used for replicating the microstructures in polymer materials. For polymers a large variety of mature replication techniques exist, e.g., hot compression molding, injection molding, and reactive processes including radiation curing [26]. The latter are especially suited for high-volume large-area applications. Firstly, the nickel shims are mounted onto a roller. Then, a polymer film substrate is continuously coated with a lacquer which contains a photo-active compound and pressed against the roller with the microstructured nickel shims. The lacquer is hardened while in contact with the nickel shim by UV irradiation. The restriction of this process is the limited availability of lacquers with a variety of refractive indices. For some designs of sun protection system a refractive index of 1.6 or even higher is desired. Therefore, for the production of these sun protection systems hot compression molding seems to be a good alternative although it is a discontinuous process. In hot compression molding polymers with a refractive index of approximately 1.6 such as poly (carbonate) (PC) can be microstructured.

4 Opportunities and Risks

The opportunities provided by polymers in the mentioned applications arise from their superior plasticity at relatively low temperature compared to other materials. The optimization of solar systems requires sophisticated optical devices which can be made by replication of surface-relief microstructures in thin polymer films or sheets. The approach to use surface-relief microstructures fulfills the most important requirements for integration into buildings and PV systems: low amount of extra material necessary, producible in high volume and on large areas, and homogeneous appearance. The latter is a very important criterion because the concerns of architects about integration of optically functional components in architectural glazing for example become much smaller if there is no obvious change of appearance apart from having translucent instead of transparent glazing.

The microstructure concept can only be successful if the microstructures can be replicated with very high precision on large areas at low cost. So far, this requirement can only be fulfilled by using polymers. Alternatives concerning materials for the mentioned applications would only be glass or inorganic films on glass. For those materials, large-area replication is much more difficult than for polymers because of the much higher glass transition temperatures and the inflexibility of the substrate glass. Therefore, much higher production costs are assumed.

There are two major risks concerning the use of polymers for the mentioned applications. Firstly, the durability of transparent polymers if exposed outdoors is not sufficient. Experiments have shown that subwavelength gratings on PMMA are destroyed rapidly when being irradiated by sunlight outdoors. Therefore, no recommendation can be given for the use of unprotected microstructured polymer surfaces outdoors at the moment. Quite different is the situation when the microstructured polymer surface is protected by a UV-absorbing pane in front of it as is the case for the daylighting and sun protection systems as well as for CPV applications. Here it is assumed that the durability will be sufficient. The second risk is that all the mentioned applications are relatively new fields of research. Only in the case of CPV appreciable experience exists and only CPV systems with microstructured polymers are commercially available so far. Therefore, further work has to be done in order to know whether the concept or the polymer materials used give rise to further risks.

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Polymer Membranes for Sustainable Technologies

Jochen Meier-Haack, Martin Müller, and Klaus Lunkwitz

Abstract Membrane-based processes have found wide acceptance and are used as powerful alternatives for conventional techniques such as distillation, extraction, or energy production. Frequently, membranes prepared from commodity polymers do not have the desired properties for the various applications. For example, fouling is still an unsolved problem in membrane applications, which is closely related to surface properties of both the membrane and the foulant. To meet the requirements for the various tasks, membranes with tailor-made properties are needed. In this contribution on the one hand surface modification techniques are described, which are used to (a) obtain microfiltration membranes with low-fouling tendency and (b) to prepare membranes with required properties in pervaporation separation applications. On the other hand modification/functionalization of polymers for use as ion-exchange membranes in energy-producing systems (fuel cells) are discussed. The focus is set on surface modification with polyelectrolytes and polyelectrolyte multilayer systems. This versatile technique enables the preparation of porous membranes with adjustable surface charge and low-fouling tendency without interference of permeate quality. Dense pervaporation membranes based on polyelectrolyte multilayer systems, with high selectivities and moderately high flux were obtained. The performance of such membranes can be controlled by the polyelectrolytes used (charge density) and the preparation conditions (e.g. temperature). Finally, a short introduction of new membrane materials based on fully aromatic polymers as alternatives to perfluoroalkylsulfonic acids, such as Nafion, is given.

Keywords Fuel cells, Grafting, Membranes, Polyelectrolyte complexes, Sulfonated polymers, Surface modification

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Contents

Abbreviations

α	Separation factor
ε	Porosity
η	Dynamic viscosity of the permeate (Pa s)
σ	Ion conductivity (mS cm^{-1})
$\Delta P_{tr}=(P_1–P_2)$	Transmembrane pressure difference (kPa)
d	Effective capillary length (m)
F	Membrane area (m^2)
IEC	Ion-exchange capacity (mmol g^{-1})
J_V	Volume flux ($m^3m^{-2}min^{-1}$)
r_P	Mean pore radius (m)
t	Time (min)
V	Volume (m^3)
VOC	Volatile organic compound

1 Introduction

Membrane-based separation processes are recognized as environmentally friendly alternatives to conventional separation techniques such as distillation or extraction. The field of large-scale applications covers the range of drinking water processing, potable water production, waste-water treatment, application in the food and pharmaceutical industries, recovery of aroma and active substances as well as sterile filtration of pharmaceuticals and clarification of beverages.

