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ENVIRONMENTAL CHEMISTRY

11

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Polymers - Opportunities and Risks I

General and Environmental Aspects

Springer

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Volume 11

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Polymers – Opportunities and Risks I

General and Environmental Aspects

Volume Editor: Peter Eyerer

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The Handbook of Environmental Chemistry
ISSN 1867-979X e-ISSN 1616-864X
ISBN 978-3-540-88416-3 e-ISBN 978-3-540-88417-0
DOI 10.1007/978-3-540-88417-0
Springer Heidelberg Dordrecht London New York

Library of Congress Control Number: 2010931701

Cover design: SPi Publisher Services

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

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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
Martin Weller
Volume Editors

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Plastics: Classification, Characterization, and Economic Data

Peter Eyerer

Abstract This chapter defines “Environmentally Friendly Polymer Engineering” as the basic organizational system of the first volume of these two books. The classification of plastics, and a list of their main characteristics, follows. This chapter closes with some economic data.

Keywords Characteristics of Plastics, Characterization, Classification, Economic data, Environmental Polymer Engineering

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P. Eyerer (ed.), *Polymers – Opportunities and Risks I: General and Environmental Aspects*, Hdb Env Chem (2010) 11,
DOI 10.1007/978-3-540-88417-0_1,

1 Introduction

Plastics are high molecular organic compounds, produced either by conversion of high molecular natural materials or by additive chemical combination of low molecular building blocks, so-called monomers, in a variety of different chemical reactions. This leads to the differentiation between converted natural materials and synthetic plastics. The synthetic plastics are the more widespread and various of the two groups. Their variety is due to the many potential combinations of monomeric building blocks and the different ways of combining them to form high molecular chains (linear, branched, crosslinked). Although new synthetic plastics are still occasionally discovered through ongoing research and engineering efforts, the number of chemical modifications of existing plastics by means of copolymerization or blending is now much greater.

Plastics (*polymers*) are materials, so the study of plastics is part of material science. The aim is to use the materials *in construction of useful solids* that can be processed, used, and recovered beneficially from the point of view of engineering, economics, and the environment.

Plastics are “tailor-made” materials, with all of the *opportunities and risks* this high level of adaptability entails, whereby the risks often result from improper handling of the material and are thus avoidable.

In most cases, opportunities can only be properly exploited if inherent potentials are developed and implemented with a degree of technical expertise. Risks, on the other hand, can often not be neutralized, or at least reduced to tolerable levels, without suitable development and management efforts and expenditures. The challenge is to master both – opportunities and risks.

2 Environmentally Friendly Polymer Engineering

The development of parts, components, systems – and of products in general – requires a *holistic point of view*.

Polymer engineering (see also [1]) thus includes synthesis, processing, construction design, tooling, production systems, production, surface characteristics, recycling and disposal as well as education and advanced training in these areas (see also Fig. 61 of Chapter “Processing (Primary Forming) of Plastics into Structural Components”).

Plastics or polymers result from chemical reactions that convert monomers into polymers, so-called *polymerization*.

Depending on the types of reinforcing materials used – fibers (short, long), balls, wafers, or fiber textiles/weaves – the properties of polymers are highly variable.

Working with plastics and composites presupposes knowledge of the *temperature and time-dependent properties* of this group of materials. The higher the degree of chemical crosslinking of the macromolecules, the basic building-blocks of every plastic, the higher the thermal and mechanical load levels it will withstand, the less it will creep under load, the better it will resist the effects of media, and the lower its emission levels will be.

Plastics and composites are *tailor-made materials*. The unrestricted freedom this implies has been reduced in the past 20 years by the necessity of recycling and the difficulties involved in disposal. Recent years have seen more development and use of specific functional and gradient materials that can hardly be economically recycled in pure form. In these cases, the utilitarian advantages of the material override the recycling aspect.

Further important advantages of plastics include the many *economical processing potentials of these materials*, combined with the freedom of form and design and the *integration of various functions*. The potential for innovation in processing of polymers and composites remains enormous.

Combinations of different processes open up new horizons. In the future, pressing of graded fiber composites will become an attractive alternative. A breakthrough in automotive engineering based on use of this group of materials is on the way.

The competitiveness of materials is influenced to a considerable degree by how much time is required to produce prototypes (*rapid prototyping*) and tooling techniques (*rapid tooling*). The integration of rapid engineering with simultaneous engineering (CAD, CAE, CIM, TQM . . .) is now considered the state of the art. A further opportunity is presented by the continued intensive development of *products suitable for inmold assembly techniques*.

As soon as economical processing methods for parts with large surface areas with integrated *in-line, nondestructive testing* become available, polymer-fiber composites will see large series production, for example in the automotive industry for exterior and interior applications and in the construction industry (including load-bearing structures). Composites are already irreplaceable in the fields of mechanical engineering, medical technology, electrical engineering, and construction engineering.

Surface engineering is a key technology for applications with plastics and composites. Consumers demand top quality, but do not see the consequences for the natural environment. In the future, product manufacturers especially in automotive industry should cooperate to cut back exaggerated surface qualities as a contribution to the preservation of natural resources.

Water-based and single-layer paints, overspray reductions, solvent recovery, paint sludge recycling, and through-dyed basic materials are some of the areas in which *environmental problems* can be approached, including plastics recycling.

Nearly all plastics can be reused. The purer the recovered material, the better. Composites based on different matrices must be viewed much more critically in this sense. At present, material recycling is still struggling with economic and logistical problems.

Disassembly costs are largely ignored in product pricing. The incineration of plastics is still often the most economical solution. It makes little practical sense to consider plastics recycling within an isolated framework.

Holistic balances are decision-making aids that are helpful in the selection of materials and processes during product development. Qualified judgments cannot be forthcoming until production, processing, utilization, and recycling/disposal have been analyzed in the form of a closed cycle, completely and objectively (applying understandable, clearly defined framework conditions). Interactive databases and standardized evaluation methods are needed for this purpose.

Materials under consideration for future use can only be analyzed and evaluated properly within an all-inclusive product engineering framework. When it comes to plastics and composites, this means *polymer engineering* and also applies to polymers made from renewable raw materials (matrix and fibers).

In addition to the technical aspects, *education and advanced training* must also be integrated into product engineering. Improved teaching and learning approaches are going to have to replace the old podium lecture. For example, the training program TheoProx [11] integrates students, teachers, and industrialists in serious project work.

3 Classification of Materials

Materials can be generally classified as metals and nonmetals, with composites as a variable subset. Plastics are organic materials, subcategorized as either natural materials such as lignin (bio resin of wood) or latex or as synthetic materials, including their conversion from natural original raw materials.

4 Classification of Plastics

As shown in Fig. 1, plastics are classified as thermoplastics, elastomers, and duroplastics. In practice, classification is made in accordance with a number of different aspects. In Fig. 1, thermoplastics are categorized in physical terms (according to structure), elastomers in chemical terms (double bond), and duroplastics according to process pressure.

Thermoelastics (more of a special case) and the significant group of thermoplastic elastomers (TPE) are shown in Fig. 1 above thermoplastics with rubber elements

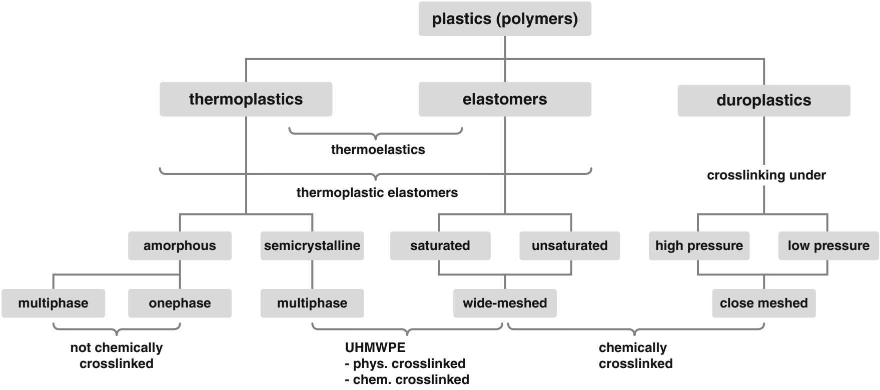


Fig. 1 Classification of plastics [2]

chemically integrated into the molecular chains. Their integration is either uncrosslinked or crosslinked.

5 Classification of Composites

Composites are defined as follows:

- They consist of *two or more components* (phases)
- that are *mutually insoluble*
- with properties optimized for specific applications
- *macroscopically*, they are *quasi-homogeneous*

The preconditions for a composite design are:

- The properties of the phases must differ by greater than a factor of 3 and
- each *phase* must account for *more than 10% by mass* (1–3% by mass of particles with large specific surface (nano particles) are sufficient for reinforcement)

Table 1 shows the classification of composites in general use along with examples of applications.

Table 1 Classification: composite materials and their applications [2]

Geometry		Particle composites	Fiber composites	Material composites, layered composites
Matrix materials	Reinforced materials	Glass, beads, talcum, quartz powder	Glass fibers, whiskers, C fibers	Sandwich: – High-strength sheets/films – Oriented fibers, layers, etc.
Metals		Femur-head (block carbides)	Piston head, piston recess edge	Combustion chamber (CHG), flat gasket
Inorganic materials	Glass	Sintered foamed glass	Wire-reinforced glass	Safety glass
	Ceramics	Protective plates for gliders	Valves, turbine vanes	Piston head, piezo actors
	Cement	Concrete	Steel, carbon fiber-reinforced concrete	CFP layer bridge repairs
	Carbon	–	Brake linings	Flat gaskets
Polymers	Thermoplastics	Pump casings	Fan impellers, frontend, underbody	Surfboard, packaging, dashboard
	Duroplastics	Grinding wheels	Bumpers, implants, aircraft structures	Headlamp reflector, plywood
	Elastomers	Car tires (tread)	Rubber tubing	Membranes, rubber-metal composites

6 The Main Characteristics of Plastics (According to [3])

Thermoplastics are *uncrosslinked* plastics up to their decomposition temperature. Flow or melting (Fig. 2) occurs above the softening point of the amorphous structure in *amorphous thermoplastics* and above the melting temperature of *semicrystalline thermoplastics*. In this thermoplastic state, the viscous liquid can be processed. Form strength is achieved by cooling. Meltdown, solidification, and crystallization can be repeated any number of times.

TPE are multiphase plastics with molecular segments characterized by elastic deformability into which fusible amorphous thermoplastics are integrated, rendering them thermoplastically deformable.

Thermoelastics are chemically or physically wide-meshed crosslinked plastics that become elastic above the softening temperature (glass transition temperature) or fusing temperature, but do not flow viscously up to the decomposition temperature, making them nonprocessable as thermoplastics. Below the softening temperature, their characteristics are similar to thermoplastics.

Elastomers are chemically *wide-meshed crosslinked* plastics that are elastic from lower temperatures (below 0 °C) up to the decomposition temperature (Fig. 2). As a result of the wide-meshed crosslinking, macrobrownian movements (molecular

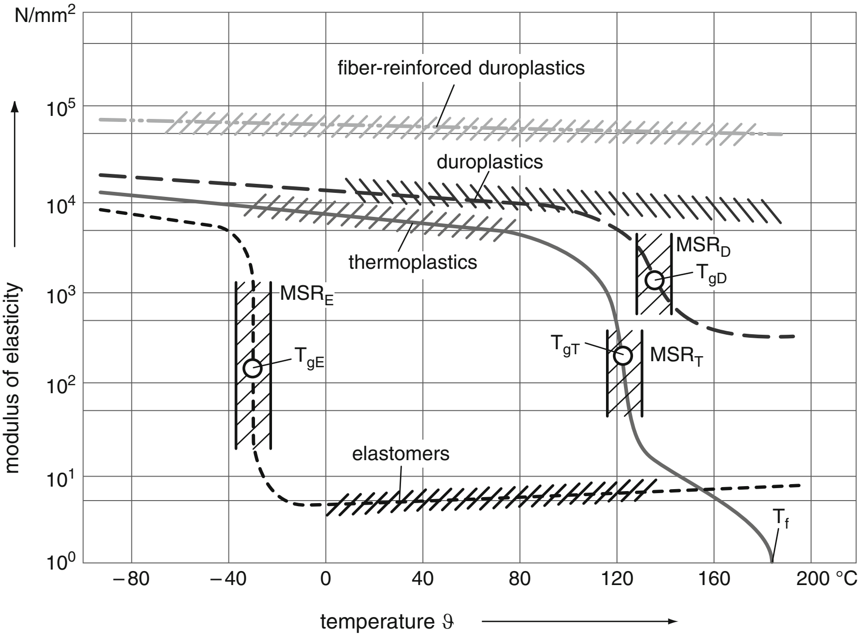


Fig. 2 Temperature-dependence of the modulus of elasticity (Young's modulus) of plastics (diagram). As an alternative to this modulus, tension σ can also be plotted against constant elongation ε or viscosity υ, or other properties [2]. $MSR_{E,T,D}$: main softening range of elastomers, thermoplastics, duroplastics, T_g: associated glass transition temperature, T_f: flow point of the amorphous thermoplastic, ////////: application range, \\\\\\\\\\\\\\\\: application range

chain sliding) are not possible at any temperature. Above the softening temperature (glass transition temperature) – above −80 °C to +20 °C, depending on the plastic – chain segment mobility becomes possible, facilitating greater deformations depending on the temperature and external force loads. Flow processes (processing) are hardly possible after crosslinking (vulcanization) (Fig. 2).

Duroplastics are chemically close-meshed plastics up to the decomposition temperature, and normally amorphous. As a result of crosslinking, the macromolecules no longer show microbrownian motion (rotation of chain segments). Limited chain segment movements resulting in limited creep processes become possible only above the softening temperature (glass transition temperature) – i.e., at over 50 °C. Flow processes (processing) are no longer possible after crosslinking.

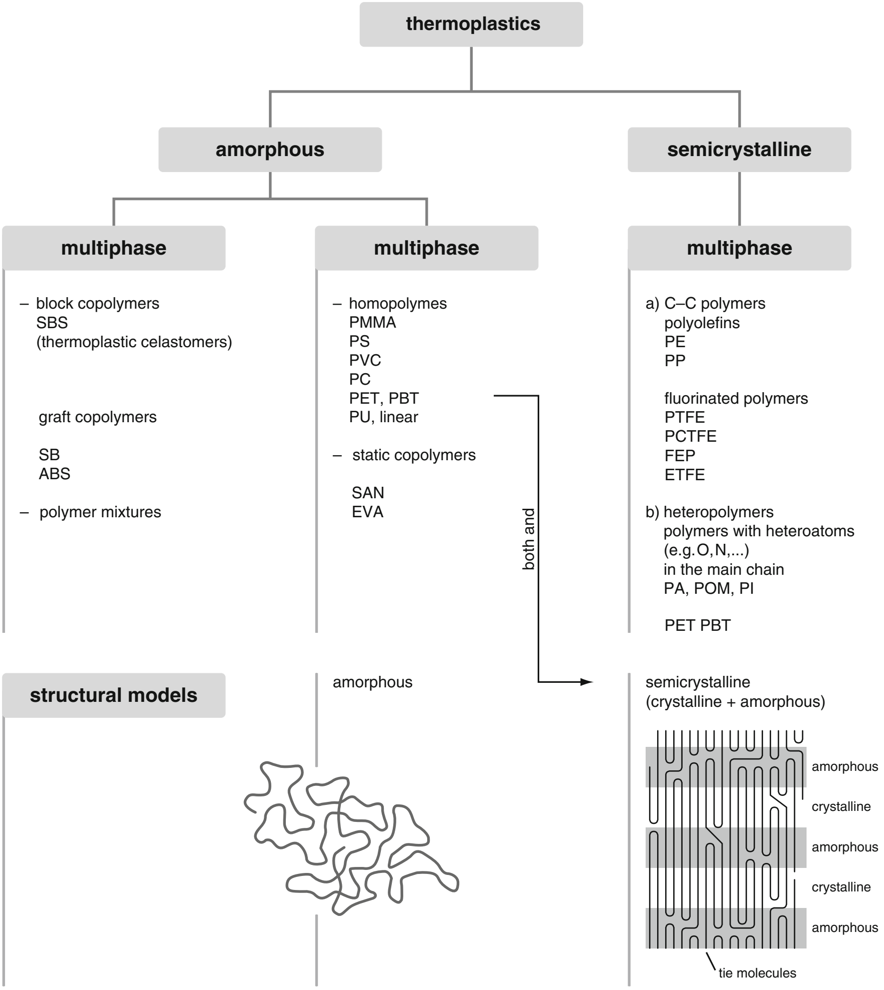


Fig. 3 Classification of thermoplastics according to structural characteristics [2]

Thermoplastics and TPE are meltable; elastomers and duroplastics are not meltable. All plastics are subject to greater and lesser degrees of softening and freezing.

The temperature-dependent characteristics result essentially in the following curves (in fact, each group of plastics is characterized by large numbers of different curves), see Fig. 2.

The following presentations and information contribute details on the main properties of plastics.

Thermoplastics can be classified in accordance with Fig. 3 (in reality: three-dimensional). The arrangement of the macromolecules is shown schematically.

A tire formula is presented as an application of elastomers in Table 2.

Table 2 An example of a tire formula (according to Goodyear Research Center) in percent by mass

10 %	Steel cord	Example of a passenger car tire formula:
3 %	Textiles and bead wire	60 % SBR
42 %	Elastomer (rubber) ⟶	20 % NBR
27 %	Carbon black	12 % BR
11 %	Oil	3 % IIR
1 %	Chemical fillers	5 % other

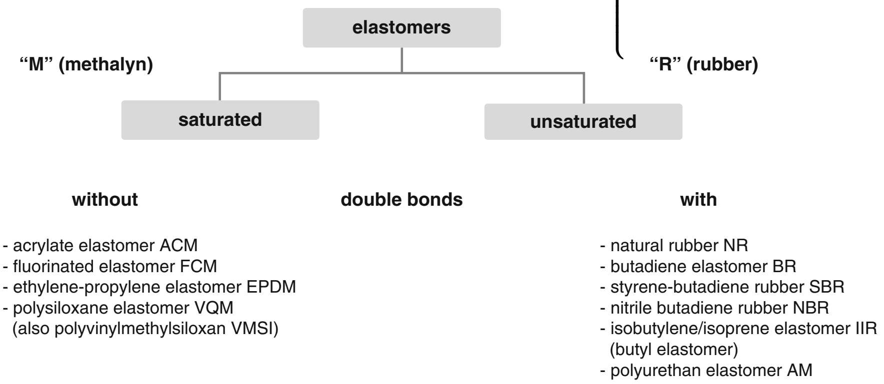


Fig. 4 Classification of elastomers according to their structural characteristics [2] (for more details see Table 3)

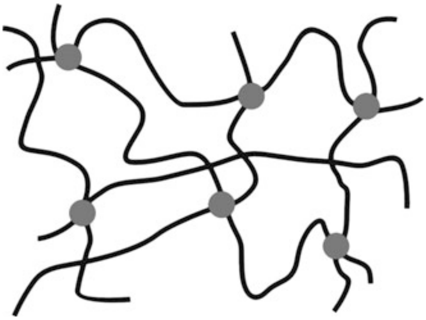


Fig. 5 Structural model of a wide-meshed, chemically networked elastomer with little crosslinks (wide deformable meshes)

Table 3 Summary of the most important types of elastomers with their main applications [4]

Elastomers		Abbrev.	Typical applications	
Chemically crosslinked elastomers (vulcanizates)	Natural rubber	NR	Apparatus linings, shoe soles, rubber boots, gloves, adhesives	
	Styrene-butadiene rubber	SBR	Vehicle tires	Technical articles
	Butadiene rubber	BR	Vehicle tires	Shoe soles, technical articles
	Isoprene rubber	IR	Vehicle tires	Thin rubber articles
	Chloroprene rubber	CR	Technical rubber articles, e.g., conveyor belts, gaskets, tubes, roller surfaces, container linings	
	Acrylonitrile-butadiene rubber (nitrile rubber)	NBR	Standard rubber for technical applications: O-rings, groove rings, sealing bellows, rotary shaft seals, gangway bellows, membranes, tubes, seals resistant to oil and fuels	
	Polyurethane	PUR	Wear-resistant, steaming machine parts, linings, shoes	
	Ethylene–propylene terpolymers (diene)	EPDM	Energy-absorbing external vehicle components such as front and rear spoilers, bumpers, cable insulations, mixed components for thermoplastics (PP) profile packings	
	Butyl rubber	IIR	Tubes for tires, seals, membranes, damping elements, linings in apparatus construction up to 140°C (abrasion-resistant), electrical insulations in cable industry	
	Silicone rubber (polysiloxane)	VQM	Mold seals and packing masses with high levels of heat resistance and cold flexibility	
	Fluoroelastomers	FKM	Seals that are highly resistant to heat and chemicals	
Physically “crosslinked” elastomers (TPE)	Thermoplastic polyolefin elastomers (ethylene–propylene block copolymers)	EPR (EPM)	Energy-absorbing car parts such as spoilers and bumpers	
	Styrene–butadiene block polymers	SBS	Soles for shoes, mixed components for thermoplastics	
	Thermoplastic polyurethanes	TPE-U	Ski boots, wear protection layers, damping elements	
	Thermoplastic polyether esters	TPE-E	Hydraulics, pneumatics (oil-resistant and thermally stable)	
	Thermoplastic polyamide elastomers	TPE-A		

Elastomers can be classified in accordance with Fig. 4 (in reality: three-dimensional).