For water-treatment processes such as drinking water or potable water production, reverse osmosis (desalination), nanofiltration, and ultrafiltration are mainly used. In these processes often a microfiltration stage is implemented as the first cleaning stage for the removal of dissolved organic matter, colloids and particles from the source.

Membrane-based separation processes are also used in large-scale applications with closed water recirculation. Examples for such processes are electrophoretic coatings in the automotive industry, or the work-up of detergent solutions and caustic solutions from the beverage industry or water from dye baths. The use of membranes in such processes reduces on the one hand the demand on fresh-water.

On the other hand the amount of waste-water is reduced to a minimum. Both factors lead to reduced environmental pollution.

In sewage treatment membranes are used to concentrate the sewage sludge (dewatering), so that the amount of solid deposits, which has to be treated as special solid waste is reduced drastically. Therefore, the costs for disposal are minimized and environmental pollution is reduced for two reasons. Firstly, the demand for the disposal area is reduced and secondly, energy for the refuse incineration is saved and the amount of off-gas is reduced.

Another important field of membrane application is the production of chlorine by the chlor-alkali-electrolysis process. Here the mercury-electrode process has been replaced by the so-called membrane process and diaphragm cell electrolysis.

The dewatering of organic solvents and the removal of volatile organic compounds (VOC) from ground water and from contaminated air can also be done by membrane-based separation processes. Especially in the dewatering of organic solvents e.g. alcohols, the membrane-based process, namely pervaporation, is favorable, because azeotropic mixtures can be overcome without any extraction processes. Furthermore, the pervaporation technique is suitable to separate close-boiling mixtures. Although, the advantages of this membrane-based separation technique are well-known, and some plants have been installed, pervaporation has to be considered as a niche-application.

A survey of large-scale membrane applications is for example given in the textbook of Nunes and Peinemann [1].

The latest developments, in which membranes are involved, have been recorded in the field of fuel cell technology [2]. Here, polymer membranes with chemical and mechanical stability, ion-conducting properties, and, for application in DMFC systems, low methanol permeability are used. The fuel cell technology excels by low or no emission of hazardous gases and by a higher efficiency compared to conventional combustion engines. The development in fuel cell technology is driven in part by regulatory pressure, especially by the US government and the growing shortage of fossil fuels like natural gas and oil.

The cited examples show that each separation problem needs a certain membrane-based process and a matching membrane with designed properties.

In principal, the membranes used in the various separation processes can be roughly divided into two groups, namely the porous membranes and dense membranes. However, there are some cases where it is not clear whether the membrane can be classified as porous or dense. According to the definition of the International Union for Pure and Applied Chemistry (IUPAC) porous membranes are those, having static transport channels or capillaries (pores) with a mean diameter larger than 2 nm. Porous membranes can simply be treated as very fine sieves, which grade particles on a molecular level of size. Corresponding to the above definition for porous membranes, dense membranes are those with a mean pore diameter less than 2 nm [3]. In dense membranes the pores are treated as nonstatic.

The mass transfer through the membranes is achieved by application of an external driving force. The mass transport through porous membranes is enabled by a hydrostatic pressure difference (driving force) between the feed-side and the permeate-side of the membrane and can be described by a modified version of the well-known Hagen–Poiseuille's law, taking the capillary structure, free diffusion, and Knudsen flow into account (1).

$$J_V = \frac{V}{F \cdot t} = \frac{r_P^2 \cdot \varepsilon \cdot \Delta P_{tr}}{8 \cdot \eta \cdot d} \tag{1}$$

The mass transfer in dense membranes takes place by diffusion in the free volume between the polymer chains of the membrane material. The external driving force for this process is a difference of the chemical potential $\Delta\mu_i$ of the permeating species i on either side of the membrane. This difference can be expressed as a concentration difference Δc_i, a partial pressure difference Δp_i, or an electrical potential difference ΔE. The transport mechanism involves three distinctive steps, (a) selective adsorption of the feed components to the membrane, the feed components are dissolved in the membrane material; (b) diffusion of the dissolved species through the membrane, and (c) desorption of the permeating species at the permeate-side of the membrane assisted by an applied sweep gas or vacuum.

The mass transfer is described by the so-called solution-diffusion-model. Because of the very complex nature of this transport mechanism different mathematical models have been developed ranging from empirical to theoretical approaches, to predict the mass transfer [4].

A survey of membrane separation techniques and the applied external driving forces is given in Fig. 1, in which the mean pore diameter of the membranes and the particle size are compared with the respective separation process.

Because of the low cost and easy processing (manufacturing) polymers are the preferred material for the production of membranes. However, the field of inorganic membranes derived from ceramics is growing very fast. Common polymers used for membrane fabrication and the membrane types derived therefrom are summarized in Table 1.

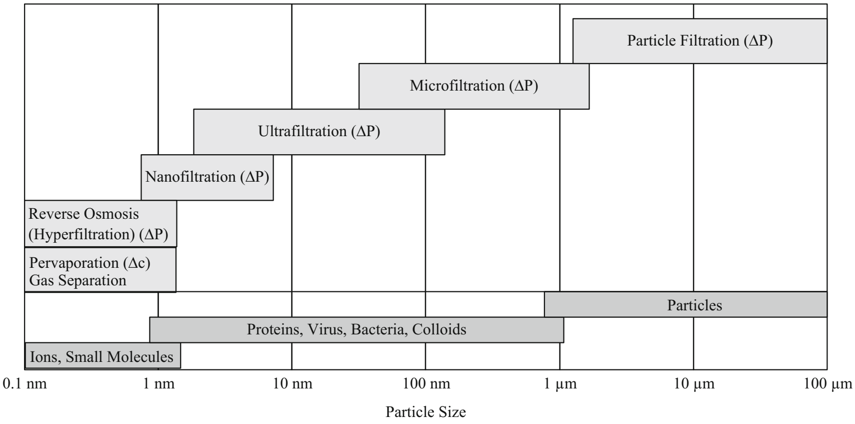

Fig. 1 Survey of membrane-based separation methods

Table 1 Common polymers used for production of commercial membranes

Membrane material	Membrane process
Regenerated cellulose	Dialysis, ultrafiltration, microfiltration
Cellulose nitrate	Microfiltration
Cellulose acetate	Gas separation, reverse osmosis, dialysis, ultrafiltration, microfiltration
Polyamide	Reverse osmosis, nanofiltration, dialysis, ultrafiltration, microfiltration
Polysulfone	Gas separation, ultrafiltration, microfiltration
Poly(ether sulfone)	Ultrafiltration, microfiltration
Polycarbonate	Gas separation, dialysis, ultrafiltration, microfiltration
Poly(ether imide)	Ultrafiltration, microfiltration
Poly(phenylene oxide)	Gas separation
Polyimide	Gas separation
Poly(vinylidene fluoride)	Ultrafiltration, microfiltration
Polytetrafluoroethylene	Microfiltration
Polypropylene/Polyethylene	Microfiltration
Polyacrylonitrile	Dialysis, ultrafiltration, microfiltration
Poly(vinyl alcohol)	Pervaporation
Polydimethylsiloxane	Pervaporation, gas separation

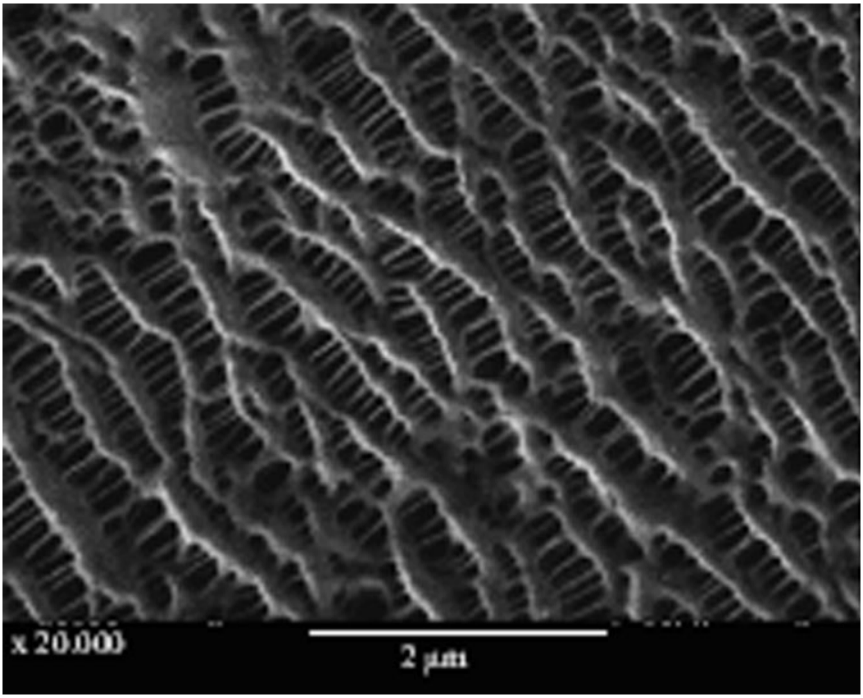

Fig. 2 Celgard membrane (stretched polypropylene (PP) film)

Membranes can be prepared from the polymer melt or from polymer solutions by different methods and techniques leading to membranes with the desired pore size, thickness, and morphology and structure. Porous membranes can be obtained