Figure 5 shows the *structural model* for elastomers. Table 3 presents the classification and applications of elastomers. TPE are two-phase or multiphase plastics (block copolymers) with elastic properties similar to those of elastomers, but with a melting temperature that allows for processing as with thermoplastics. Figure 6 illustrates the classification of TPE.

Duroplastics are classified as shown in Fig. 7. The chemical crosslinking reaction takes place in the molding tool (usually heated). Table 4 describes, based on the example of polyolefin blends, their advantages over thermoplastics and elastomers.

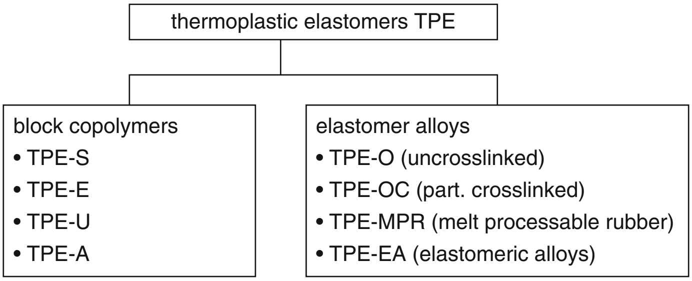


Fig. 6 Classification of thermoplastic elastomers (based on Osen and Sckuhr [5])

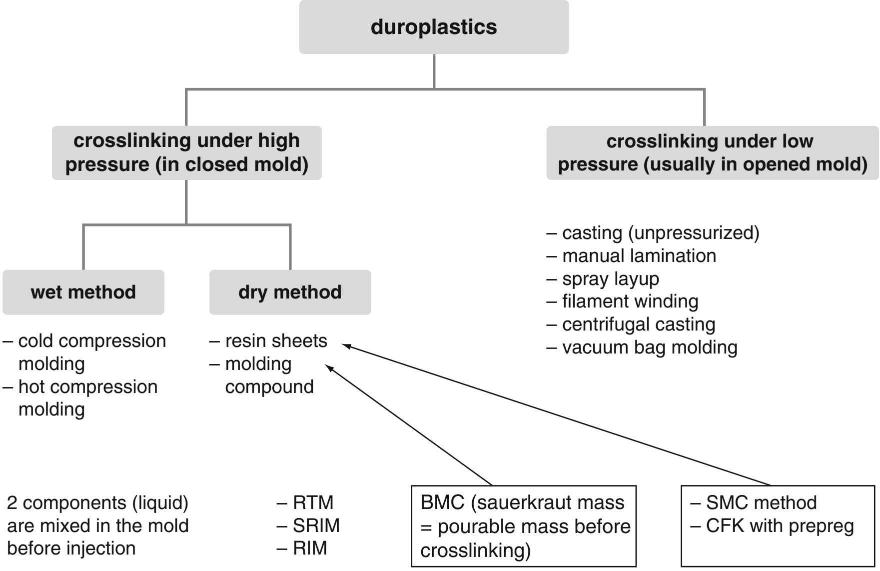


Fig. 7 Duroplastics grouped according to processing method [2]

Table 4 Thermoplastic elastomers (example of TPO); characteristics

Thermoplastic elastomers (e.g. polyolefin blends TPO)

Advantages of polyolefin blends (TPO) compared to thermoplastics	Advantages of polyolefin blends (TPO) compared to elastomers
• improved resilience	• lower processing costs
• higher utilization temperatures	• increased productivity, reduced energy costs
• contain no plasticizers	• recyclability of production wastes and used components
• improved resistance to abrasion	• enlarged processing potential
• improved cold flexibility	• readily welded and colored

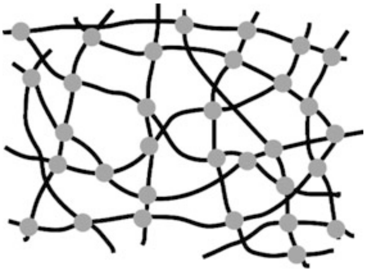


Fig. 8 Narrow-meshed, chemically crosslinked structural model for duroplastics

The *structural model* for duroplastics in Fig. 8 (in reality: three-dimensional), shows the close-meshed crosslinking of the macromolecules resulting from the high density of the chemical crosslinks.

Table 5 provides information on the most important abbreviations used in the field of plastics. For a detailed list see [6].

7 The Economic Significance of Plastics

7.1 Economic Data on Thermoplastics [7]

Figures 9 and 10 provide current economic data on thermoplastics.

For extensive additional data go to the homepage of Plastics Europe (http://www.plasticseurope.org).

Table 5 Plastics abbreviations (a selection)

ABS	Acrylonitrile butadiene styrene	POM	Polyoxymethylene
ASA	Acrylonitrile styrene acrylate	PF	Polyformaldehyde; phenolic resin
EP	Epoxide, epoxy resin	PP	Polypropylene
EPDM	Ethylene propylene diene methylene rubber	PPA	Polyphthalamide
LCP	Liquid crystalline polymer	PPE	Polyphenylene ether
PA 11	Polyamide 11	PPS	Polyphenylene sulfide
PA 12	Polyamide 12	PPSU	Polyphenylene sulfone
PA 4.6	Polyamide 4.6	PS	Polystyrene
PA 6	Polyamide 6	PSU	Polysulfone
PA 6.6	Polyamide 6.6	PTFE	Polytetrafluoroethylene
PA 6.10	Polyamide 6.10	PUR	Polyurethane
PA 6.6/6T	Polyamide 6.6/6T	PVC	Polyvinyl chloride
PAEK	Polyarylether ketone	PVDF	Polyvinylidene fluoride
PBT	Polybutylene terephthalate	SAN	Styrene acrylonitrile
PC	Polycarbonate	SB	Styrene butadiene
PE	Polyethylene	TPO	Polyolefin-based thermoplastic elastomer
PEI	Polyether imide	TPU	Polyurethane-based thermoplastic elastomer
PEEK	Polyetherether ketone	UP	Unsaturated polyester
PES	Polyether sulfone		
PET	Polyethylene terephthalate		
PEK	Polyetherketone		
PMMA	Polymethylmethacrylate		

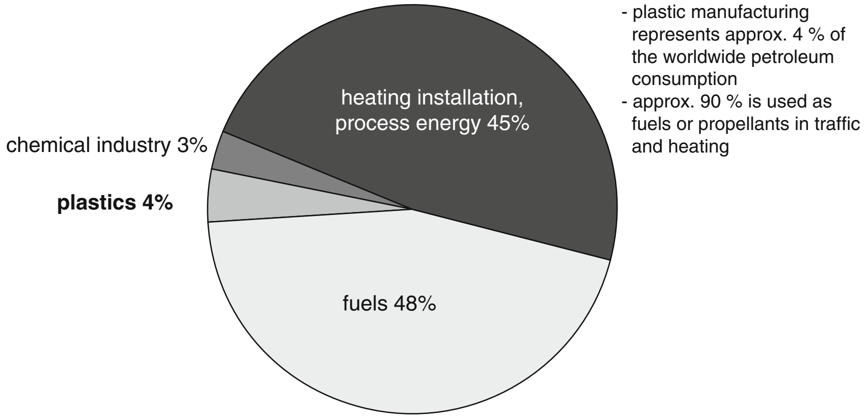
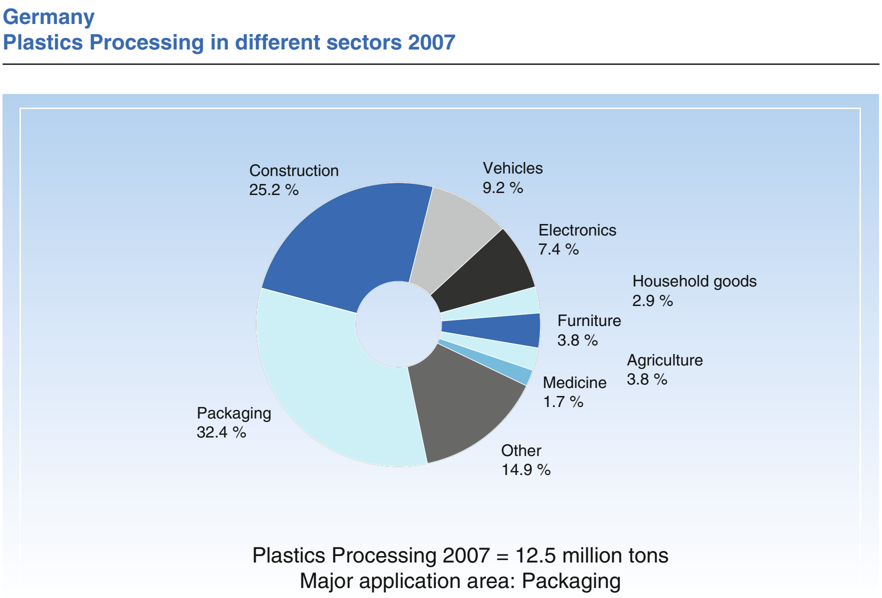


Fig. 9 Petroleum consumption for production of plastics

7.2 Economic Data on Duroplastics [8]

For current economic data on duroplastics as well as additional figures and information, go to www.avk-tv.de.



Source: Consultic Marketing & Industrieberatung GmbH

Economic data and charts concerning the plastics market 2007/2008; last update 03/09

Fig. 10 Fields of application of plastics in Germany, volumes of processed plastics for 2007 [7]

Table 6 Pricing margins per kilogram of plastic granulate (selection) in € for Q1/2009 (order of magnitude) [10]

Plastics/metals	Euro (€)	Plastics/metals	Euro (€)
PE-HD[a]	0.78–0.87	PA 11	7.50–11.50[b]
PP[a]	0.83–0.86	PA 12	7.50–11.50[b]
PS[a]	0.98–1.02	PA 6[2]	2.36–2.58
PVC[a]	0.81–0.85	PA 6 GF[c]	2.67–2.88
ABS[c]	1.33–1.49	PA 6.6[c]	3.08–3.21
PC[c]	2.70–2.82	PBT[c]	2.89–3.02
PMMA[c]	2.77–2.89	POM[c]	2.49–2.57
PEI	10.00–17.00[b]	PET	0.95–1.09
SAN	1.50–2.50[b]	PPS	3.00–10.50[b]
SB	0.90–1.50[b]	PTFE	~12.50[b]
PSU	13.50[b]	LCP	~50.00[b]
		PEEK	~60.00[b]
For comparison		TPO	2.50–5.00[b]
St 37	0.30–0.50[b]	TPU	3.75–6.25[b]
Al	0.70–1.00[b]	UP	2.60–5.00[b]
Mg	1.50–2.00[b]	PF (prepolymerized)	1.00–3.00[b]
Ti	4.00–5.00[b]	EP	4.00–10.00[b]
CF fabric	80–120[b]		

[a] Twenty ton truck load

[b] Pricing margins per kilogram of plastic granulate in € for 2007

[c] Single orders between 3 and 10 ton

7.3 Economic Data on Elastomers [9]

For current economic data on elastomers as well as additional figures and information, go to www.vke.de.

7.4 Pricing Margin for Plastics

Table 6 lists pricing margins for a selected spectrum of plastics and metals.

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The Economic Significance of Plastics

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Synthesis (Manufacture, Production) of Plastics

Peter Eyerer

Abstract Addition polymerization (chain reaction, multistep reaction) and condensation polymerization are very briefly summarized from an engineering perspective. The influences of synthesis on opportunities and risks of raw materials for plastics are listed. This chapter closes with some brief examples of plastics chemical production.

Keywords Influences of Synthesis on Properties, Polymerization, Process Engineering, Synthesis (Manufacture, Production)

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P. Eyerer (ed.), *Polymers – Opportunities and Risks I: General and Environmental Aspects,*
Hdb Env Chem (2010) 11,
DOI 10.1007/978-3-540-88417-0_2,

1 Overview of Polymerization

This chapter has been kept intentionally brief in view of the intended use of this book as an engineer's manual. The material used here was derived in large part from the transparency collection of the *Verband der kunststofferzeugenden Industrie* (Association of the Plastics Producing Industry), VKE [1]. For a deeper study, [2, 3] are recommended. Also pay attention to the section "Further Reading" at the end of this chapter.

Polymers are classified according to the reaction in which they are produced as follows:

- Synthetic plastics
  - Addition polymers
    Chain reaction (polymerization)
    Multistep reaction (polyaddition)
  - Condensation polymers
- Converted natural materials

Each of these groups includes both linear, i.e., thermoplastic, and cross-linked plastics. Depending on the degree of cross-linking, either

- highly elastic plastics (elastomers)
  or
- highly rigid plastics (duroplastics) are produced

2 Polymerization (Synthetic Chemistry)

2.1 Addition Polymerization

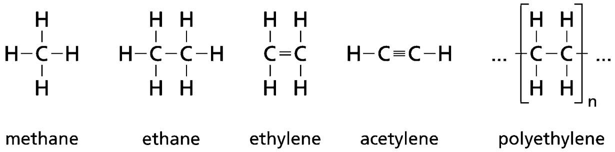
2.1.1 Chain Reaction (Polymerization)

Double bonds are the basis of the polymerization process. The force that holds most macromolecules together is the bonding strength of the carbon, i.e., its capacity for bonding to its own and other atoms. Valence is the property that determines the number of potential bonds. Carbon is tetravalent, i.e., the C atom has four bonding arms.

The structural formulas of methane and ethane show that each bond of the C atom is occupied by a hydrogen (H) atom. These are known as saturated bonds.

In the structural formula for ethylene, the two C atoms are, in contrast to ethane, interconnected by a double bond. Such bonds are unsaturated, examples being the monomers of the olefins (ethylene) and the vinyl monomers. They can be restored to single bond status by means of a reaction. However, each of the two C atoms then has a free bond on the outside seeking saturation and is unsaturated as long as this state persists. Free bonds are not stable.

In the case of ethylene, application of heat, high-energy radiation (e.g., UV or X-rays), or in the presence of initiators or catalysts, the double bond is separated. The ethylene base units combine to form polyethylene.



The index *n* (degree of polymerization) at the foot of the brackets indicates how many monomeric building-blocks have been combined to form the particular macromolecule.

The degree of polymerization of plastics is within the range of 100 to one million. Of course the individual macromolecules have different numbers of building-blocks, so that one can only speak of an average degree of polymerization.

Polymerization is an exothermal reaction because the polymer contains a lower level of energy than the unsaturated monomers. The polymerization heat of ethylene, for example, is very high. This heat must be dissipated during the synthetic (production) process, since otherwise explosions would result. During polymerization, a chemical reaction between the monomer and the polymer causes a volume reduction (shrinkage), also resulting in increased density. In the case of vinyl chloride, the shrinkage factor amounts to 34.4 % and with styrene 14.7 %. The conversion yield in each case is calculated on the basis of the change in density.

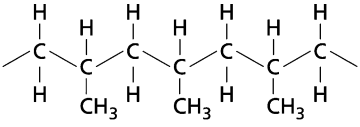
Of the three polymerization types radical chain, ion chain, and stereoregulated polymerization, the latter has become the most important, above all in polymerization of the higher α-olefins.

The familiar polymers polyvinyl chloride (PVC), polystyrene (PS), and polymethylmethacrylate (PMMA), which were produced in the 1930s and 1940s in large-scale production plants, are examples of so-called *radical chain polymerization*. One way of replacing the high-pressure polymerization method used for ethylene (ICI), which involved radical catalysts, with a low-pressure process, was provided by *anionic coordinative catalysts*, for example titanium tetrachloride plus aluminum triethyl as a cocatalyst in the method according to K. Ziegler (1953).

In 1953, Ziegler's work then inspired Giulio Natta of Milan to apply these insights to the *stereoregulated polymerization* of propylene. This work led to discovery of isotactic, syndiotactic, and atactic PP as well as to research into their structural property differences. The CH_3 groups can be arranged in various different orders along the carbon chain, a property termed tacticity [3].

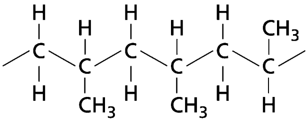
The following forms of polypropylene are differentiated in the stereoregulated polymerization of this polymer:

Isotactic polypropylene, in which all CH_3 groups are arranged along the same side of the carbon chain or extend outwards in accordance with their spiral arrangement.



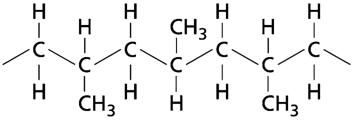
isotactic polypropylene

Atactic polypropylene, in which the CH_3 groups are arranged randomly.



atactic polypropylene

Syndiotactic polypropylene, in which the CH_3 groups are located on regularly alternating sides of the carbon chain.



syndiotactic polypropylene

The material type that is currently the most important is the isotactic polypropylene obtained by means of stereospecific catalysts according to Ziegler/Natta. It is high crystalline because the regularly formed chains are readily arranged. The softening point is therefore 165 °C (crystallite melting point) as compared to 128 °C for atactic polypropylene.

The large family of polyolefins ensures, and will continue to ensure, an unlimited supply of many items in daily use with an annual production volume exceeding 65 million tons worldwide.

The major application significance, and resulting economic importance, of the polyolefins were not completely satisfactory. The main characteristics of this material included a molar mass distribution that was very wide, in addition to which its tacticity was not uniform. These aspects affected its properties and processing and restricted its applicability. The cause of these difficulties lay in the fact that the Z/N catalysts comprised solid bodies on whose surface large numbers of chains grew at varying rates, resulting in wide molar mass distribution.