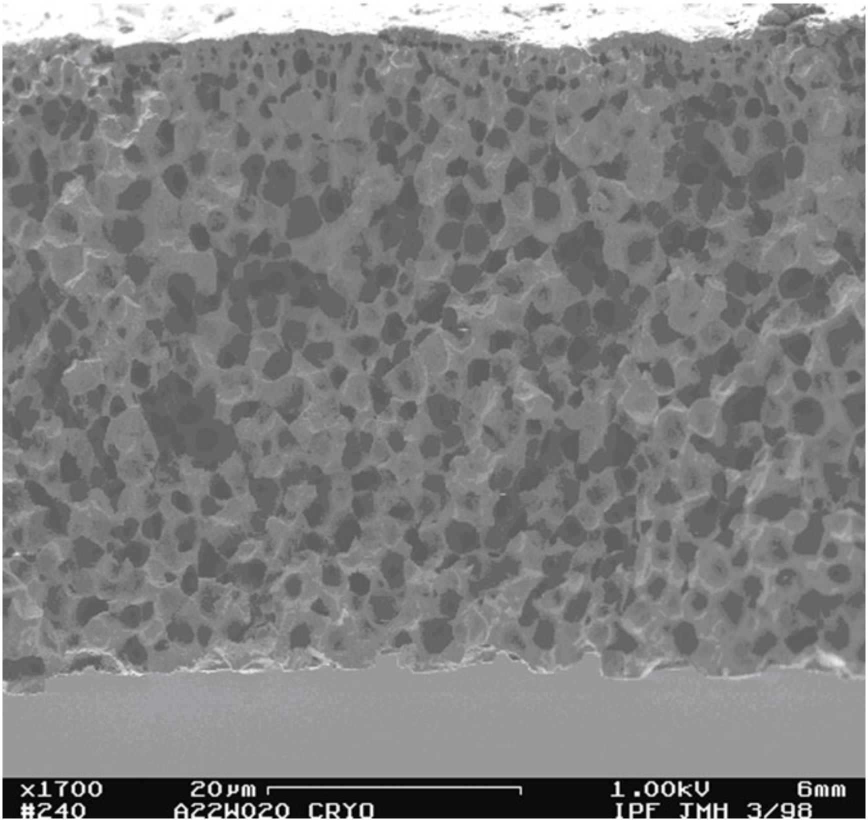

Fig. 3 Cross section of a polyamide-membrane (phase inversion process)

by stretching extruded films from semicrystalline polymers such as polypropylene (PP), polyethylene (PE), polyvinylidenfluoride (PVDF), or polytetrafluoroethylene (PTFE) [5–13]. Another way to prepare porous membranes, is to irradiate polymer films derived from polycarbonate (PC), poly(ethylene terephthalate) (PET), or PP with ions and a subsequent selective etching of the damaged structures (track-etch membranes) [14–16]. With this method porous membranes with ideal tube-like pores are obtained. The so-called phase-inversion process is one of the most common methods to prepare porous as well as dense membranes [17]. A polymer solution is cast onto a substrate and after an appropriate time, during which the solvent is partly evaporated, the polymer film is immersed into a coagulation bath. The morphology and pore size of the resulting membranes depend on the evaporation time, added pore forming agents, and the system solvent/nonsolvent. A variation of this process is the thermally induced phase separation (TIPS) [18]. Here, the polymer is only soluble in the solvent at elevated temperatures. As in the phase-inversion process, a polymer film is cast onto a substrate. On cooling the cast film, the polymer precipitates and the membrane is formed. This process is

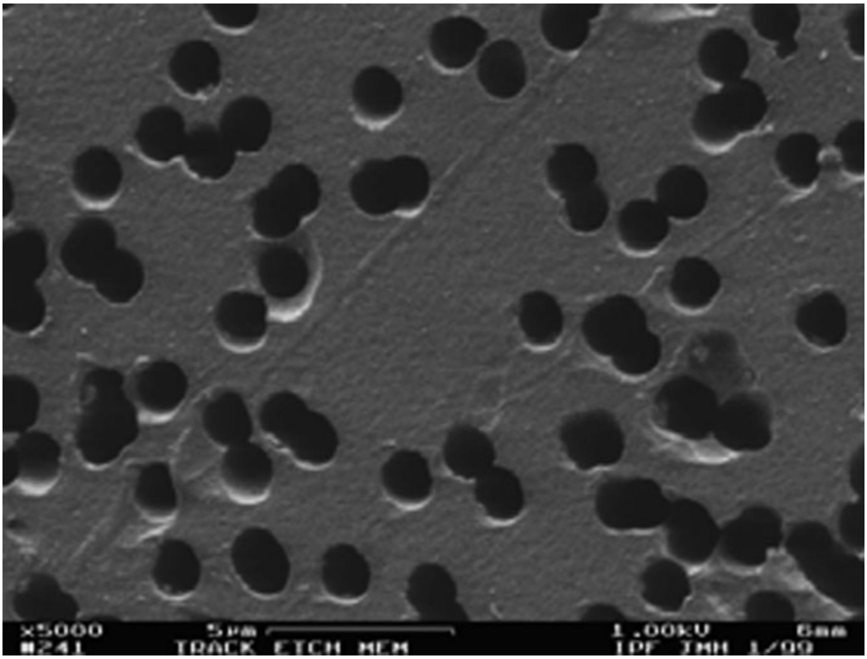

Fig. 4 Poly(ethylene terephthalate) (PET) membrane (track-etch)

preferably used for the preparation of polyolefin membranes. The SEM micrographs in Figs. 2–4 show some examples of membranes prepared by the methods described above.

2 Membrane Fouling

Despite the progress that has been made in membrane science, fouling is still a serious problem in many membrane-based separation processes. The expression fouling covers all events during operation of a membrane unit, that lowers the membrane performance e.g. permeate flux and is one of the major factors limiting the use of membranes in separation applications. Fouling is caused by undesired deposition of feed components on the membrane surface which is in the case of organic material favored by hydrophobic interactions (van der Waals) between the membrane material and the feed components [19, 20]. Up to now only periodical cleaning methods such as backflushing with air or water or chemical cleaning are used to remove the fouling products from the membrane surface. Furthermore, special module designs have been introduced in the past which induce a turbulent flow above the membrane surface and which should reduce the deposition of feed components on the surface [21, 22]. Particularly the back flushing and the use of