A decisive improvement in the polymeric properties, and much-improved applicability, were brought about by the metallocene catalysts that have been known since the 1980s.

Metallocene catalysts, for example dicyclopentadienyl zirconium dichloride, in combination with the cocatalyst methylalumoxane, helped establish a regulated set of properties, making it possible to customize molar mass, molar mass distribution, tacticity, heat resistance, rigidity, hardness, cold impact strength, and transparency. Added to these advantageous physical properties is the reactivity of this catalyst combination: With only a single gram of zirconium, 100 kg of ethylene can be polymerized into PE. One advantage of these metallocene catalysts is their high rate of reaction, 10–100-times faster than the catalysts previously in use. A further aspect, and indeed an essential one, is that the small volumes of catalysts required no longer have to be removed from the polymer [3].

The typical structure of metallocene catalyst molecules is reminiscent of that of enzyme molecules, which also catalyze the uniform synthesis of a biopolymer molecule. Metallocenes are also capable of determinate control of polymerization reactions of a given tacticity and chain length, for example the synthesis of isotactic polypropylene with a uniform molar mass [4,5].

A milestone was reached in 1993 with development by Dow of the Insite® technology, resulting in development of the polyolefin elastomers Affinity® and, 3 years later, Engage®.

mPP fibers and films also have a wide spectrum of applications. These products, Engage® polyolefin elastomers and new types of Nordel® EPDM rubber are more readily customized to meet specific customer requirements as to processability and performance characteristics than older synthetic rubber products, opening up a wide range of high-quality polyolefins to customers.

Copolymerization

The polymers considered up to this point have all consisted of uniform monomers in series. The precondition for polymerization was in each case the presence of at least two points of linkage.

The deeper science penetrates into the fine structure of high polymer materials, the more skills it acquires to wield the agents that influence the properties of the homopolymers by means of *copolymerization of one or more monomers*. Other methods of changing the properties of these materials are known, mainly physical processes such as mixing, plasticizing, cross-linking, and drawing, but copolymerization is always preferred when the molecular properties of polymers are to be changed.

The following arrangements are possible, depending on the reactants and reaction conditions:

- Static copolymerization
- Alternating copolymerization
- Block copolymerization
- Graft copolymerization

Copolymerization is by no means restricted to two monomeric components.

Copolymerization is also the term used to describe the uniting of linear polymers or polycondensates that still possess a reactive component (trifunctional monomers) with polymerizable (bifunctional) monomers. The result is a cross-linked plastic, for example unsaturated polyester + styrene → cross-linked polyester resin.

Monomers for addition polymerization in a chain reaction [1] thus always possess at least one C=C double bond. The two C atoms in the double bond may carry hydrogen, other atoms, or even entire groups of atoms. In technical applications, the monomers used almost always have only one H atom substituted either by another atom or a pendant group, usually quite small.

Six different monomers were selected for the polymerization reactions shown in Fig. 1.

A number of different polymerization reactions can be used (radical, ionic, stereoregulated) to convert monomers to polymers as a chain reaction in addition polymerization.

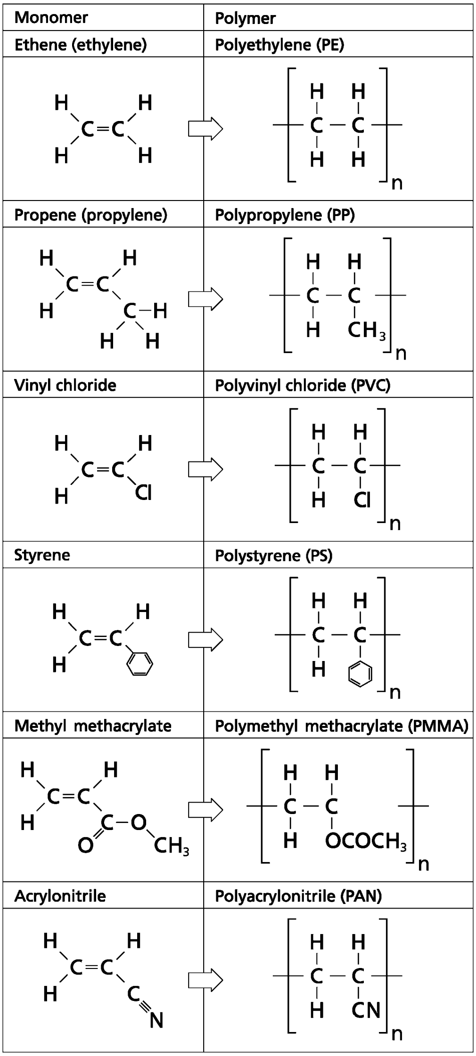


Fig. 1 Monomers for addition polymerization (based on [1])

Radical Polymerization [1]

Figure 2 shows a general summary of the process of radical polymerization. The double bonds, as functional groups, react by opening a bond. The C atoms form the chain. This is illustrated in a very schematic way in the upper section of Fig. 2.

The lower section of Fig. 2 provides more detail. Here we see a polymerization process started by a radical generating agent or initiator, in this case dibenzoyl peroxide. The radical resulting from the decomposition of the radical generating agent, designated R•, attacks the first ethene molecule in the *start reaction*, producing another radical with a free electron that can then attack a further ethene molecule. The carbon chain is propagated pairwise; this process is known as *chain growth* (*or propagation*). After a while, *chain breakage* (*or termination*) results when two chain ends come into contact with a lone electron, forming a chemical bond.

Ethene bears on its periphery only H atoms. In propene, one H atom is replaced by a methyl group, in styrene by a phenyl ring, in vinyl chloride by a Cl atom. In Fig. 2, this type of substitution is indicated by an X. Monomers with more than one substitution (e.g., polytetrafluorethylene) are used to make high-grade halogenated plastics.

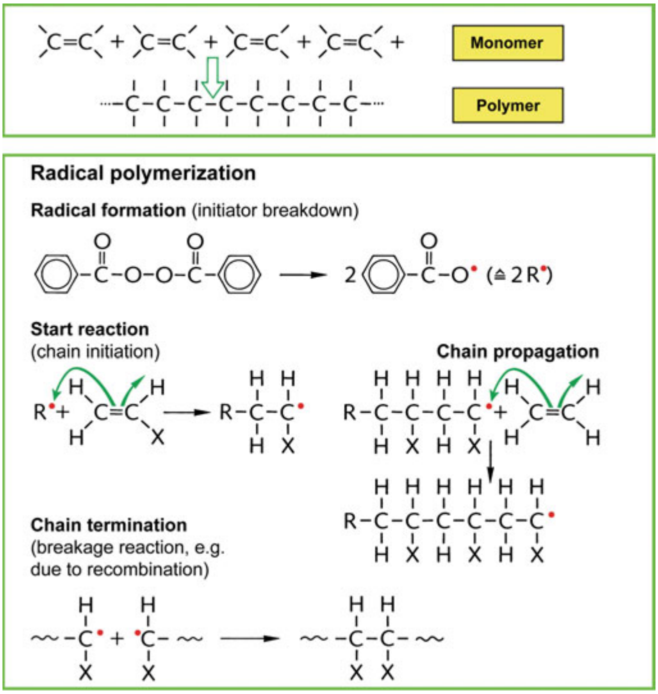


Fig. 2 Reactions – radical polymerization [1] – a *dash* symbolizes a chemical bond involving two electrons

Radical polymerization is a balanced reaction in which the balance is usually well in favor of the polymer. High pressure further enhances this effect. Raising the temperature accelerates the formation of the radicals. Pressure and temperature also influence the molar mass (chain length), molar mass distribution, and the degree of branching.

Radical polyethylene does not have a purely linear structure as shown in Fig. 2. If one chain end comes into contact with a lone electron on the inner part of another chain, an H atom may be removed and a side chain substituted for it. High pressure polyethylene therefore has a branched molecular structure and a resulting low density of 0.915–0.94 g/cm^3.

In addition to the radical type, there is also *ionic polymerization*. It is initiated by ions (cations or anions), dissociation of which is naturally heavily dependent on electrostatic effects, in particular solvation by the solvent. As in radical polymerization, the ionic process consists of a chain reaction. In the *start reaction*, a Lewis acid or Lewis base attaches to one C atom of the double bond of a monomer. This produces a charge at the other C atom. Whether anionic or cationic polymerization takes place depends on the nature of this charge. *Chain growth* involves repeated attachment to a double bond, whereby the charge "jumps" two C atoms further. In ionic polymerization there is no chain breakage due to recombination. Termination has to be induced by adding water, alcohols, acids, or amines. If this is not done, the reaction comes to a halt when all of the monomer is used up, whereby the reactivity is maintained for some time.

This is characterized as a "living polymer" state. Ionic polymerization may often take place at very low temperatures at a rapid rate. An example of this is polymerization of isobutylene with boron trifluoride as the catalyst. This process is run at –100 °C in liquid propane.

Catalytic Polymerization [1]

Figure 3 is a schematic diagram of the two types of *catalytic polymerization* currently used to produce polyethylene on an industrial scale. Common to both is that the reactions are run at relatively low pressures and temperatures, hence the term *low pressure polyethylene*. The product is designated as high density polyethylene (HD-PE). In chemical terms it is more uniform, and more of its substance crystallizes to a solid, than is the case with LD-PE, which is why HD-PE is denser than LD-PE.

The *Ziegler–Natta catalysts* are metal–organic mixed catalysts. These catalysts result from mixing compounds of the metals of the secondary groups IV–VIII with metal alkyls or hybrids of groups I–III in the periodic table. Combinations of $TiCl_4$, $TiCl_3$, or $VOCl_3$ with aluminum alkyls or aluminum alkyl halogenides[1] are

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[1] The aluminum reduces the metal compound and does not contribute to the polymerization reaction.

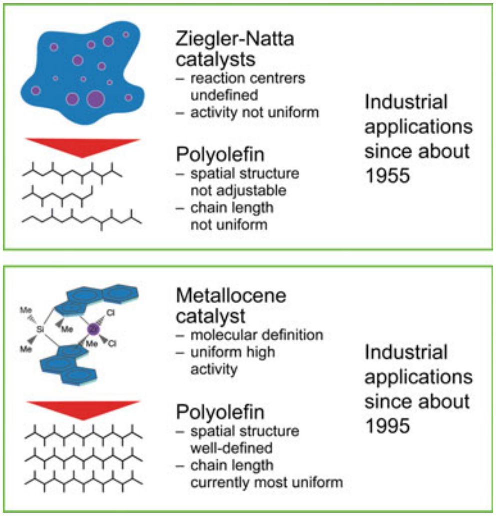


Fig. 3 Reactions – catalytic polymerization [1]

particularly effective. In polymerization of ethylene, additional ethylene molecules get between titanium or vanadium atoms and the ethyl groups, thus extending the chains stepwise by two C atoms. In the polymerization of propylene, the synthetic process is for the most part stereospecific, with the methyl groups rotated in one direction in quite a uniform manner (isotactic). Ziegler–Natta catalysis results in up to 95 % isotactic polypropylene, see above [3].

Industrial applications of *metallocene catalysts* are a recent development. All of them possess in their reaction center two aromatic rings, between which a complex bond holds a metal atom, in most cases zirconium. This type of catalysis produces polymers with exceptionally uniform structures. The chain lengths of the individual molecules closely approximate one another. The spatial structure is therefore well-defined. Polypropylene, for instance, is completely isotactic. It is even possible to produce polypropylene in which the pendant group orientation alternates between right and left. The resulting substance is known as a syndiotactic polypropylene (see above) [3].

Catalytically manufactured polyethylene has a mainly linear structure with Ziegler–Natta catalysis and a completely linear structure with metallocene catalysis. The macromolecules of low pressure polyethylene may therefore come to lie very close together, resulting in polyethylene with a high density of 0.95–0.98 g/cm^3. Parts of the molecules line up in parallel structures to form microcrystallites (small crystalline structures). Low-pressure polyethylene film shows a much higher level of breaking strength than high-pressure polyethylene film. The rubbing together of the microcrystallites is what causes plastic film material made of low pressure polyethylene (e.g., in bags) to “crackle.”

Side chains (short branches) can be intentionally added to low pressure polyethylene. To achieve this, a certain amount of longer alkenes (olefins) such as butene-1 or octene-1 are mixed into the ethylene. Metallocene catalysts then insert them in the chain in a highly uniform manner. In this way, low pressure polyethylene with a low density (LLD-PE) can be produced as well.

2.1.2 Multistep Reaction (Polyaddition)

A multistep reaction, polyaddition, is a polyreaction of at least two bifunctional or higher functional compounds. Polyaddition can result in either linear polymers (thermoplastics) or cross-linked plastics (duroplastics), depending on the specific functionality. Cross-linked products are obtained by means of a reaction of a bifunctional reactant with a trifunctional one. The more polyfunctional the reactant, the more closely meshed the cross-linking will be. That is why the polyols in polyurethane or epoxy resin production are frequently replaced by polyesters and polyethers containing large numbers of OH groups. Polyaddition, like polycondensation, is a multistep reaction, Fig. 4. Important polyadducts include linear and cross-linked polyurethanes as well as epoxy resins (see [2]).

Monomers for Polyadditions [1]

Epoxy resins [1] are duroplastics. Polyaddition initially produces an essentially linear macromolecule that still possesses numerous OH groups. This addition product is either placed in a mold or applied to surfaces in liquid form. This is followed by chemical curing, and this process often involves heat application. Because of their reliable adhesion to metallic substrates, epoxy resins are excellent primer coats for automobile paints and can also be used as metal adhesives. A further important field of application is electronics, where they serve as structural

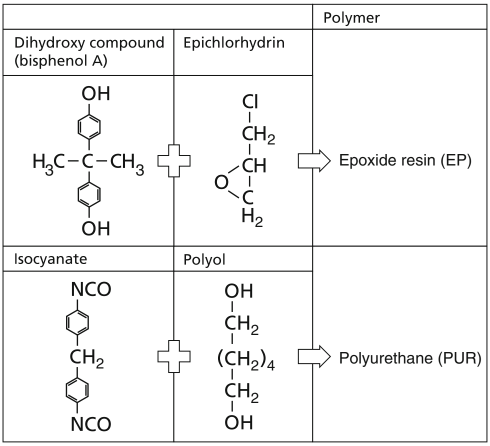


Fig. 4 Monomers for multistep reactions (polyaddition) (based on [1])

materials in printed circuit boards (PCBs) for semiconductors. Reinforced with glass or synthetic fibers, epoxy resins are also used in boat and aircraft construction.

Polyurethanes can be produced in both linear (thermoplastic) and cross-linked (duroplastic) configurations. In the latter case, both dialcohols and trialcohols are used to induce cross-linking of the polymer chains. Polyurethane can also be foamed with blowing agents. Current practice is to derive most of the blowing agent from the reaction mixture. Adding small amounts of water splits off CO_2 from isocyanate groups, which quickly form bubbles. Foamed polyurethane is used among other things in furniture and automobile upholstery as well as for heat insulation applications, for instance in refrigerators and prefab housing. All kinds of shoe soles can also be made of polyurethane: from comfortable, robust hiking shoes to high-performance track shoes.

Reactions: Polyaddition [1]

Figure 5 illustrates polyaddition using the example of polyurethane. As in esterification, only the functional groups are essential to descriptions of the reaction, as

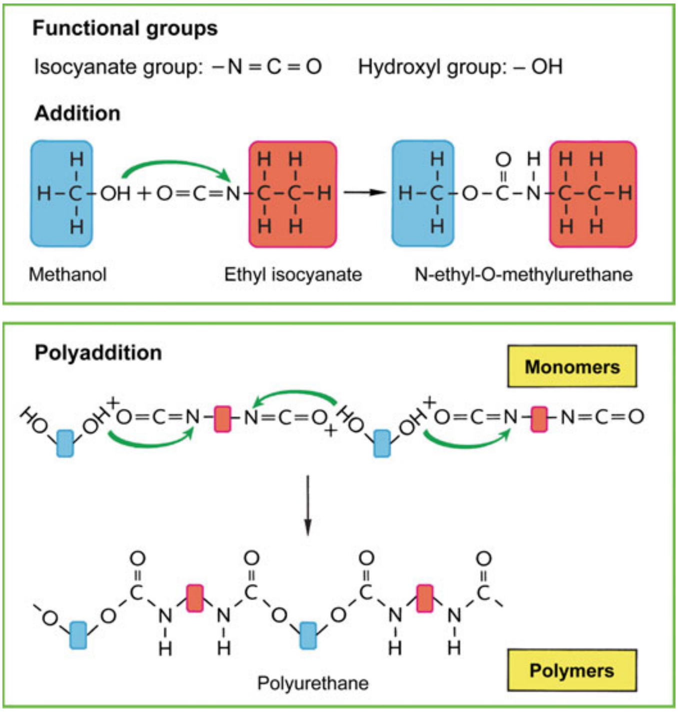


Fig. 5 Reactions – polyaddition [1]

seen here with the reaction of methanol and ethylisocyanate to produce *N*-ethyl-O-methylurethane. Polyurethane is then produced when bifunctional monomers are used. The structures shown in Fig. 5, with their "encapsulated" central sections, once again represent a variety of diols or diisocyanates.

The functional groups react with one another, whereby the H atom of the hydroxyl group attacks the N atom of the isocyanate group. No low molecular secondary products are produced. Polyaddition thus also proceeds stepwise.

The foaming process widens the spectrum of applications of polyurethanes. It can be induced by addition of a blowing agent or by a slight excess of isocyanate and addition of a little water. In this case, CO_2 is split off from the isocyanate, then forms fine, evenly distributed bubbles. Polyurethane foam can be produced with either hard or elastic properties. The former type is used in applications such as heat insulation material in refrigerators, the latter for furniture and car seat upholstery.

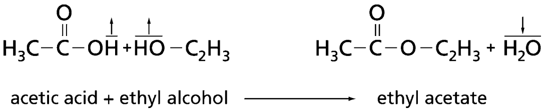
Epoxy resins make excellent primers for automobile paints. Now most cars are coated with epoxy resins before coats of colored paint are applied. These resins adhere very well to metallic substrates. They render car bodies practically rust-proof. In aircraft and boot construction, fiber-reinforced epoxy resins are used to create extremely light, high-strength structures. PCBs for electronic devices are a further field of application.

2.2 Condensation Polymerization

Polymerization is an addition reaction of a basic building-block that remains chemically unchanged, except for the absence of the double bond, after the reaction. Condensation polymerization is a substitution reaction. Two groups of reactive compounds of the same or different types react with one another. Low molecular secondary products such as water, ammonia, hydrogen chloride, alcohols, etc. are produced in the reaction.

If the condensation reactants have only one reactive group, low molecular compounds are produced along with the corresponding low molecular components (see [2]).

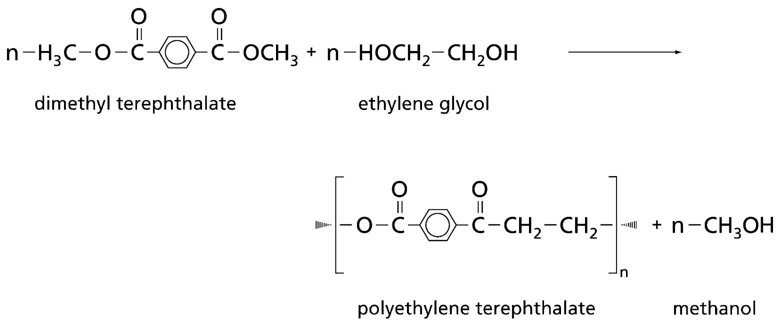
Example: Esterification with acid + alcohol, water is split off.



$$H_3C-\overset{\overset{O}{\|}}{C}-O\overset{\uparrow}{H}+\overset{\uparrow}{HO}-C_2H_3 \qquad H_3C-\overset{\overset{O}{\|}}{C}-O-C_2H_3+\overset{\downarrow}{H_2O}$$

The familiar linear chains are produced from the bifunctional reactants (thermoplastic).

Example: Terephthalic acid dimethyl ester + glycol → polyethylene terephthalate + methyl alcohol (re-esterification).



Close-meshed steric cross-linked three-dimensional networks are produced from trifunctional or polyfunctional reactants (duroplastic).

Example: Phenol + formaldehyde → phenol resin + water.

Condensation polymerization is an example of polyaddition in single, independent steps. Its heat tonality is endothermic, i.e., energy is introduced into the reaction. The intermediate products that form can be isolated and stored for a certain amount of time. Under suitable working conditions, the interrupted reaction can then be continued. The plastics industry makes use of this feature to produce molding compounds by mixing in fillers or various precondensates to reduce the process cycle times.

2.2.1 Monomers for Condensation Polymers [1]

The examples shown in Fig. 6 are used to make important industrial products.

Polyester: polyethylene terephthalate (PET), the polycondensate of ethandiol (glycol) and terephthalic acid, is now known even to the layman in two of its applications. More and more nonalcoholic beverages are being filled into PET bottles that can easily endure 30 return and refill cycles. As is the case with other polyesters, PET also serves as a fiber raw material marketed under brand names such as Trevira, Diolen, and Terylen and processed to produce textiles that are highly wrinkle-resistant. This also opens up new potentials for recycling of bottles that can no longer be reused. After they are removed from circulation, the bottles are made into fibers that are used for insulation padding in warm winter parkas. Polyester fibers add a great deal of tear-resistance to car airbags. In an accident, gas enters the airbag explosively, creating within seconds a cushion that can prevent or reduce injuries.

Polycarbonate is a very tough (resilient) polymer from which objects with high levels of impact strength can be manufactured. This material is also so transparent that it can be used for glazing purposes like acrylic glass. Finally, polycarbonate can also be sterilized and has therefore been found suitable for applications in refillable systems for milk and dairy products. However, washing with hot water may split off bisphenol A, which can permeate into foods, for instance from baby bottles, so that

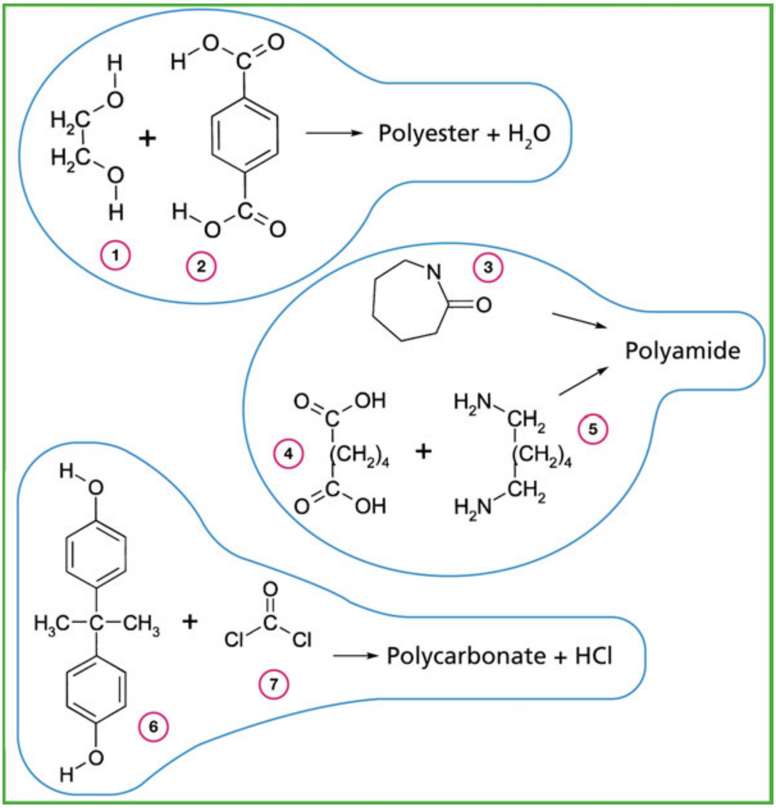


Fig. 6 Monomers for condensation polymerizations. Structures: 1 = Diol (ethandiol = ethylene glycol), 2 = Dicarboxylic acid (terephthalic acid), 3 = ε-Caprolactam, 4 = Dicarboxylic acid (adipic acid), 5 = Diamine (hexamethylene diamine), 6 = Dihydroxy compound (bisphenol A), 7 = Dicarboxylic acid chloride (phosgene)

polyamide is recommended for this purpose instead. For further risks involved in the use of polycarbonate, see Sect. 4 in chapter “Properties of Plastics in Structural Components.”

Caprolactam is an elegant example of a bifunctional monomer. The ring of this cyclic internal amide can be opened by catalysts, for example water. This triggers formation of the monomer for polycondensation, which can then be converted into a *polyamide*. Only a small amount of water must be added for this purpose. Theoretically, for every monomer to be built into the growing macromolecule, a water molecule is first consumed, then released again in the polycondensation reaction. In fact, the reaction continues without a further contribution from water once it has been induced. Nylon and Perlon are the most familiar brand names for polyamides. Fibers of these plastics provide the textile raw material for sheer women’s stockings and high-strength rope.

2.2.2 Reactions: polycondensation [1]

Figure 7 presents polycondensation using the *example of polyesterification*. As in the reaction illustrated above of ethanol and ethanoic (acetic) acid, producing acetic acid ethylester (ethyl acetate), only the functional groups are essentially important in describing esterification. Bifunctional monomers are required for polycondensation. In the example of polyesterification, diols such as ethandiol (glycol) and dicarboxylic acids such as terephthalic acid are used.

The structures with encapsulated central components in Fig. 7 stand for various diols or dicarboxylic acids.

The functional groups react with one another, whereby water is split off. The first step produces a molecule with a carboxyl group at one "end" and a hydroxyl group at the other.

Esterification can therefore be continued at either "end." Polycondensation is thus propagated stepwise in both directions.

Polycondensation is a *multistep reaction*. As such, it first produces *oligomers,* i.e., molecules comprised of only a small number of monomers. Continuation of the process to produce polymers can either take the form of step-by-step addition of

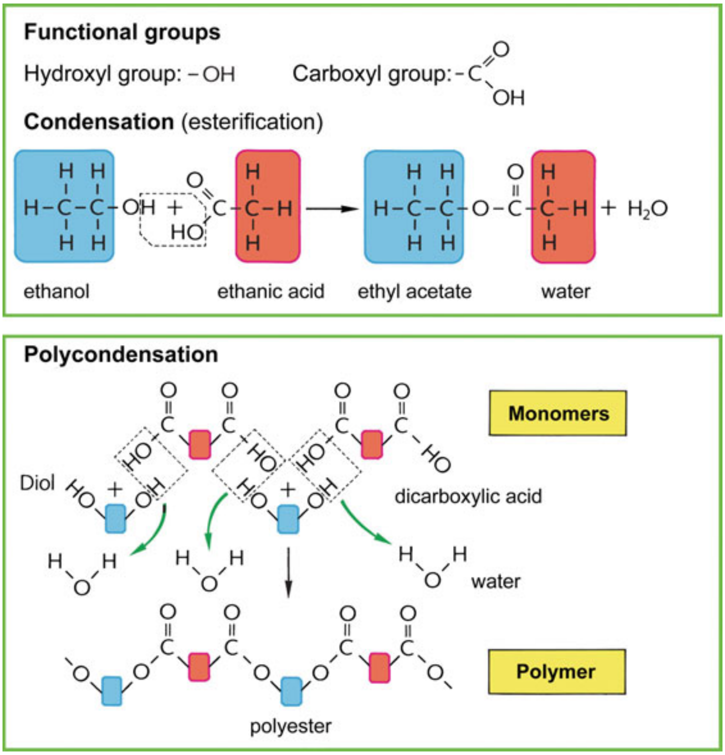


Fig. 7 Reactions – polycondensation [1]

further monomers or the union of oligomers. There is no typical chain termination reaction. One might take the form of a “head-to-tail” reaction, resulting in a cyclic polyester, although the probability of this occurring is minimal considering the high initial concentrations of the monomer. It is much more likely that the ends of different molecules will come into contact than the beginning and end of the same molecule. In practice, high concentrations are obtained by induction of the reaction among the monomers without solvents.

The low molecular reaction products of condensation reactions have to be removed constantly. This results in a shift in the balance in favor of the polycondensate. Water is removed by distilling it off. This is done by heating the monomers in the presence of catalysts. The product obtained is a polymer melt that can either be granulated in the case of polyesters and polyamides or pressed through a fine sieve to produce fibers.

Examples of *polycondensates* are polyesters, polyamides, polycarbonates, and polysiloxanes (silicones).

Mixing in monomers with more than two functional groups results in cross-linkage, which increases the hardness of the polycondensates. Three-dimensional cross-linking is also possible with polyester resins in which monomers with double bonds such as maleic acid are used. The polyester produced in this way can subsequently be cross-linked with peroxides, resulting in a duroplastic. In addition to polycondensates with a uniform chain structure, mixed polycondensates can also be produced. Polyesteramides are one example, in production of which dicarboxylic acids are converted with diols and diamines.

3 Influences of Synthesis on Opportunities and Risks (Properties) of Raw Materials for Plastics

Table 1 summarizes important influential factors, listed separately for uncross-linked plastics (thermoplastics) and cross-linked plastics (elastomers/duroplastics).

Table 1 Influence of polymerization on material properties [6]

Thermoplastics	Elastomers/Duroplasticics
Molar mass	Degree of cross-linkage influences rigidity, strength, chemical resistance, softening temperature, . . .
Molar mass distribution	Copolymerization (sequence length, etc.)
Degree of branching	Low molecular components, e.g., isocyanates, amines, phenols, formaldehydes
Tacticity	
Residual monomers, e.g., styrene, VC	
Residues, e.g., emulsifiers, solvents and precipitants (in UHMW PE[a] diesel oil)	

[a] Ultra high molecular weight polyethylene

3.1 Thermoplastics

The *molar mass* influences, among other things, melt viscosity and therefore processability. A low molar mass means a low melting temperature and a low melt viscosity, therefore requiring lower processing pressures and lower mold clamping pressures. Mold filling tends to be faster and more complete. On the other hand, there is also a tendency to spew, necessitating additional reworking and a return to higher clamping pressure settings.

The properties of low molecular thermoplastics tend towards:

- Low levels of strength and rigidity
- Lower levels of resilience
- Greater creep tendency under long-term loads

Chain branching may influence these qualities one way or the other, depending for example on the crystallization tendency.

Very high levels of molar mass, for instance in ultrahigh molecular weight polyethylene, significantly increase:

- Wear resistance
- Impact strength
- Form stability

In principle, a wide *molar mass distribution* (dispersity) has a similar effect: High proportions of low molecular components soften the material and slide readily against one another at higher temperatures, making for better processing quality and poorer long-term material properties. On the other hand, close distribution with high proportions of long-chained components makes for poorer processing quality and improves the long-term material properties.

The *degree of branching* has a considerable influence on the crystallinity of the molecular structures as well as a pronounced impact on the mechanical and transport-related properties of plastics (permeation). High impact strength with a high degree of branching is a potential result. On the other hand, the fusing temperature and glass transition temperature (cold impact strength) drop noticeably.

The influence of *tacticity* on polypropylene in particular is covered in Table 1. A 95 % level of isotactic polypropylene resulting from metallocene catalysts raises many properties to the desired level of technical versatility.

Residual monomers or *residues* from polymerization may be harmful to health (e.g., vinyl chloride from PVC) or alter technical properties, for example residues of emulsifiers that reduce the insulating quality of PVC cabling. Solvent residues (diesel oil, toluene, etc.) from precipitation polymerization migrate over a period of years following implantation, albeit in the microgram range, from joint endoprostheses such as hip acetabula into body tissues.

3.2 Duroplastics

The *degree of cross-linking* significantly influences the glass transition temperature and the deterioration of properties in the main softening range. As the degree of cross-linking rises, strength and rigidity increase, whereas elongation capacity decreases.

For example, disc brake linings are cross-linked step-by-step with phenol resin and elastomeric binder in complex curing processes lasting approx. 20 h at temperatures as high as 250 °C.

The width of the molecular network mesh (*sequence length*) plays a central role in copolymerization (thermoplastics and elastomers/duroplastics) and determines material properties during elastic deformation.

Low molecular components are evaluated critically when considering in particular long-term applications in interiors (automobiles, living quarters), since they tend to give off emissions.

Shrinkage/memory effect: What is usually meant by the term shrinkage is the actual contraction of the volume, for instance due to increased packing density of the macromolecules as a result of crystallization or cross-linking.

Shrinkage therefore implies an actual reduction in part volume, as well as a change in dimensions, whereas the form is preserved ($v \neq$ const).

The memory effect, on the other hand, is defined as a retraction or "relaxation" of oriented macromolecules, usually at raised temperatures. The length is decreased and the cross-section increased (v = const).

Example: When a deep-drawn cup made of PS or polypropylene is placed in an oven, it is warped (PS at approx. 120 °C, PP at approx. 160 °C) and returns to the form of the plate from which it was originally molded.

The volume of plastic remains unchanged, but the form and dimensions are changed completely.

Three types of shrinkage are differentiated:

- Synthesis shrinkage,
- Processing shrinkage, and
- Aftershrinkage.

The polymer always has a greater density than the monomer, i.e., the volume shrinks during polymerization.

In practice, shrinkage is often used as a parameter for reaction yield.

Low shrink (LS) and low profile (LP) systems have been developed over the past 20 years for large-surface parts in car bodies such as bumpers, trunk lids, doors, fenders, etc.

LS and LP systems are obtained by dissolving suitable thermoplastics in the *UP*[2] *starting resin*. They show finely distributed precipitation during the curing reaction, since the added thermoplastics apparently dissolve in the styrene monomer, but not

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[2] Unsaturated polyester.

in the PS being produced. The precipitated thermoplastic particles contain monomeric styrene that shows a delayed reaction, generating fine bubbles due to evaporation caused by the reaction temperature. These bubbles compensate the shrinkage and press the surface of the molded part being formed against the molding tool wall, see also Sect. 5.1 in chapter "Properties of Plastics in Structural Components."

The LP system contains so much thermoplastic that uniform dyeing of the mass is no longer feasible. It can, however, be painted (e.g., like a car body).

3.3 Elastomers

Schobert et al. [7], in a critical appraisal of the range of raw materials used in the rubber industry [8], revealed the following qualitative limitations ([7]; see also [9]).

Polymers: Aspects that must be taken into account include potential monomer content, impurities deriving from the production process and stabilizers added during production.

Antioxidants: These substances are absolutely essential from the point of view of the functionality and useful life of elastomer products, for which reason they are irreplaceable despite the fact that almost all groups are potentially harmful to skin and mucosa. (Cause of most of the allergies observed in the rubber industry. The problem can be managed by means of "hygienic measures").

Fillers: The discussion on carbon black toxicity resulting from surface-adsorbed polycycles has now abated for the most part since animal trial models did not reveal any reactions. The risk represented by inhaled black and light-colored filler particles is controlled by limiting air dust content, whereby asbestos and talcum types containing asbestos must be mentioned here.

Plasticizers: The important thing here is that although aromatic mineral oils do contain a certain amount of polycycles requiring hygienic measures, substitute product development has been ongoing. Some of the synthetic products (e.g., DOP, DOA, DBP, DOS, and phosphates) are also controversial.

Processing Agents: The situation with these agents is analogous to the aromatic plasticizers: Attention must be directed to the aromatic hydrocarbon resins and to the components resorcin and formaldehyde, with their enhancing effects on adhesion to structural elements, as well as to isocyanates and some peptizers.

Pigments, blowing agents: The organic pigments now in preferred use are harmless compared to the inorganic pigments used previously (mainly metal oxides or sulfides). Most blowing agents used in production of expanded products require careful handling.

Activators: These inorganic oxides can cause mucosal irritations. Their concentration levels in waste air are subject to the *TA Luft* (German airborne emissions standards). In this connection, the frequently used stearates and substances such as triethanolamine and diethylene glycol must be carefully dosed and handled.

Cross-linking agents: Only ground sulfur, still in frequent use, is comparatively harmless. Most of the sulfur donors and organic peroxides used must be viewed critically as potentially harmful to skin and eye mucosa.

Vulcanization accelerators: None of these chemical substances can be categorized as absolutely harmless. Most of them are potential skin and mucosa irritants. The thioureas are particularly critical in this sense. Most of the thiuram products and dithiocarbamates are problematical with regard to nitrosamines, which will be addressed in greater detail in chapter 7.3.

Antiscorching agents: Here as well, hygienic measures must be realized to prevent, or at least drastically reduce, negative effects.

Solvents: Solvents must be included in this list due to their widespread use in the rubber industry. The concentration limits applying to most solvents have been lowered over time. Products containing halogens and lower-boiling aromatics are now no longer used.

Overall, it can be stated that the published body of knowledge concerning the risks to workers in the rubber industry has grown significantly in recent years based on animal experiments and epidemiological studies. Occupational protection and hygiene measures have now been developed to address most of the remaining problems effectively.

Here is a current to-do list of measures for the industry:

- Replacement of hazardous materials with less hazardous ones;
- Engineering changes that reduce or prevent human contact with these chemicals;
- Binding of dust, gases, and vapors by means of encapsulation of facilities, extraction, granulation, pasting, etc.;
- Compliance with regulations, occupational hygiene limits and industrial safety measures in general;
- Personal cleanliness of all staff members to minimize contact with chemicals;
- Intensification of toxicological research on rubber chemicals with subsequent modification of the substances used so as to reduce risks;
- Development of new products with reduced toxicity levels;
- Product safety data sheets/standard operating procedures providing information on the risks involved and safety measures required in use of specific substances;
- Intensified worker health monitoring within the framework of occupational medicine [8].

4 Plastics Production (Process Engineering) [1, 3]

4.1 General Aspects of Plastics Production

The production of plastics is always an industrial process. For mass-produced plastics such as polyethylene, polypropylene, PS or PVC, production is carried out in facilities with per annum capacities of several hundred thousand tons.

A production plant often encompasses several such facilities, one next to the other, amounting to a total annual production plant capacity exceeding 500,000 tons. In Germany alone, approximately 20 million tons of plastics were produced in the year 2008.

Large-scale plastic production facilities are in continuous operation. The plastic produced is thus continuously removed from the reactor and replaced with new monomer. Unconverted monomer, catalyst, radical generating agents (initiators), and possibly solvents as well, are separated out of the plastic product and recycled into the process. Quality control is practiced throughout the process, i.e., to maintain constant settings of average chain length, chain length distribution, and degree of branching (see [3]).

In most cases, each facility is responsible for only a few specific reaction steps. Polyethylene or polypropylene production facilities are supplied with the monomer material, from which they then produce the plastic in a single reaction step. In PS and PET production, a few additional steps are required to produce the monomer. The technical "know-how" covers the chemical structure of the polymer molecules, the catalysts, and the process engineering. The end result is comprised of high-performance materials with specifically engineered application properties. For instance, PS types are produced that are either highly transparent (clear as glass) or particularly impact resistant.