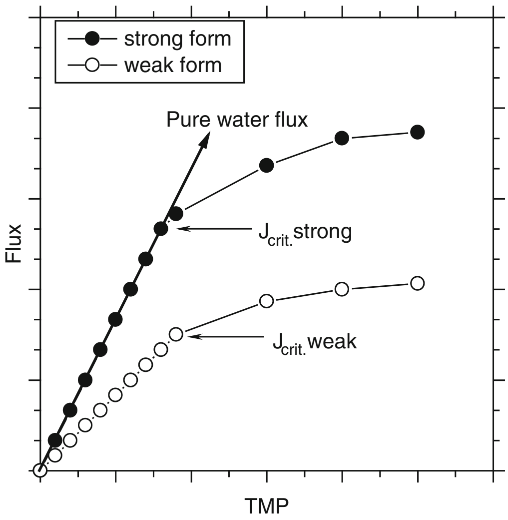

Fig. 5 Forms of critical flux as originally defined by Field et al. [25]

aggressive chemicals for membrane cleaning increases operational costs and therefore lowers the competitiveness of membrane-based water-treatment systems [23].

In order to suppress fouling, a new concept called "the critical flux concept" was introduced by Howell and co-workers in the mid-1990s [24, 25] and has been subject to a recently published review [26]. This concept describes a permeate flux below which no deposition of colloids and therefore no irreversible fouling occurs. In an early paper, Field et al. defined two types of critical flux: the strong form, where the transmembrane pressure (TMP) deviates from a certain point on from the (linear) pure water line and the weak form, where already at the starting point fouling occurs and the TMP-flux relationship is still linear but below the pure water line (Fig. 5) [25]. At the critical flux $J_{\text{crit.}}$ the TMP-flux relationship becomes nonlinear.

Hydrophobic membrane materials have the advantage of high chemical and mechanical stability, but the hydrophobic properties promote fouling by hydrophobic interactions. On the other hand more hydrophilic materials exhibit lower tendency for fouling, but these materials have also a lower chemical and pH resistance. Several methods to combine the good mechanical and chemical properties of hydrophobic materials with the low-fouling properties of hydrophilic polymers have been described in the literature. In large-scale production of for example polysulfone or polyaramide ultra- or nanofiltration membranes, hydrophilization is achieved by using blends of the base polymer and poly(vinylpyrrolidon). However, only small amounts of the hydrophilic polymers can be used in these blends due to restricted miscibility and film-forming properties.

The same problems occur on bulk modification of membrane polymers. The introduction of hydrophilic functionalities to the initially hydrophobic polymer may alter the film-forming properties to such an extent, that membrane formation is restricted to materials with a low degree of modification.

To overcome these disadvantages, surface functionalization and modification of hydrophobic membrane materials has found growing interest in the past. This technique leads to membranes with tailor-made filtration properties like permeate flux and retention as well as an effective reduction of fouling. A review article published by Ulbricht gives a good overview of the various activities in this field [27]. The creation of a positive charge to the membrane surface by for example grafting of polycations or adsorption of chitosan, introduces antibacterial properties [28–30].

Maartens et al. modified ultrafiltration membranes by adsorption of nonionic surfactants Triton X-100 and Pluronic F 108 [31]. Although a reduced fouling was observed, the modification was not stable under filtration conditions, due to the physisorption of the surfactants to the membrane surface by hydrophobic interactions.

A more promising method to obtain membranes with stable modification under filtration conditions is the chemical fixing of hydrophilic functionalities on the membrane surface for example by the grafting technique. The permanent hydrophilization and/or the permanent introduction of surface charge alters the interactions between the feed components and the membrane surface to such an extent, that the feed components show a lower tendency to adsorb at the membrane surface resulting in a reduced membrane fouling. Beside chemical and physical methods such as plasma-treatment, the grafting and adsorption of polyelectrolytes and polyelectrolyte complexes to membrane surfaces has been recognized as a versatile technique to introduce and control hydrophilic properties and/or sign of surface charge of membranes [32–52]. Especially the build-up of polyelectrolyte multilayer systems by consecutive alternating adsorption of oppositely charged polyelectrolytes is a very effective method to reduce membrane fouling substantially and to design and control filtration properties e.g. permeate flux and retention capability. The formation of polyelectrolyte multilayers (PEM) by the layer-by-layer adsorption of polyelectrolytes was taken up and further developed by Decher and coworkers in the early 1990s [53, 54]. Furthermore the surface charge and therefore the (electrostatic) interactions between the feed components and the membrane surface are determined by the outermost adsorbed polyelectrolyte layer, which can easily be controlled by ending the formation process with the adsorption either with a polyanion (negatively charged surface) or a polycation (positively charged surface). The reversal of surface charge on adsorption of polyanions and polycations was monitored for example by zeta-potential measurements as shown in Fig. 6.

We have used the layer-by-layer technique in our laboratories to modify PP microfiltration membranes [35, 55]. In a first step the PP membranes were treated with CO_2-plasma to create peroxide functionalities on the surface. These groups were used in a subsequent step, grafting polyacrylic acid onto the surface. The chemical anchoring of the first polyelectrolyte layer is advantageous compared to physically adsorbed polyelectrolytes onto a plasma-treated surface for two reasons. Firstly, the amount of grafted polyelectrolyte is much higher than that of the adsorbed one and secondly the grafted layer is much more stable under filtration conditions.