4.2 Plastics Production: Example of PS: Technical Process [1]

Plastics are produced in large-scale technical processes. PS, for example, is made from the basic chemicals benzole and ethene, Fig. 8.

Benzole and ethene are transferred to a reaction vessel, in which ethyl benzole is produced at 85–95 °C and normal pressure. In the downstream section of the facility, this substance is then dehydrated to make styrene, which is collected in a storage tank.

The styrene is transferred from the storage tank into a water-cooled reaction vessel. Following the addition of water and additives, it is polymerized to make PS while being mixed constantly (emulsion polymerization, see Table 2). The reaction mixture is then drained into a cooling vat, from where it enters a centrifuge in which water, residual monomer and additives are separated out. The pure PS, obtained in powder form, then requires only drying.

PS is one of the most important mass-produced plastics. It has been produced on an industrial scale since 1930. Not knowing what he had discovered, E. Simon described PS as early as 1839 as a solid mass produced from styrene when heated. Some time later, M. Bertolet realized that the process involved was polymerization. The first patent for production of PS was awarded to Englishman F. E. Matthews in 1911. The first technically efficient production method, Staudinger thermal polymerization, was developed in 1929.

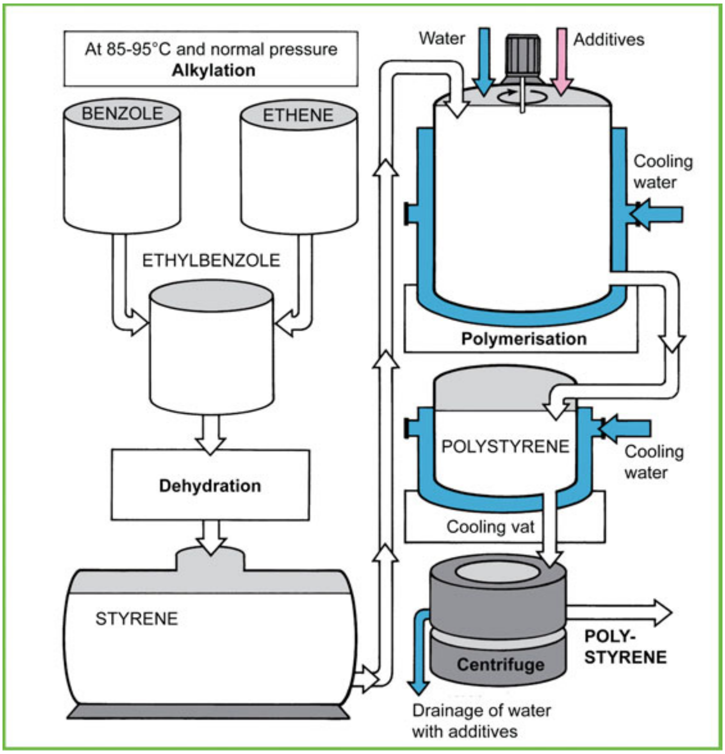

Fig. 8 Example: polystyrene engineering process [1]

In contrast to alkylation of benzole, *dehydration of ethyl benzole* is endothermic. This process is carried out at high temperatures of 550–600 °C by means of heterocatalysis. The resulting styrene, to which a polymerization inhibitor has been added, is then vacuum-distilled before further processing. This complex purification procedure is made necessary by the close proximity of the boiling points of ethyl benzole and styrene.

PS is polymerized in very large-scale facilities with yield volumes of several thousand tons per year. PS in the form of small beads is obtained from a mixture of water and styrene and must then still be separated from water, initiator, protective colloids, residual monomer and catalyst, Fig. 8.

PS is glass-clear with a light transmittance level in the visible range of 90 %. The material is hard, dimensionally stable, relatively brittle, and provides smooth, high-quality surfaces when processed. PS is tasteless and odorless and suitable for contact with foods in every respect. Every other C atom of the PS molecule bears a phenyl pendant group extending either to the right or left of the chain. The distribution of these rings is accidental in technical, or *atactic* PS. The irregularly arranged phenyl pendant groups are bulky. No crystallization takes place.

Table 2 Polymerization process engineering, overview [10]

Polymerization	Reaction partner	Phase structure[a] with allocation to reaction partner	Examples	Form in which polymer is produced	Remarks
Homogeneous in substance = substance polymerization	Initiator	So in $\underline{M}$	PS, UP, PMMA, PA 6 (cast PA), EP, PCYA	Compact	Pure polymer, mold casting with extremely high molar mass and molding strength possible; melt processing not possible (ship's propellers and cable pulleys made of PA 6, bulletproof glass made of PMMA), molar mass shows little uniformity. High level of polymerization shrinkage. High risk of overheating – polymerize gradually!
	Polymer Monomer is reaction medium, see third column	So in $\underline{M}$			See specific substances for more processing information.
Homogeneous in solution = solution polymerization	Monomer Initiator Polymer	So in $\underline{M}$ D or So in $\underline{M}$ D in $\underline{M}$	PVAC (paint), PIB, S/B, ABS, HDPE	Solution	Highly efficient dissipation of polymerization heat. When paints and adhesives are made of PVAC the plastic solution is produced ready for use, i.e., expensive and high-energy separation of polymer and solvent is not required. HDPE can be polymerized at > 100 °C, e.g., in cyclohexane solution and precipitates when cooled.
Precipitation from solution = precipitation polymerization	Monomer Initiator Polymer	So in M D or So in $\underline{M}$ D in $\underline{M}$	HDPE, PP, PMMA, PS, PVC, SAN	Powder	In all of these polymerization methods, the polymer is produced in a finely distributed, heterogeneous form. Viscosity remains low, efficient heat dissipation, and therefore rapid Important example: Low-pressure polymerization of HDPEP or in hydrocarbon (HC) solvent. PMA, PMMA also in HC, PS in methanol, PAN in water
Precipitation from substance	Initiator Polymer Monomer is reaction medium, see third column	So in $\underline{M}$ D in $\underline{M}$	PVC, PAN from liquid LDPE or LDPE made from gaseous monomer	Powder	Polymerization, is possible. Separation of the polymer from the reaction medium causes no problems, even at high molar mass levels. LDPE is precipitated from the ethylene gas by means of high-pressure polymerization. PAN is nonmeltable, is dissolved in dimethyl formamide and spun into threads

(*continued*)

Table 2 (continued)

Polymerization	Reaction partner	Phase structure[a] with allocation to reaction partner	Examples	Form in which polymer is produced	Remarks
In emulsion = emulsion Polymerization	Monomer Initiator Polymer	E in W So in W D in W (emulsifier)	E-PVC, PVAC, S/B, NBR, SBR, ABS	Powder	Water-soluble initiator e.g., $[O_3S–O–O–SO_3]_2$ Polymer particles 0.05–0.1 mm in diameter Emulsifier residues reduce electrical insulating properties High molar mass possible. Readily processable
In suspension = suspension or bead polymerization	Monomer Initiator Polymer (protective colloids)	Su in W So in M Su in W	PS, PMMA, PVAC	Powder	Polymer particles up to 1 mm in diameter. Due to small amounts of protective colloid residues, the degree of purity is somewhat lower than in substance polymerization, but still much higher than in emulsion polymerization
Precipitation in suspension	Monomer Initiator Polymer (protective colloids)	Su in W So in M D in M finally Su in W	S-PVC	Powder	

[a] The main component of the single-phase or multiphase system (reaction medium) is underlined. So solution; E emulsion; M monomer; W water; D dispersion; Su suspension; Sol solvent (usually organic)

The styrene molecules form irregular tangles that can only be "untangled" by application of high levels of energy. This explains the high softening temperature for an amorphous plastic of nearly 100 °C. It also explains the high light transmittance of PS: No semicrystalline structures form that would disperse the light.

In a facility scheme that appears quite complex, only a few formulae suffice to illustrate where in the system the few chemical reactions take place. Often, polymers are produced on the basis of monomers as delivered without further chemical transformations. The monomer is supplied by a large petrochemical plant located many kilometers away near a refinery. Ethylene is transported in Europe in a special pipeline along the Rhine. Propylene and other raw materials for polymerization processes are transported in tanks by road, rail, and ship.

In the case of PS, ethylene and benzole from petrochemical plants are converted into styrene in only two steps. Purification of the intermediate products to achieve high molar masses accounts for most of the technical effort and expenditure required.

Every impurity in a polymerization process results in low molecular products, for which reason considerable time and effort goes into purification of the monomers.

The removal of water from the reaction mixture requires application of much greater levels of energy consumption and separation technology. Re-esterification of the methanol ester with glycol makes it easier to separate the methanol.

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Properties of Plastics in Structural Components

Peter Eyerer and Volker Gettwert*

Abstract The properties of plastics are discussed and summarized, sometimes in comparison with metals and other materials. The temperature and time dependence of the properties related to the polymer structure (thermoplastics, elastomers, thermoplastic elastomers, thermosets, and fiber-reinforced plastics) are dealt with. Additives are discussed in a separate section, Sect. 6 because of the importance of these factors for the use of environmentally friendly plastics.

Keywords Functional additives, Organic and inorganic additives, Properties (mechanical, thermal, chemical, physical), Structure

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*Volker Gettwert contributed Sect. 6.1.3 "Fire protection agents" to this chapter

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P. Eyerer (ed.), *Polymers – Opportunities and Risks I: General and Environmental Aspects*,
Hdb Env Chem (2010) 11,
DOI 10.1007/978-3-540-88417-0_3,

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1 Introduction

As is the case with all structural materials, users are most interested in the properties a material exhibits in the useful structural component made from it, i.e., subsequent to design, construction, processing, production, and surface finishing.

In addition to material factors such as chemical, physical and technical structure and factors related to production (in the case of plastics: synthesis), processing methods including tooling and design engineering may change the properties of the resulting structural component in highly significant and specific ways. Figures 4 and 7 in the Chapter "Processing (Primary Forming) of Plastics Into Structural Components" illustrate this in addition to other factors that act upon the structural component externally and may also influence its properties in decisive ways [1].

These considerations apply in principle to all materials. Here we will of course focus on plastics and include data on metals for comparative purposes.

2 Structure of Plastics

Engineers considering plastics applications generally have a good knowledge of metals, so we present some comparative data on metals and plastics in this section. Whereas the structure of a metal is determined at the atomic level, plastic structures are molecular [81] and [107].

The metallic lattice consists of positive ions, whereby the valence electrons move around freely within it similarly to a gas (*electron gas*). The resulting negative spatial charge produces a force (*metallic bond*) that is greater than the repulsive force between the ions. The bonding energy between, for example, iron atoms is about 395 kJ mol^{-1} [2, 3].

In contrast to the metallic bond between atoms (metallic crystal lattice), the properties of plastics are determined by the *covalent bond* (primary valence bond) and *intermolecular bond* (secondary valence bond).

The covalent atomic bond is a result of electron pairing, i.e., the equal probability that certain electrons will be found in several different atoms. Carbon, C, and silicon, Si, are capable of forming crystalline lattices based on shared valence electrons, examples being diamonds and quartz. However, by means of saturation of two of the four valence “arms” of carbon and silicon, the molecular chains that provide the basic framework of plastics can also be formed, either in chains (aliphatic) or rings (aromatic).

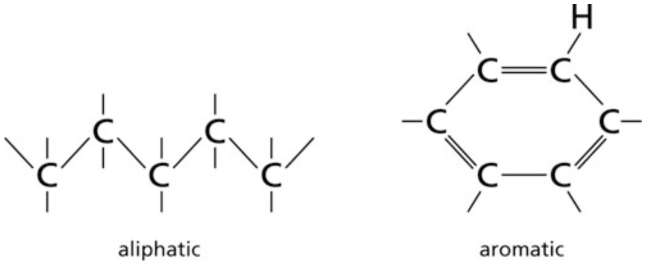
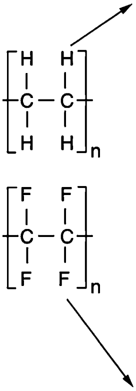


Table 1 lists a number of the important bonding partners, distances and energy levels for plastics, from which properties of the resulting solids can be derived in qualitative terms.

For example, the bond length of two carbon atoms is shorter, and the bond energy that much greater, in a ring than in a chain. Therefore, ring compounds show, for instance, greater thermal stability than linear chains of molecules, whereby steric inhibition also plays a major role. Another example is the C–F bond compared to the C–C bond. The greater bond energy in C–F results in the high levels of thermal and chemical stability of polytetrafluoroethylene (PTFE).

In addition to the primary bonding forces at work in the molecular chain between C or Si or intercalary atoms (heteroatoms), the intermolecular bonding forces are important determinant factors in the properties of plastics. In general, only weak attractive forces due to molecular polarization are active between covalently bonded molecular chains.

Table 1 Bond energy levels and lengths for covalently bonded atoms [4]

Example	Bonding partners	Bonding distance [nm]	Bonding energy [kJ mol^{-1}]	Remarks
	C–C (aliphatic = chain)	0.154	approx. 350	∢CCC 109° ± 2°
	C–C (aromatic = ring)	0.140	approx. 560	∢CCC 124° ± 2°
	C=C	0.135	610	no rotability
	C≡C	0.120	832	no rotability
	C–H	0.109	413	∢CCC 107° ± 4°
	C–O	0.143	351	ready rotability
	C=O	0.122	708	
	C–N	0.147	293	
	C–CI	0.177	339	
	C–F	0.131	485	
	N–H	0.102	389	
	Si–O	0.164	444	ready rotability

The intermolecular bonding forces are highly dependent on temperature and bond length and are as a rule less than 12 kJ mol^{-1}. The ratio of the secondary bonding force B_S to the primary bonding force B_P is approx.

$$B_S : B_P \approx 1/20 \text{ to } 1/100.$$

The results in terms of general properties of plastics are

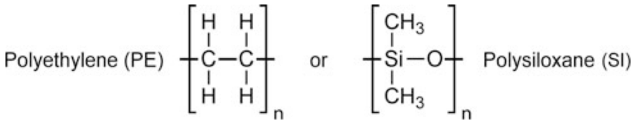
- Highly direction-dependent properties in materials with oriented macromolecules
- A high level of temperature dependence
- A high level of time dependence
- A high level of dependence of the material properties on the load applied.

2.1 Chemical Degrees of Order

The chemical and physical structure of plastics, and their resulting properties, can be described by the terms constitution, conformation, and configuration.

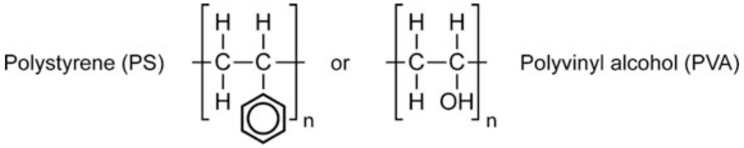
The atom-based chemical structural principle of a molecule (*constitution*) is described by the following typology:

- Type and linkage of atoms in the basic molecular chain



$$\left[-\mathrm{CH_2}-\mathrm{CH_2}-\right]_n \quad \text{or} \quad \left[-\mathrm{Si(CH_3)_2}-\mathrm{O}-\right]_n$$

- Type of end groups and substituents



- Type and length of branches
- Molar mass and its distribution
- Insertion of foreign atoms or molecules

The *configuration* designates the spatial arrangement of the atoms and groups of atoms in molecules of the same constitution, for example the tacticity of the CH_3 group in polypropylene (Fig. 1).

In the process of polymer synthesis as described above, the CH_3 groups are arranged alternately at front and back, thus achieving a higher degree of order of the macromolecular chains (crystallinity), resulting in greater strength and rigidity with improved temperature stability.

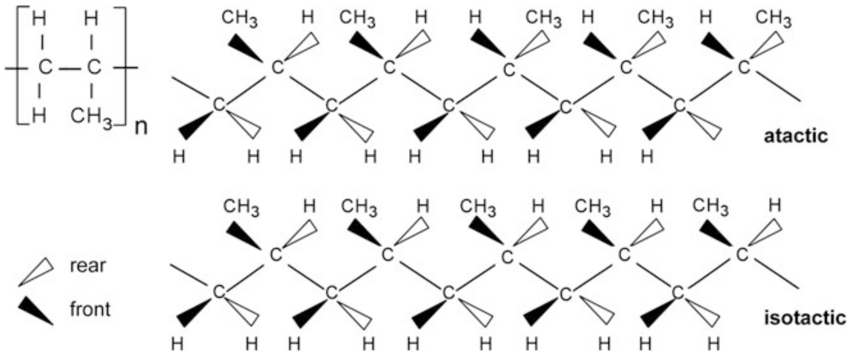
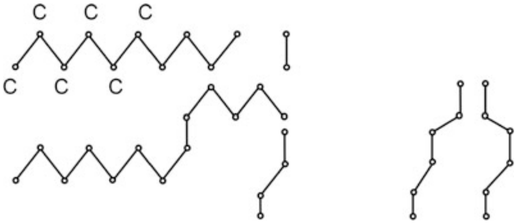


Fig. 1 Tacticity (configuration) of the CH_3 groups in polypropylene

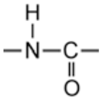
Conformation designates the spatial structure assumed by macromolecules of the same configuration by means of rotation about their bond axes. The schematic drawing shows this in frontal and lateral views of two macromolecule chains



2.1.1 Influence of Linkage Types Within the Basic Molecular Chains on Properties

Table 2 shows examples of different types of linkage (insertion of heteroatoms) in the basic molecular chain of plastics.

The connection between the altered basic molecular chain and macroscopic properties is explained using the example of a polyamide structure. Polyamides are nitrogenous thermoplastics the base units of which (CH_2) are interlinked by carboxylic acid amide groups (short form: amide groups).



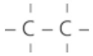
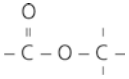
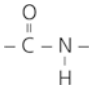
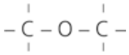
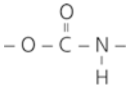
$$-\overset{\overset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle O}{\|}}{C}-$$

Production is realized by means of condensation polymerization (polycondensate). Two groups are differentiated:

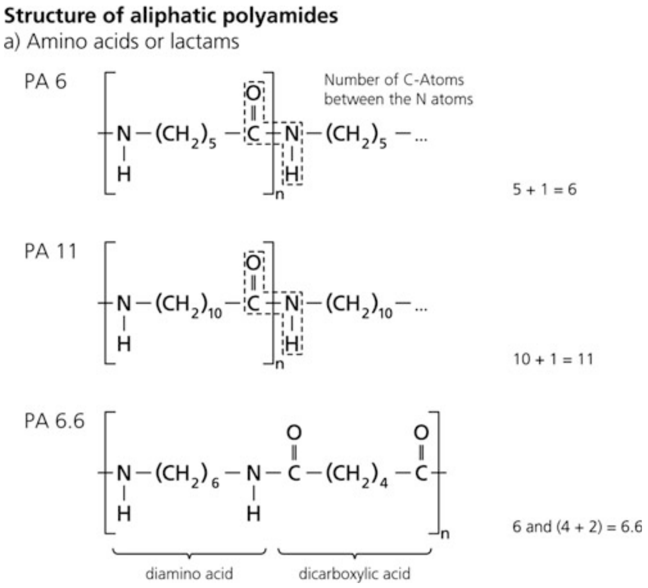
(a) The group of *amino acid types*, also known as lactams (*one base unit*)
(b) Polyamides of the aliphatic *diamino*–dicarboxylic *acid type* (*two base units*)

The chemical structural formulae of different polyamides as shown below (PA 6 and PA 11 as examples of type (a) one base unit; PA 6.6 as an example of type (b)

Table 2 Linkage types of atoms in the basic molecular chain [4]

Bond type	Structural symbol	Example of	
		Synthetic macromolecules	Natural macromolecules
Carbon bonds	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$	Polyolefins, vinyl, styrene, acrylic polymers	Rubber Guttapercha
Esteric bonds	 $-\overset{O}{\overset{\Vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$	Linear, saturated polyesters	Nucleid acids
Amide bonds	 $-\overset{O}{\overset{\Vert}{C}}-\underset{H}{\underset{\vert}{N}}-$	Polyamides	Proteins, wool, silk
Etheric bonds (acetal bonds)	 $-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$	Polyoxymethylene (polyethylene oxide)	Polysaccharides, cellulose, starch, glycogen
Urethane bonds	 $-O-\overset{O}{\overset{\Vert}{C}}-\underset{H}{\underset{\vert}{N}}-$	Polyurethane (TPU)	

two base units) illustrates their structures comprising CH_2 groups of varying length with interspersed NHCO groups. The nomenclature refers to the number of C atoms between the N atoms.