In a simple dipping procedure one additional layer of poly(diallyldimethyl ammonium chloride) (PDADMAC; polycation) and polyacrylic acid (PAAc;

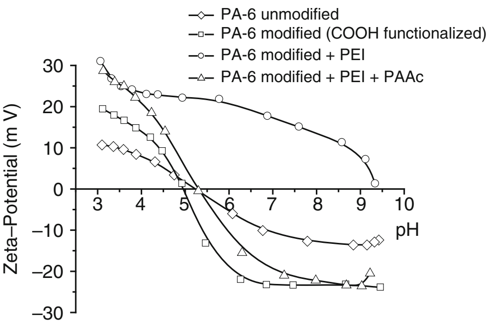

Fig. 6 ζ-potential versus pH curves of modified PA-membranes (reproduced from [82] with permission from Wiley-VCH)

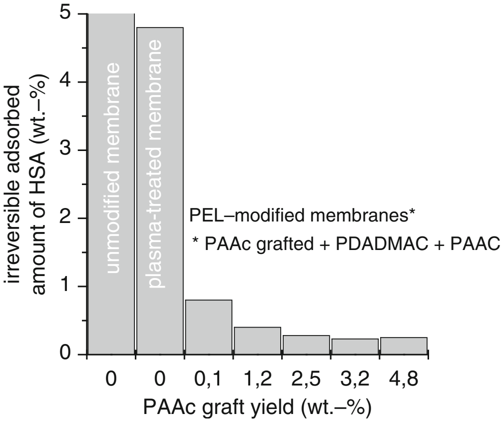

Fig. 7 Effect of graft yield and polyelectrolyte deposition on the irreversible fouling of PP membranes with Human-Serum-Albumin (HSA) (pH 6.5)

polyanion) were adsorbed to the grafted layer, resulting in a negatively charged surface. Investigations on a lab-scale showed a highly reduced irreversible adsorbed amount of protein (Human-Serum-Albumin; HSA) after filtration of an aqueous protein solution when the membrane surface and the protein are equally charged (Fig. 7). Furthermore, the permeate flux of the polyelectrolyte complex membrane is double that of the just-grafted membrane without any loss in retention. This anti-fouling effect of the modified surface is attributed on one hand to the repulsive electrostatic forces between the membrane surface and equally charged protein molecules or agglomerates. On the other hand the adsorption due to the more hydrophilic membrane surface and the resulting reduction of hydrophobic interactions between the membrane and the protein also contributes to the anti-fouling effect. These anti-fouling effects at PEM-modified polymer membrane materials were also confirmed on planar thin polymer films or silicon crystals modified with analogous PEM systems under variation of several media parameters [56–59]. Moreover, especially the PEI/PAAc system has been also found useful for the selective repulsion or separation of proteins out of binary protein mixtures by changing the pH value [60].

But also attractive interactions between the membrane surface and feed components might have a positive impact on membrane performance [36, 61, 62]. In this case a PP hollow-fiber was graft-modified with PAAc using a pre-adsorbed macroinitiator as the starting agent for the graft process. The results of the filtration experiments are displayed in Fig. 8. Filtration of water containing calcium ions and natural organic matter (NOM) through such modified membranes leads at low graft yields (ca. 4.5 wt.-%) to a similar flux-time dependence (fouling rate) as observed for the unmodified membrane. At higher graft yields (ca. 7 wt.-%), the initial flux is only approximately 25 % that of the unmodified membrane, but starts to increase with prolonging experimental time. After reaching a flux maximum, which is approximately 30% that of the unmodified membrane, the permeate flux remains nearly constant. The permeate quality is not influenced. In this case we have two counter acting effects influencing the membrane performance. On the one hand the positively charged calcium ions or in general multivalent cations interact with negatively charged PAAc which are initially in an extended rather than a coiled conformation attributed to repulsive electrostatic forces between equally charged groups on the polyelectrolyte backbone. The calcium ions can act as a crosslinker forcing the grafted polyelectrolyte layer into a more coiled conformation. This change in conformation results in a flux enhancement due to increased effective pore radius. On the other hand adsorption of NOM leads to pore blocking and decrease of permeate flux. In the case, when both effects, the flux enhancement by calcium binding and flux decrease by NOM adsorption equal each other, a constant flux is observed. The interplay of various features such as feed composition, graft yield, interaction between graft layer and feed, will all determine the potential for improved membrane fouling performance by polyelectrolyte graft modification.

Moreover, ultrafiltration membranes derived from polyaramide were successfully modified by electron beam irradiation [63]. As displayed in Fig. 9, an increase in retention capability without any change in permeate flux was achieved, due to chemical reactions leading to crosslinks and to the introduction of hydrophilic groups into the polymer backbone.

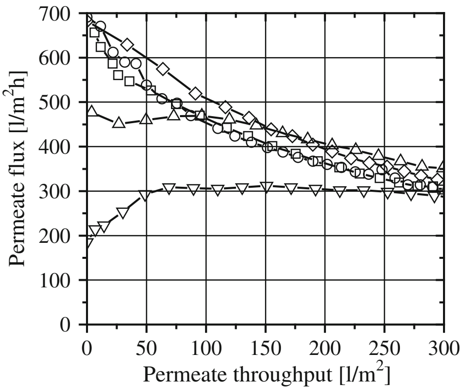

Fig. 8 Effect of anionic grafting on the fouling by NOM at pH 6.5 for a graft yield of 3.7 wt.% (□), 4.5 wt. % (◇), 5.5 wt.% (Δ) and 7.0 wt.% (∇), (non-grafted membrane (○)) (reproduced from [36] with permission from Elsevier)

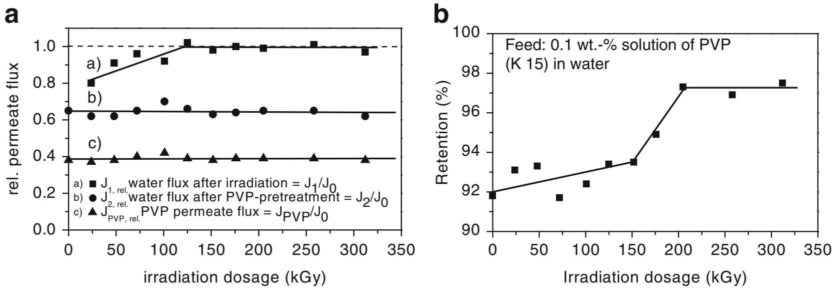

Fig. 9 Effect of electron beam irradiation on the performance of a polyaramide ultrafiltration membrane. (**a**) Permeate flux, (**b**) Retention (reproduced from [63] with permission from Wiley-VCH)

3 Dense Membranes

Dense membranes are used for the separation of small molecules and ions. Typical applications are reverse osmosis, hyperfiltration, pervaporation, or gas separation (see for example [64,65] and the references cited). Thin separating layers are recommended as the transport through dense membranes is diffusion controlled. This requirement can be satisfied by the so-called composite membranes consisting of a highly permeable support layer coated with a thin highly selective separating layer. It has been demonstrated that the layer-by-layer deposition of oppositely charged polyelectrolytes onto nonselective high-flux supports is useful to prepare such composite membranes [38–40, 66, 67]. The thickness of the polyelectrolyte multilayer system is only a few nanometers and can be controlled by the number of adsorbed layer pairs and preparation conditions. The selectivities and permeabilities of the composite membranes depend strongly on the chemical structure and the charge density of the polyelectrolytes used. It was found that the selectivities of the membranes increased with increasing charge density of the polyelectrolytes. When weak polyelectrolytes with high charge densities like PAAc or PEI are employed for the build-up of the complex layer systems, a small number of polyelectrolyte layers (six double layers) are already sufficient to obtain membranes of high selectivities in the dewatering of low molecular weight alcohols [40]. For example, separation factors higher than 10,000 have been reached in the dewatering of 2-propanol and ethanol with composite membranes consisting of a polyamide-6 support and six double layers of PEI/PAAc or PEI/Alg. Furthermore, the number of ionic groups in the supporting materials plays an important role in the build-up and stability of the polyelectrolyte multilayer systems since these groups act as anchors for the first polyelectrolyte layer.

In general, due to the broad variety of polyelectrolytes the consecutive alternating adsorption of oppositely charged polyelectrolytes is an easily accessible and powerful method to tailor membranes to the desired properties. Recently, the author of this contribution reported on a highly selective pervaporation membrane with only one or two polyelectrolyte double layers [68]. The membranes were obtained by increasing the adsorption temperature from 25 to 80°C. Even in the separation of water/methanol mixtures high water-selectivity was observed. Therefore and for the reported ion conductivity [69], those membranes might be of interest for application in DMFCs.

4 Ion-Exchange Membranes

In the past two decades, fuel cells and in particular ion-exchange membranes have become a top priority topic in material research. Fuel cells are seen as promising alternative energy conversion systems replacing the combustion-based techniques. Among the various types of fuel cells, the low-temperature fuel cells like the polymer electrolyte membrane fuel cell (PEMFC), DMFC, or alkaline fuel cell (AFC) are the most flexible ones concerning range of applications e.g. portable, automotive, and stationary.

An overview on the latest research on PEMFC is for example given in a special issue of Advances in Polymer Science [2] or the Journal of Membrane Science [70].

Compared to the PEMFC the AFC has the advantage that no precious metal catalysts for the oxidation of hydrogen at the anode are needed. However, the classical AFC is operated with a highly concentrated potassium hydroxide solution (50 wt.-%) as electrolyte. This strong base adsorbs carbon dioxide. The formed carbonate tends to precipitate inside and consequently plugs the small structure inside the fuel cell. Therefore, only highly purified hydrogen and oxygen can be used with this type of fuel cell. In the past years some effort has been made to develop anion-exchange membranes, which will withstand the harsh conditions in an AFC (high pH, high temperature) [71, 72]. Usually polymeric trimethyl-alkyl ammonium salts are used, but these compounds decompose at elevated temperatures (Fig. 10) [73, 74]. At the moment maximum working temperatures of membrane-based AFC are around 70°C, leading to a much lower power output compared to PEMFCs [75].