The NHCO groups of adjacent polyamide molecules form so-called hydrogen bridges with the hydrogen atom on the nitrogen and nearby oxygen atoms on the C. They possess two to three times the strength of normal intermolecular bonds.

Table 3 illustrates the consequences of this in terms of material properties.

The more NHCO groups are contained per CH_2 group (or vice versa, the fewer CH_2 groups there are per NHCO group) in the polyamide molecule, the higher the melting temperature of the lactams (one base unit, e.g., 220 °C at PA 6), and the greater the maximum water uptake, since NHCO exhibits a very high affinity to H_2O.

The situation is similar with the diamino–dicarboxylic acid types (two base units). Why is the melting temperature of PA 6.6 much higher than that of PA 6? The macromolecule of PA 6.6 shows point symmetry if the symmetry point is posited at the center of a monomer unit. Short-range order hydrogen bridges were already able to form with a high "hit quota" in the melt since the distances are always right and will then be fixed in long-range order at crystallization.

The macromolecule of PA 6 is not symmetrical. Only if adjacent macromolecules assume the counter-direction will the distances be amenable to formation of hydrogen bridges.

This is less frequently the case here than in the point-symmetrical PA 6.6, so that PA 6 shows a lower degree of crystallization, and a lower modulus of elasticity, than PA 6.6.

Another example of the influence of the molecular chain structure (conformation) on the properties of plastic materials is polyamide PA 4.6. As a polymer, its structure is less regular than, for example, that of PA 6. These "inhomogeneous" molecular chains result in a low degree of crystallization, but at the same time a higher level of impact strength. The molar mass has a similar effect: The higher the molar mass, the greater the impact strength a_k.

For example: PA 6 normal $a_k = 65\ \mathrm{kJ\ m^{-2}}$

PA 6 higher molecular $a_k = 100\ \mathrm{kJ\ m^{-2}}$

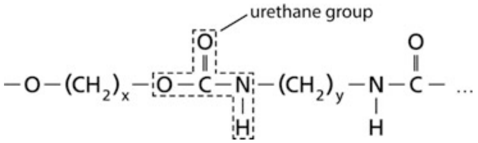
The influence of the structure of the macromolecular chain is demonstrated by the following presentation of aromatic polyamides, carbon fibers, and graphite.

Table 3 Aliphatic polyamide nomenclature [4]

PA type	Structural formula	Density [g cm^{-3}]	Number of CH_2-groups	Melting point [°C]	Max. water uptake in % by mass
PA 6	$+\mathrm{NH(CH_2)_5CO}+ \ldots (5 + 1 = 6)$	1.14	5	220	10
PA 11	$+\mathrm{NH(CH_2)_{10}CO}+ \ldots (10 + 1 = 11)$	1.04	10	190	2
PA 12	$+\mathrm{NH(CH_2)_{11}CO}+ \ldots (11 + 1 = 12)$	1.02	11	170	1.7
PA 6.6	$+\mathrm{NH(CH_2)_6CO{-}CO(CH_2)_4{-}CO}+$ $\ldots$ (6 and $(4 + 2) = 6.6$)	1.15	5	265	8.5
PA 6.10	$+\mathrm{NH(CH_2)_6CO{-}CO(CH_2)_8{-}CO}+$ $\ldots$ (6 and $(8 + 2) = 6.10$)	1.08	7 average $\frac{6+8}{2}$	226	3.5

The more ring structures are integrated in a molecular chain, in graphite the ring structure only, the higher the glass transition temperature T_g. In other words: the less mobile (the more rigid) the molecular chains become, the greater the high-temperature stability of the material (Tables 4 and 5).

Linear polyurethanes (*TPU*) have a structure very similar to that of polyamides.



$$-O-(CH_2)_x-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_y-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\ldots$$

As with polyoxymethylene (POM), see Table 6 and polyethylene terephthalate (PET), the oxygen atom (heteroatom) has a sort of *hinge effect* within the molecular chain. Generally speaking an oxygen atom in the chain lowers the glass transition point T_g, but also enhances the tendency towards crystallization due to the increased rotatability – depending on the constitution – and thus raises the melting point.

2.1.2 Substituent and End Group Types

In addition to the chemical structure of the basic molecular chain, the arrangement (configuration) and form (conformation) of substituents (and end groups) also influence the properties of plastics in important ways.

Table 4 Structure of "aromatic" polyamides (product names, e.g., Aramide) [4]

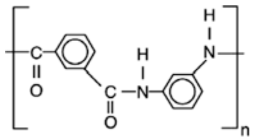
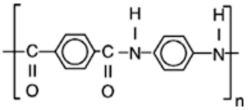
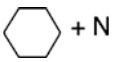
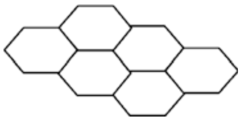
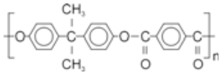
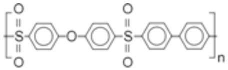
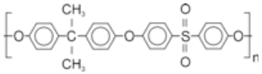
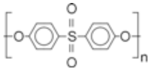
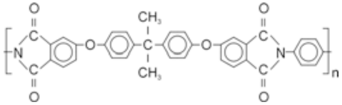
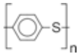
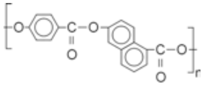
		Influence of chemical structure on glass transition temperature T_g
(a) Meta position A		T_g PA aliph. ~30 °C T_g meta: 220 °C commercial name: e.g., Nomex
(b) Para position B		T_g para: 290 °C commercial name: e.g., Kevlar
Carbon fibers		Hardly any T_g
Graphite structure	 e.g., pencil; ring levels show some shift	No T_g

Table 5 HT (high-temperature) thermoplastics (a selection). Structure, designation, characteristic temperatures

	Structure	Common name	Commercial name	T_g °C	T_m °C
1		Polyarylate (PAR)	® Apec ® Ardel ® Durel	192	*
2		Polyarylsulfone (PAS)	® Radel ® Astrel	290	*
3		Polysulfone (PSU) (PSO)	® Udel ® Ultrason S	187	*
4		Polyether sulfone (PES)	® Victrex PES ® Ultrason E	190	*
5		Polyetherimide (PEI)	® Ultem	200	*
6		Polyphenylene sulfide (PPS)	® Ryton ® Fortron	185	274
7		Liquid crystal polymer (LCP)	® Vectra ® Ultrax ® Xydar	280	*

(*continued*)

Table 5 (continued)

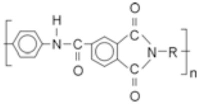
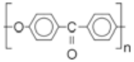
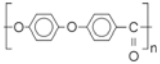
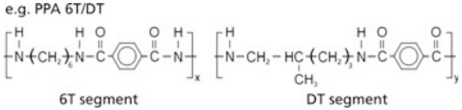
	Structure	Common name	Commercial name	T_g °C	T_m °C
8		Polyamideimide (PAI)	® Torlon	274	*
9		Polyetherketone (PEK)	® Victrex PEK ® Hostatec ® Ultrapek	158	365
10		Polyetheretherketone (PEEK)	® Victrex PEK	145	355
11		Polyphthalamite (PPA)	® Amodel ® Zytel ® Grivory	90–140	300–310

Table 6 Examples of atoms or atom groups as substituents [4]

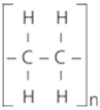
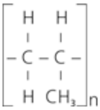
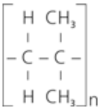
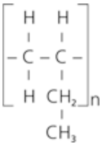
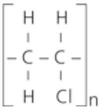
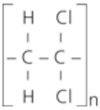
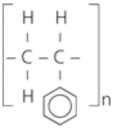
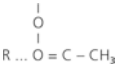
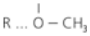
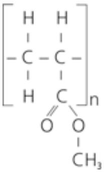
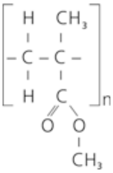
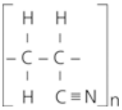
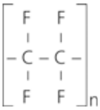
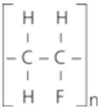
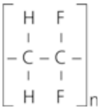
Polyolefins	Polyethylene (PE) 	Polypropylene (PP) 	Polyisobutylene (PIB) 	Polybutene 1 (PB-1) 
Vinyl compounds	Polyvinyl chloride (PVC) 	Polyvinylidene chloride (PVDC) 	Polystyrene (PS) 	Polyvinyl alcohol (PVAL) R ... OH Polyvinyl acetate (PVAC)  Polyvinyl ether (PVE) 
Polyacrylates	Polymethyl-acrylate (PMA) 	Polymethylmeth-acrylate (PMMA) 	Polyacrylonitrile (PAN) 	
Fluorinated polymers	Polytetraflouro-ethylene (PTFE) 	Polychlorotrifluoro-ethylene (PCTFE) 	Polyisobutylene (PIB) 	Polyvinylidene fluoride (PVDF) 

Table 6 divides thermoplastics into groups and provides examples of atoms and atom groups as substituents.

Substituents exert a decisive influence on the polarity (dipole moments) and mobility (steric inhibition) of macromolecular chains.

Polarity, for example, has an influence on chemical stability (chlorine atom in polyvinyl chloride). Bulky pendant groups (phenyl residue in polystyrene) for example, move the glass transition temperature up and produce brittle, stiff plastics.

The distances and the valence angle between the carbon atoms are almost impossible to deform; a high level of mobility of a molecular chain results from nearly free rotation around the C–C axis (conical projection).

The energy threshold for rotation is quite low, for example 11 kJ mol^{-1} for the ethane molecule and 16.7 kJ mol^{-1} for the polyethylene molecule. This segment rotation is more or less hindered by substituents attached to the main chain (atoms or atom groups) or branches (*steric inhibition*), for example, less so in polyethylene, more so in polystyrene due to the residual phenyl.

The rotatability of the basic molecular chain is decisive for the rigidity of a plastic.

The following two examples serve to illustrate the influence of the rotatability of the basic chain and substituents on the engineering properties of plastics:

2.1.3 Type and Length of Branches

Despite the fact that they are made up of the same atomic building blocks, plastics vary widely in their properties, in most cases because the specific chemical buildup, either per se or influenced by the conditions of polymerization, exercises a decisive influence on the structure of the polymers. The bonding distances of the molecular chains influences the intermolecular bonding forces. The regularity of the chain structure is another decisive factor in the properties of the plastic material produced.

Branching (Constitution)

Depending on the polymerization process used, a larger or smaller number of lateral branches of varying length are produced along the main (or backbone) chain of linear chain molecules, for example polyethylene, see Table 7.

The formation of branches along the main chain changes the structure of the polyethylene inasmuch as branches act as spacers between the macromolecular chains and result in a larger number of defects in the molecular structure.

As a result, the degree of crystallization is reduced and many properties are altered.

Table 7 provides qualitative data on the tendencies of these property changes. For example, the melting temperature drops as the degree of branching increases. The intermolecular bonding forces are reduced because of the increased distances resulting from branching, defects grow, chain slipping processes are facilitated at higher temperatures. Gas permeability and the tendency to swell under the influence of liquids increase for the same reasons.

Table 7 Effects of the degree of branching on the properties of polyethylene [4]

Branching type short-chain branched	Type of PE	Polymerization process	Effects of increased branching (semicrystalline thermoplastics)
Low level of branching (length: 2–6 C atoms) average number of pendant groups 3 CH_3/1,000 C atoms	HDPE high density $\rho = 0.96\ \text{g cm}^{-3}$	Low pressure process acc. to Ziegler with complex catalysts or stereospecific catalysts (200 bar)	Density↓ Degree of crystallization↓ Rigidity↓ Flowability↑[a] Melting temperature↓ Heat conductivity↓ Impact strength↑ Elongation at rupture↑ Light permeability↑ Gas permeability↑
High level of branching average number of pendant groups 21 CH_3/1,000 C atoms	HDPE low density $\rho = 0.92\ \text{g cm}^{-3}$	High pressure process (radical activation) (max. 4,000 bar; 200 °C)	

[a] Increases due to cross-linking degree; usually molar mass decreases at polymerization process

At least the direction of qualitative property changes can therefore be estimated on the basis of knowledge of these simple molecular aspects of plastics engineering.

Properties of polymers can be altered by the chemical structure (constitution), for example branching. Other factors that can change them include.

2.1.4 Isomerism (Configuration)

This term designates the varying spatial arrangement of the atoms or atom groups (substituents R) in molecules of the same composition and structure (as a rule: carbon chains).

A differentiation is made between:

Structural isomerism
and
Stereoisomerism (tacticity)

The spatial arrangement of the substituents along the chain may differ. The specific polymerization procedure (process and catalysts used) results in plastics with a “steric configuration,” see Fig. 1.

As a rule, technical plastics contain atactic, isotactic, and syndiotactic moieties. The ratio of these moieties to one another is decisive in terms of the plastic material properties. In polypropylene, for example, the atactic moiety is only 2–5 %. This means the degree of crystallization is potentially very high in polypropylene. The more regular the arrangement of the substituents, the greater the probability that crystalline structures can form.

2.1.5 Molar Mass and Molar Mass Distribution

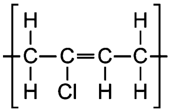
In addition to the type and magnitude of the bonding forces, the branching and isomerism, the properties of plastics are also decisively influenced by the molar mass (constitution).

The size of a macromolecule is expressed as its molar mass (normally the mean molar mass M_w or the mean degree of polymerization n):

$$n = \frac{M_{\mathrm{w,polymer}}}{M_{\mathrm{w,monomer}}} = \text{number of base units in a macromolecule.}$$

The molar mass of the monomeric unit of a plastic is the sum of the individual atomic masses multiplied by the degree of polymerization n

Polychlorobutadiene (CR)



$$\left[\mathrm{-CH_2-CCl{=}CH-CH_2-}\right]$$

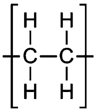
$4C + 1Cl + 5h$

$48 + 35 + 5 = 88$

n...: 10^2 to 2×10^3

$\overline{M}_w$ 10.000 to 500.000

e.g. Polyethylene (PE)



$$\left[\mathrm{-CH_2-CH_2-}\right]$$

$2C + 4H$

$24 + 4 = 28$

n...: 10^3 to 2×10^5

$\overline{M}_w$ 28.000 to ~ 6 million (UHMWPE)

Table 8 illustrates the connection between appearance and technical applicability on the one hand and molar mass on the other hand in technical polystyrene.

Causes of many property changes when molar mass increases:

- Increase in number of primary bonds per unit of volume
- Reduced short-range and long-range order

Table 8 Connection between appearance, technical applicability and molar mass in a technical polystyrene (BASF, Ludwigshafen)

Molar mass M [g $\mathrm{mol^{-1}}$]	Degree of polymerization n	Appearance after reprecipitation of solution	Appearance after melting and cooling	Technical application
200–1,000	2–10	Liquid, solid	Partly crystallized and friable, brittle	Oligomers
1,000–20,000	10–200	Powdery	Less friable, more solid, slightly filmogenic	Paints
20,000–75,000	200–750	Somewhat fibrous	Viscous, glassy	Thermoplastic injection molding compounds
75,000–1,500,000	750–15,000	Long-fibered	Highly viscous glass types elastic when hot	Films and strips

- Increase in number of loopings and entanglements between two or more molecular chains (physical cross-linking)

Therefore, the main flow properties of plastics in the widest sense are influenced by the mean molar mass. These properties include melt viscosity, modulus of elasticity and shear modulus above the glass transition range, creep behavior, stress cracking behavior, strain at break, mechanical strength, solubility and swelling behavior, etc.

Figures 2 and 3 illustrate the quantitative influence of molar mass $\bar{M}_w$ on a number of technical and physical properties of amorphous and semicrystalline thermoplastics.

Amorphous Thermoplastics, for example PMMA

The temperature range between the glass transition range and the flow or fusion (melt) range, in which the shear modulus remains nearly constant, becomes wider as the molar mass grows. The plastic is then described as entropy or rubber elastic, or even thermoelastic (as opposed to thermoplastic).

Semicrystalline Thermoplastics, for example PE

With increasing molar mass (growing chain length), the numbers of chain loopings (*physical cross-links*) in the individual macromolecules also increase. The viscosity

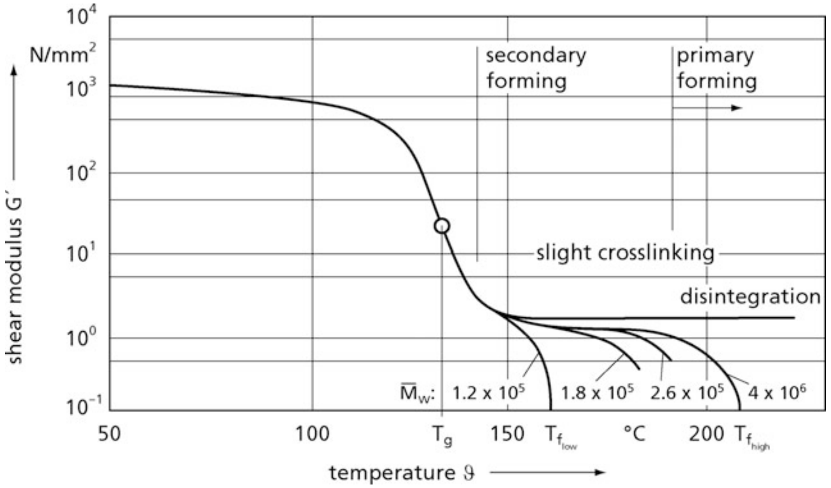


Fig. 2 Temperature-dependence of shear modulus G′ for PMMA molding compounds with different mean molar masses [5]

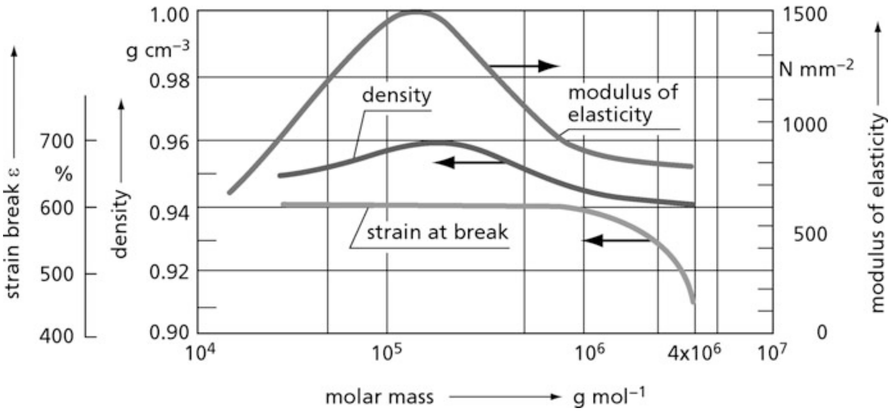


Fig. 3 Influence of molar mass on properties of polyethylene (measured at 23°C)

of the melt increases and the mobility of the macromolecules in the melt (chain slipping processes) decreases. This renders injection molding more difficult. It also reduces the crystallization capacity when very high molar masses solidify, and results in lower packing density as well.