Though not fulfilling all requirements for fuel cell application (e.g. operating temp. $>100°C$), the poly(perfluoroalkylsulfonic acid)s (PFSA) like Nafion, Hyflon, or Dow-Membrane are still state of the art membranes in the field of PEMFC, because of their high proton conductivities (under high humidification) and high chemical stability. The shortcomings of the PFSA-membranes and the prospect of lower production (material) costs have forced the development of hydrocarbon-based ion-exchange materials. In particular the research activities have been focused on the well-known high-performance polymers such as poly(arylene ether) (PEEK, PSU, PES) in their sulfonated form (the reader is referred to [2, 70] and the herein cited literature). However, aromatic sulfonic acids are susceptible to desulfonation at elevated temperatures and low pH, especially when attached to electron-rich aromatic rings [76]. Furthermore, sulfonic acids attached to aromatic rings are much less acidic than those connected to a perfluoroalkyl chain. Thus, a much

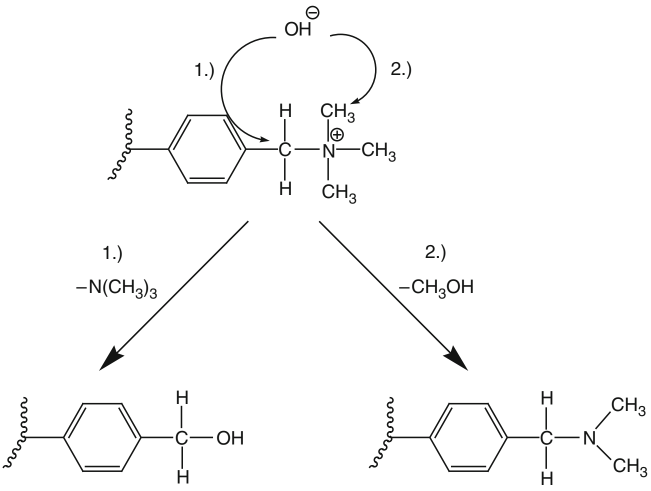

Fig. 10 Decomposition pathways of tetra-alkyl ammonium salts under basic conditions at elevated temperatures

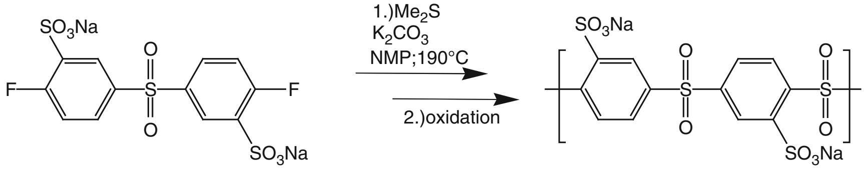

Fig. 11 Structure of and reaction scheme towards sulfonated poly(p-phenylene sulfone)

higher concentration of functional groups has to introduced into the polymer chain to achieve a similar proton conductivity as the PFSA-based membranes. On the other hand this high content in functional groups leads to higher water-uptake/ swelling of the hydrocarbon membranes, which results in a substantial loss in mechanical properties. Recently, Kreuer et al. introduced an ion-exchange membrane for medium-temperature PEMFC based on sulfonated poly(phenylene sulfone) (sPSO$_2$) [77–80] (Fig. 11).

Sulfonated poly(phenylene sulfone)s with an ion-exchange capacity of 4.57 mmol g^{-1} (sPSO$_2$-220) and 2.78 mmol g^{-1} (sPSO$_2$-360) showed over a wide range of humidification a proton conductivity superior to that of Nafion 117. More significant is the conductivity at low humidification levels and high temperatures. For example at 135°C and 30% relative humidity the conductivity of sPSO$_2$-220 is seven times higher and that of sPSO$_2$-360 is twice as high as that of Nafion 117 [80]. These outstanding properties were attributed to a highly ordered structure with very narrow hydrophilic channels (ca. 1.4 nm in sPSO$_2$-220) [80]. Furthermore, sPSO$_2$-samples exhibit a high thermal and hydrolytic stability due to the attachment of the sulfonic acid group to an electron-poor aromatic ring [79].

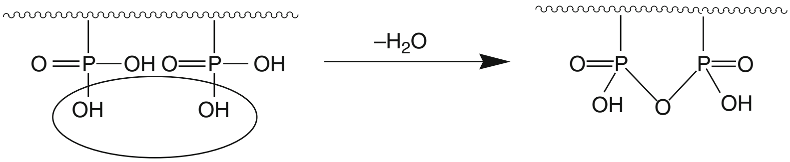

Fig. 12 Formation of anhydride structures in poly(phosphonic acid)s

The aspect of desulfonation has motivated the search for ionomers with acidic functionalities other than the sulfonic acid group. The phosphonic acid group shows higher thermal and chemical stability as compared to the sulfonic acid group, and, shows no "dephosphonation." An overview of the research activities in the field of poly(phosphonic acids) has for example been published by Rusanov et al. [81]. However, the low acidity and the limited number of complex synthetic procedures available for phosphonation has been the main obstacle in the development of ion-exchange membranes based on phosphonic acids. Furthermore, the low acidity of the phosphonic acid groups makes it necessary to introduce even a higher number of ion-exchange sites into the polymer backbone than in the case of sulfonated polymers with all known consequences. Finally, the formation of phosphonic anhydride (Fig. 12) during operation at high temperatures limits the application of poly(phosphonic acid)s.

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