The modulus of elasticity curve can be explained analogously in terms of molar mass, Fig. 3, starting with stronger effects of intermolecular forces resulting from increasing crystallization and, beginning at a certain chain length, a lower degree of order. With increasing chain length, higher force levels are transferred into the chains via the secondary bonds, resulting in greater efficiency of individual chain strength utilization. Chain slipping is inhibited. If the effective intermolecular forces are great enough to rupture the primary bond in a chain, a longer chain length can no longer increase the strength level. The reduced increase in tensile strength above $M_\mathrm{w} = 10^5$ clearly demonstrates that, despite the increasing share of looped longer chains, an increase in chain length will no longer increase strength.

The decrease in strain at break in PE with an increasing molar mass as shown in Fig. 3 is also due to an increase in “physical cross-links”. This is without effect in PMMA, since the strain at break in this plastic is less than in PE by two powers of ten.

Molar Mass Distribution

Synthetic polymers are *polydisperse*, i.e., they feature a continuous distribution of molecular chains with different molar masses. A well-known example of a “monodisperse polymer” is the naturally occurring substance insulin.

The curve and/or definition of different mean molar masses, Fig. 4, characterize the flow properties of (thermoplastic) plastic melts or the behavior (e.g., the long-term properties) of solid plastics. For example, a high molecular moiety combined

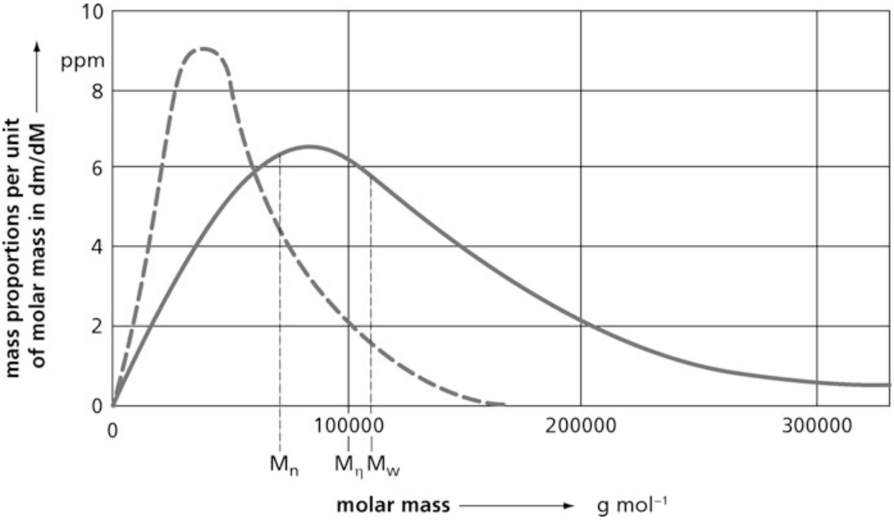


Fig. 4 Typical differential molar mass distribution curve, example of polystyrene: ——— wide distribution, - - - - - narrow distribution [6]. M_n . . . numeric mean of the molar mass, M_η . . . mean viscosity of the molar mass, M_w . . . mean mass of the molar mass

with a relatively low degree of polymerization raises the viscosity of the melt and improves the mechanical properties of the finished part. Inversely, a low molecular moiety can render a melt more readily processable, whereby the mechanical properties may suffer.

Nonpolar plastics usually have a relatively high molar mass. This compensates lesser intermolecular forces (no dipole forces) (strong tendency to crystallization, chain entanglements). Polar plastics, on the other hand, often have a relatively low molar mass.

The datum mean molar mass makes little sense for cross-linking plastics, since the macromolecules are combined to make single molecules with a very high molar mass. It therefore makes more sense in the case of duroplastics and elastomers to consider the mean cross-link density, the mesh width so-to-speak, or the content level of cross-linking agents (e.g., sulfur content of rubber).

Table 9 lists the degree of polymerization and mean molar mass of a number of thermoplastics.

These are general reference values that cover the usual qualities. More closely defined values can be obtained for specific qualities.

Summary:

- The mean molar mass influences the flow properties of plastics mainly in the fusion and flow ranges.
- As a result of molecular chain slipping processes, solid properties also depend to a greater or lesser degree (depending on constitution and configuration) on the mean molar mass.

Table 9 Degree of polymerization and mean molar mass M_w [g mol^{-1}] of a number of thermoplastics

	Degree of polymerization n	Mean molar mass M_w
Polyethylene low density (LDPE)	1,000–5,000	30,000–150,000
Polyethylene high density (HDPE)	1,800–10,000	50,000–300,000
Ultrahigh molecular weight polyethylene (UHMWPE)	70,000–200,000	approx. 2–6 million
Polypropylene	7,500–18,800	300,000–750,000
Polystyrene	1,500–2,500	150,000–250,000
Polyvinyl chloride	1,000–2,500	60,000–150,000
Polyoxymethylene	1,000–2,000	30,000–60,000
Polymethacrylate	20,000–30,000	~2–3 million
Polytetrafluoroethylene	~10,000	~500,000

- Long-chain amorphous plastics are usually more mechanically rigid and show greater chemical resistance (chain entanglements prevent slipping); short-chain plastics are more readily molded.
- The molar mass distribution within a mean molar mass has analogous effects on the properties and processing of plastics. High molecular moieties increase melt viscosity and improve the mechanical and chemical long-term properties. Low molecular moieties facilitate slipping processes both in the melt and in the solid (reduced long-term stability).
- Numeric mean, mean viscosity, and mean mass are defined to characterize plastic molding compounds. The principle as it applies to polydisperse plastics is: $\bar{M}_w > \bar{M}_v > \bar{M}_n$ (see Fig. 4 for explanation) [11].

2.1.6 The Insertion of Foreign Atoms or Molecules (Homopolymers, Copolymers, Polyblends, Plasticization)

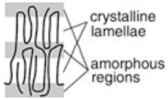
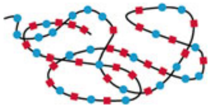
The transformation of properties by means of chemical and/or physical insertion of foreign atoms or molecules is an important process today, since development of entirely new plastics is now feasible within a limited framework only. A plastic comprising a single monomer type is called a *homopolymer*, whereas a copolymer contains two or more monomer types.

The terms *copolymer, terpolymer, and quaterpolymer* designate the number of base units integrated in the chain. The different monomer types may show statistically regular or irregular distribution. Plastics with longer sequences of a single monomer type in the chain are known as *block* (or segment) *copolymers*.

The grafting of side chains from other monomer types to the main chain (backbone chain) is called *graft copolymerization*. Physical mixtures of plastics are designated as *polyblends*. Table 10 illustrates these terms.

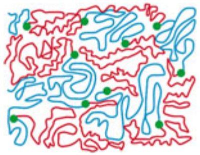
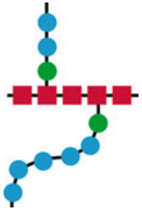
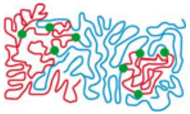
The process of copolymerization can alter the properties of plastics (medium resistance, form stability when exposed to heat, mechanical behavior, especially

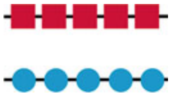
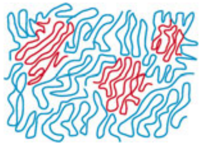
Table 10 Overview: structural scheme and linkage type in thermoplastic homopolymers, copolymers, and polyblends

Polymer			Struct. scheme		
			Monomeric units (MU) or polymer repetition units (PRU)	Linkage type, phase structure	Examples and remarks
Homopolymers	amorphous		homogenous MU 	 Single-phase plastics amorphous thermoplastics ball model	PS; PMMA; PC; PVC; PSU (thermoplastics)
	semicrystalline			Multiphase plastics: semicrystalline thermoplastics 	PE; PP; POM; PTFE; PBT; PET; PCTFE; PVFDF; PVF; PA
Copolymers	Bipolymers=2, Terpolymers=3, Quaterpolymers=4 different MU	Random (static) copolymers as amorphous thermoplastics or elastomers	heterogenous MU irregular: 	Random copolymers (single phase plastics) homogenous amorphous phase 	irregularSBR, SAN, VC/CA, EV/A, E/VAL, EPM; EPDM; FEP
		Alternating copolymers, semicrystalline or amorphous	regular:  strictly alternating MU with $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$ polymers (rare)	MU bonded by primary valence forces (usually subordinate regions)	in regular alternation: polyester (diacid MU + diol MU) polyamide (diacid MU + diamine MU) UP: cross-linking, duroplastic copolymer with relatively regular alternation of styrene MU and fumaric acid MU

(*continued*)

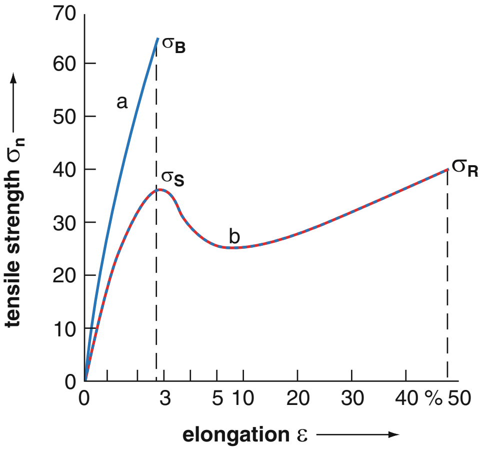
Table 10 (continued)

Polymer		Struct. scheme		
		Monomeric units (MU) or polymer repetition units (PRU)	Linkage type, phase structure	Examples and remarks
Polymer alloys	Block copolymers as thermoplastic elastomers	in blocks 	Multiphase plastics  MU bonded by primary valence forces acting along the chain‘s length	S/B/S; S/I/S; S/EBM/S (three-block copolymers) PUR; PEBA; EPTR; ETR (multiblock copolymers) disperse hard phase as physical cross-linking coherent soft phase
	Graft polymers, mainly as high-impact strength thermoplastics. The chemical bond between the hard and soft phases improves efficacy and long life of impact damping	grafted homopolymer or copolymer  backbone polymer, e.g., elastomer, soft, damping	Multiphase plastics  phases bonded laterally to the chain of the backbone polymer by primary valence forces	high-impact thermoplastics S/B; ABS; ASA; MABS; MBS; S/E; E/P-B; PEBA coherent hard phase (graft polymer) disperse soft phase (backbone polymer)

Polyblends, also in most cases as high-impact-strength thermoplastics. The soft phase is an elastomer or semicrystalline thermoplastic with a low glass transition temperature T_g	 physical mixing in melted state	Multiphase plastics  phases bonded by secondary valence forces; no primary valence linkages	(PS+BR), (PE+PP), (PA6 +PA10), (PE+PIB), (PC +ABS), PA6+PE), (PVC +PE-C), (PC+PBT) coherent hard phase (amorphous or semicrystalline) disperse soft phase (amorphous or semicrystalline) Special case: (PS+PPE)

🟥 soft elastic, 🔵 hard elastic, 🟢 primary bindings

Fig. 5 Stress–strain diagram of normal polystyrene (**a**) and of a polystyrene modified to increase its impact resistance (**b**)



under *impact stress*, etc.) in decisive ways. For example, the impact strength[1] (resilience) of polystyrene is increased by modifying it (in this case: graft copolymerization) with rubber particles.

Figure 5 [4] uses the example of stress–strain behavior to demonstrate the extent to which plastic properties can be altered, "tailor-made," by means of copolymerization. Explanations and details on Table 10.

Statistical Copolymers

Figure 6 illustrates the influence of statistical copolymerization on the modulus of elasticity curve plotted against temperature, using the example of the butadiene–styrene copolymer.

A shift in the glass transition temperature results from copolymerization of plastic A with B (A-co-B), in our example of butadiene with polystyrene. This process is also known as internal plasticization. By contrast, in block and graft copolymerization and in polyblends of two plastics C and D, their glass transition temperatures remain essentially unchanged.

Block Copolymers (Thermoplastic Elastomers, TPE)

The main properties are determined by the matrix (coherent soft phase); the disperse hard phase then shows the transformation.

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[1] Impact strength a_n (notch impact resistance a_k) is the impact energy absorbed by the un-notched (notched) test object in relation to the smallest cross-section of the test object prior to the test.

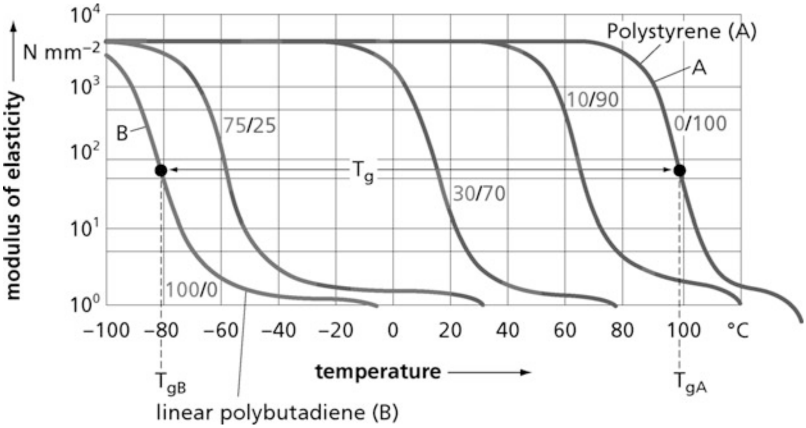

Fig. 6 Temperature dependence of the modulus of elasticity in butadiene-styrene copolymers [7]

TPEs have a two-phase system, see Table 10, i.e., an elastic soft phase and a thermoplastic hard phase. They are produced as block copolymers or polyblends.

Morphology is determined by material properties. The hard phase, as a reversible physical cross-linkage, contributes strength and stability under heat exposure, whereas the soft or disperse elastomer phase contributes the elastic properties and behavior under cold exposure (impact strength).

Important *block copolymers* include the styrene types (TPE-S), polyether esters (TPE-E), polyurethanes (TPE-U), and polyether amides (TPE-A).

Among the *polymer blends*, or polyblends, the main focus is on those with a disperse EPDM phase in a PP matrix.

The dispersed elastomer particles are *uncross-linked* (TPE-O or TPO), but may also be *cross-linked* (TPE-V). The cross-linking (vulcanization) occurs during compounding in closed mixers (batchwise) or with twin-screw extruders (continuous).

The main advantage of thermoplastic elastomers, as illustrated by the modulus of elasticity curve in Fig. 7, is their improved processability compared to cross-linked elastomers (e.g., direct in-situ shoe sole moldings).

Table 11 [8] compares the properties of TPE classes. See Table 6 in Chapter “Plastics: Classification, Characterization, and Economic Data” for the abbreviations.

Graft Copolymers and Polyblends (Polymer Blends)

There is no essential difference between the two types in the modulus of elasticity curve, Fig. 8. Within the temperature range between T_{gB} and T_{gF}, rigidity is reduced in accordance with the mixture ratio of components B and F. The modulus of elasticity curve is similar to that for semicrystalline thermoplastics. This is

Fig. 7 Schematic modulus of elasticity curve, plotted against temperature for TPE [4]. A: amorphous thermoplastic, e.g. Polyisocyanate
B: natural rubber, e.g. Polyol
C: thermoplastic elastomer, e.g. PUR

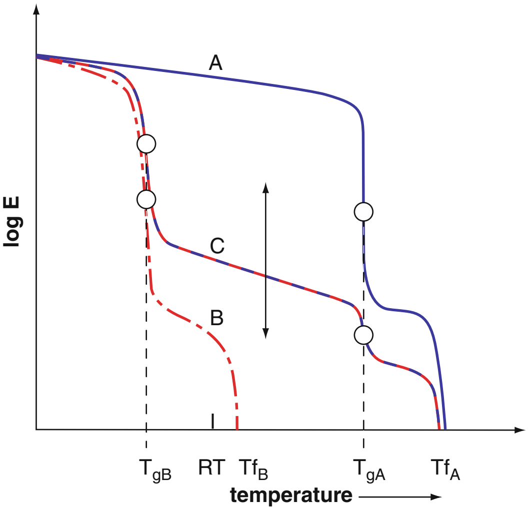

Table 11 Comparison of properties of TPE classes [8]

Property	TPE-O	TPE-V	TPE-S	TPE-U	TPE-E	TPE-A
Density [g cm^{-3}]	0.89–1	0.9–1	0.9–1	1.1–1.34	1.05–1.39	1.01–1.2
Hardness [Shore]	50 A-75 D	40 A-50 D	10 A-75 D	70 A-90 D	35 D-75 D	65 A-72 D
Lower temperature limit [°C]	−60	−60	−70	−50	−65	−40
Upper temperature limit [°C]	120	135	100	135	150	170
Residual pressure deformation, at 100°C	–	+/++	– [+/++]	O/+	O	O/+
Resistance to HCs	–	O/++	–	O/++	+/++	+/++
Resistance to aqueous media	+/++	+/++	+/++	O/+	−/−	O/+
Price level [€/kg]	1.50–3.50	3.50–7.50	1.50–6.50	5–6.50	5–6.50	6.5–12.50

++: very good, +: good, O: moderately good, –: poor

understandable, since the latter are also two-phase materials (amorphous and crystalline phase).

Whereas *incompatible partners* in polyblends usually result in heterogeneous morphologies (e.g., styrene-butadiene SB), and often in highly resilient plastics, *compatible partners* result in plastics with moderate property profiles in accordance with the mixing percentages (e.g., PC/PBT).

As opposed to copolymers, polyblends may unmix during processing. On the other hand, production of the blends is often more economical and can be realized right on the processor's premises. In many cases, the long-term properties (creep) of polyblends are less desirable (slipping of macromolecules) than those of copolymers.

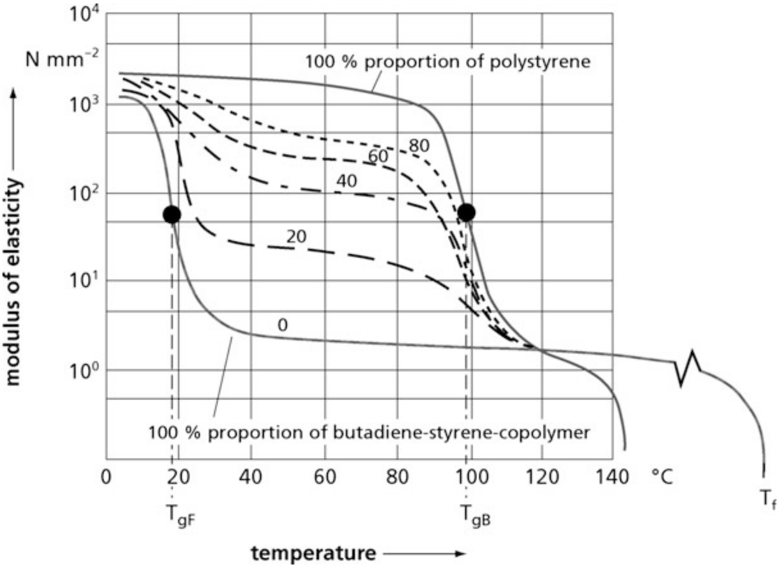

Fig. 8 Temperature-dependence of the modulus of elasticity in a polyblend of PS and 30/70 butadiene-styrene copolymer. According to [7])

Plasticization

The modulus of elasticity *E* of unfilled thermoplastics and duroplastics is between ~600 and 4,000 N mm^{-2}, that of elastomers between ~50 and 600 N mm^{-2}. Since elastomers require more complex and expensive processing due to the chemical reactions involved, the properties of thermoplastics have been altered to resemble those of elastomers, the objective being economical processing of thermoplastics. "Plasticizers" increase the toughness and formability of a plastic, whereby for example its strength, modulus of elasticity, and melt viscosity are reduced. Internal and external plasticization are differentiated.

Internal Plasticization

Internal plasticization is realized by polymerizing incorporation (statistical copolymerizing) of a second "plasticizing" component. This makes it possible to influence the mobility of molecular chains and, on the other hand, the bonding forces between the chains as well (Table 10).

Whereas polymethylacrylate (PMA) is within its main plasticization range at room temperature (T_g at 5 °C), polymethylmethacrylate (PMMA) is still in the vitreous state at this temperature (T_g at 105 °C). Because of the statistical copolymerization of MMA with MA, there a downward shift of the glass transition temperature accompanies increasing MA content, resulting in "internal plasticization" of the PMMA, i.e., MA is incorporated into the PMMA chain by means of primary bonds.

External Plasticization

Similarly to the production process of polyblends, the macromolecules are physically mixed with another substance for external plasticization. By contrast with polyblends, however, low molecular substances (monomeric plasticizers with molar masses of 350–600 g mol^{-1}) or oligomers (so-called polymeric plasticizers with molar masses of 2,000–4,000 g mol^{-1}), are used for external plasticization.

The smaller the plasticizer molecules, the better the plasticizing effect. However, these short-chain plasticizers do tend to be rather volatile due to their high vapor pressure levels (plasticizer migration). The main advantage of the oligomeric/polymeric plasticizers is their reduced tendency to exudate. Polyesters, nitrile-butadiene elastomers and, for example, ethylene-vinyl acetate terpolymers (EVA) with molar masses of up to 150,000 g mol^{-1} are seeing increasing use as polymeric plasticizers.

The external plasticizing method is applied most frequently to polyvinyl chloride (PVC). The distance between the macromolecules of the plastics is increased by incorporation of plasticizer molecules [aromatic plasticizers, e.g., tricresyl phosphate (TCP) and aliphatic plasticizers, e.g., dioctyl phthalate (DOP) or dioctyl sebacate (DOS)]. This reduces the secondary bonding forces and increases chain segment mobility. Solvents (including water in polyamides) may also act by inward diffusion in a manner similar to plasticizers [11].

"Plasticizers are liquid or solid, indifferent organic substances with low vapor pressure, mainly ester-like in nature (definition of plasticizers acc. to DIN 55 945). They are capable of mutual interaction with high polymer substances and formation of a homogeneous system with the latter, without a chemical reaction and preferably on the basis of solvent or swelling properties, but under certain circumstances without these as well. Plasticizers give systems or coatings made with them certain desirable physical properties, e.g., lower freezing point, more formability, increased elasticity, reduced hardness and, if required, stronger adhesion."

Polyamides (PA) with Varying Amounts of Water (See Also Fig. 9)

Water acts as a plasticizer in PA. The water content of the PA depends, among other things, on ambient moisture. Dry PA is brittle at room temperature. PA dries out at higher temperatures, in an anhydrous atmosphere ($T < 0$ °C) or in anhydrous fluids (oils, etc.). To avoid brittleness in PA parts in long-term use in

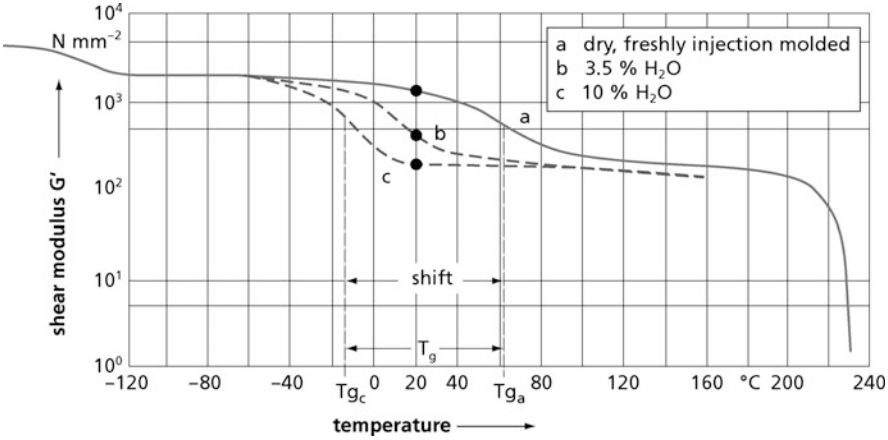

Fig. 9 Temperature and moisture dependence of the shear modulus of polyamide 6 [4]

a cold, dry atmosphere, such parts are sometimes made of PA 6 with monomer content.

Monomers act as plasticizers. They diffuse much more slowly than water molecules. A similar plasticizing effect of water is also observed with polyvinyl alcohol (PVAL) and linear polyurethane (TPU). This applies in general to swelling of plastics in solvents.

Changes in mechanical properties, for example, due to water uptake or release are a matter of concern to design engineers.

Figure 9 shows the shear modulus G′ of polyamide 6 plotted against temperature under differing moisture conditions.

The glass transition temperature can shift downwards by ~50 °C between the dry state and maximum water uptake (10 % in PA 6).

The shear modulus, for example, is reduced at a selected temperature of, say, 40 °C, from 1,000 N mm^{-2} in a dry PA 6 to ~200 N mm^{-2}.

Such extreme variations are rarely seen in actual practice. Nonetheless, the designer of a hand drill housing, for instance, has to take such potential property variations into account (drill might be left out in the rain), whereby a PA 6 housing 2 mm thick would have to lie in water for weeks before the extreme variations shown in Fig. 9 would come to bear. Internal swelling stresses will result in any case, since the outermost layers of the housing will absorb some water. Reinforcement of the structural material with glass fibers helps reduce water uptake since glass does not absorb water (the absolute water content is reduced, but the rate of water uptake and release is increased).

The incorporation of foreign atoms or molecules in existing basic molecular chains can be realized, as described above, either internally by way of chemical bonds (copolymerization) or externally by means of physical mixing of different molecular partners (polyblends, external plasticization). The properties of plastics can be engineered by these methods, whereby undesirable secondary effects must be kept in mind such as emissions from low molecular plasticizers.

2.2 Physical Degrees of Order

2.2.1 Amorphous State in Thermoplastics

Completely statistical (random) arrangements of the macromolecules without a regular order or orientation, i.e., without constant distances, are known as *amorphous states*. There is no long-range order whatsoever.[2] The valid model for such states is the statistical coil. This is the dominating secondary structure in synthetic polymers and polymeric solutions. Its determinant parameter is coil density.

This spatial coil structure represents the most favorable state from the point of view of entropy; the macromolecule tends toward this state to the extent allowed by external conditions (mobility). Under conditions of rising temperature or diffusion of solvents into the material, the mobility of the chain segments and side chains increases. Rotations and shifts are more frequent (molecular microbrownian motion).

According to the second law of thermodynamics, a macromolecule strives to attain the state of greatest possible entropy and will therefore tend to coil.

Causes of amorphous structure:

- Chain structure, pendant groups
- Cooling rate

Homogeneous, amorphous plastics without pigments or fillers are transparent. Expressed in terms of structural dimensions, this means no long-range structures are present within the order of magnitude of visible light waves (wavelength 0.4–0.75 μm). An incident ray of light is therefore not bent, since the refractive index remains unchanged in amorphous plastic. By contrast, the refractive index for an incident ray of light changes constantly in semicrystalline plastics between unordered, amorphous and ordered, crystalline areas, resulting in diffusely scattered light at the interfaces – and opacity. Theoretic considerations based on felt models for the completely amorphous state result in a density of ~65 % of crystalline-state density. The measured values were, however, between 83 and 95 %. The conclusion is that amorphous plastics must harbor areas of short-range order[2] within the random felt or coil structure.

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[2] Long-range order refers to an intermacromolecular order extending beyond the adjacent neighbors regarding intermacromolecular distance, order, and orientation. The term short-range order designates ordered states extending only to immediately adjacent neighbors, whereby it is assumed that these ordered states are constantly broken down and renewed by thermal motion.

2.2.2 Semicrystalline State in Thermoplastics

Besides the state of greatest disorder, ordered states within a macromolecule are also possible, particularly in *semicrystalline thermoplastics*. These short-range orders presumed to exist in the amorphous state develop in the melt of semicrystalline thermoplastics, then act as crystallization nuclei in the subsequent cooling process.

Linear macromolecules, either without substituents or with small ones regularly arranged, can juxtapose themselves at a microscopic level in uniform parallel aereas and form crystals. Plastics with crystalline regions always also contain more or less amorphous, unordered regions, for which reason they are termed semicrystalline. This macromolecular arrangement can be altered by a number of influences.

Crystalline structures result when macromolecules

- Exhibit a uniform chemical structure (constitution) and
- A regular arrangement of the substituents (configuration)
- Have time to reach an ordered state during cooling or
- For example if the macromolecules are shortened (degraded) during processing (by pronounced shearing in the melt or excessively high melt temperature) or during use
- Solidify under high pressure or
- Contact ordering surfaces (nucleation agents).

The PE chains, which show a zigzag structure in the planar view, arrange themselves so that any one chain is surrounded by four equidistant chains, each of which is rotated around its longitudinal axis by 82° in relation to the central chain. The size of the crystalline blocks depends largely on the cooling rate of the melt.

In semicrystalline thermoplastics, these crystalline blocks can form ordered superstructures such as spherulites. The properties of the plastics in most cases depend more on the overall behavior, size, and predominance of these superstructures than on that of the crystalline blocks.

The cohesion of the amorphous boundary layers of different crystalline blocks is determined by the number of bridging chains (*tie molecules*) and mutual chain entanglements. The tie molecules extend to as many as 15 blocks and thus contribute to material properties, Fig. 10. The amorphous boundary layer is often considered a weak point as far as strength and rigidity are concerned. However, semicrystalline thermoplastics would be brittle and useless without their amorphous boundary layers.

Degree of Crystallization

The temporal course of crystallization can be shown in schematic form as follows, Fig. 11:

Crystallization is normally not completed when a molding is produced. The postcrystallization process may continue for weeks or even months. In practice,

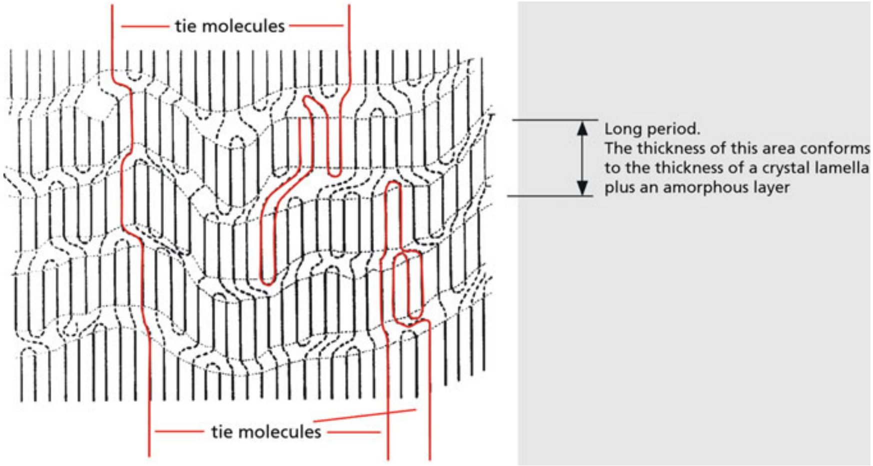


Fig. 10 Model drawing of the cross-section of a lamellar structure. The crystalline lamellae are separated by amorphous regions in which the molecules either terminate, fall back or form bridges to the lamellae above or below (tie molecules) [6]

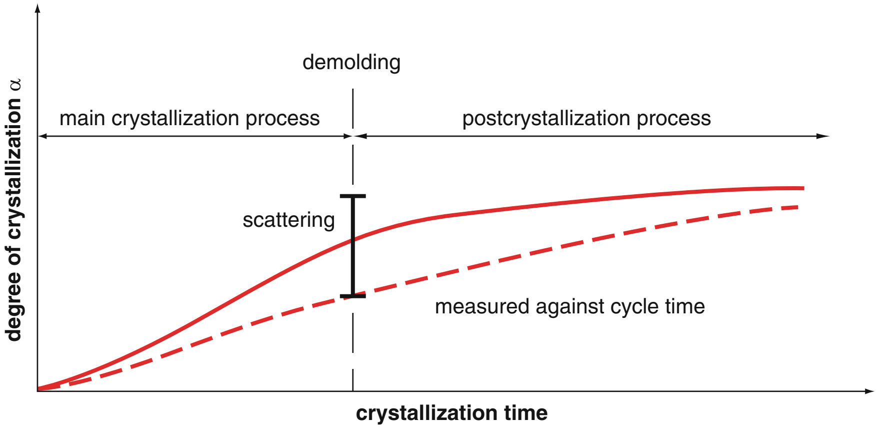


Fig. 11 Degree of crystallization α as a function of crystallization time during an isothermal crystallization process. Shrinkage V = const. (memory effect), not to confuse with volume contraction where V ≠ const

moldings that require high levels of dimensional accuracy are made in heated molds to give the chains a chance to crystallize as rapidly and completely as possible. The higher the mass and mold temperature and the greater the distance from the mold surface, the more opportunities the molecules are given to reorient themselves over a longer period.

The degree of crystallization depends in large measure on the rate of crystallization. The crystallinity in injection moldings therefore varies across the molding wall cross-section. The layers close to the mold wall solidify rapidly. The time until crystallization is brief. In polyamides, for example, nucleation is gradual, so that crystallization at the mold wall may be completely suppressed by rapid cooling (cold mold). The middle of the molding wall cross-section cools more slowly, resulting in a higher degree of crystallization.

These variations in the shrinkage process, localized depending on wall thickness, cause internal stress in injection-molded parts. Internal compression stress is usually present on the outside and internal tensile stress on the inside. This tends to compensate stress cracking tendencies, since the outside internal compression stress counteracts the tensile stress necessary for stress cracking.

The increasing density resulting from increasing crystallization also results in shrinkage processes inside the plastic material originating with the spherulite centers.

Crystallization Shrinkage

The overall shrinkage of a molding is the sum of its processing shrinkage and aftershrinkage, Fig. 12.

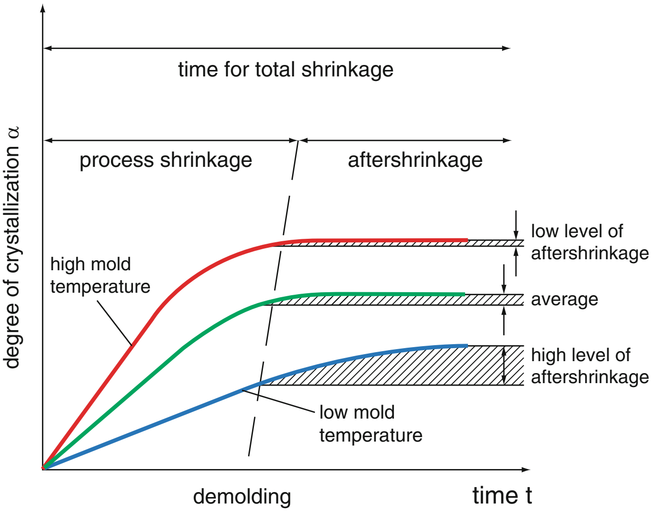


Fig. 12 Schematic course of processing shrinkage and aftershrinkage in relation to mold temperature [4]

Besides aftershrinkage, the following parameters also influence the dimensional stability of a molding in use:

- Temperature variations
- Moisture variations

Significant aftershrinkage is observed mainly in semicrystalline plastics as a result of postcrystallization. It can be reduced by selection of suitable mold temperatures.

Shrinkages processes result in tensile stress between the spherulites. The larger the spherulites, the greater the shrinkage, and stress, levels will be along the spherulite boundaries. Since only a relatively small number of chain molecules extend from one spherulite to the next, these tensile stresses can cause cracking.

Cracks and high levels of tensile stress at the spherulite boundaries reduce, in particular, impact strength and elongation at rupture, and favor stress cracking.

On the basis of the above information, it is clear that two crystallization parameters in particular influence the properties of a finished part:

- Degree of crystallization
- Size and distribution of spherulites

whereby the degree of crystallization is the more influential of the two, also with regard to internal stresses.

2.2.3 Low Cross-Linked State (Elastomers)

A wide-meshed, three-dimensional cross-linkage of linear macromolecules is characteristic of *elastomers*. Sulfur bridges are a common example of a cross-linking reaction.

The starting materials are long-chain rubbers. DIN 53001 covers the special terminology and definitions on “rubbers and elastomers.”

Thermoplastic elastomers, for example certain styrene-butadiene copolymers (see Table 10), contain so-called “hard and soft segments” that react like “cross-links” at low to medium temperatures, but fuse thermoplastically at higher temperatures and thus do not represent true chemical cross-links.

Incorporated elastomer particles (in the micro and nano ranges) may however also be chemically cross-linked.

2.2.4 High Cross-Linked State (Duroplastics)

Starting from prepolymers (reactive resins), duroplastics are produced by means of an irreversible chemical cross-linking process, usually with a high cross-linking density. The small segment lengths between the cross-links result in reduced segmental mobility, leading to low creep levels and good form stability at high temperatures.

3 Mechanical and Thermal Properties

High polymers show pronounced viscoelastic and viscous (plastic) behavior under normal mechanical loads compared to most other materials, meaning the deformations that occur are in some cases elastic (reversible), and in some cases viscous and thus plastic (irreversible). A result of this is that material parameters such as modulus of elasticity, shear modulus and other important related mechanical properties of high polymers depend not only on temperature, but rather – among other things – on load application times and rates as well.

3.1 Temperature-Dependence of Mechanical Properties

The torsional vibration test according to DIN 53445 is used to investigate temperature-dependent viscoelastic material behavior. This is a short-term test. The time-to-rupture test according to DIN 53444 registers the influence of stress duration, stress type, and temperature. The torsional vibration test provides additional information on the damping behavior of the plastics tested (mechanical loss or damping factor d), Fig. 13 [9].

Knowledge of the processes that take place in the transitional phase between the defined states:

- glass transition temperature T_g
- melting range T_m

is key to an understanding of the mechanical properties of plastics at different temperatures.

The state below the glass transition temperature is the energy elastic (hard elastic) state, in which the material is usually very brittle. The so-called micro-brownian motion still possible up to the glass transition temperature – derived from higher temperatures – has come to rest in this state. The level of the transition interval depends on the strength of the secondary bond, i.e., the stronger these forces are, the higher the glass transition temperature will be.

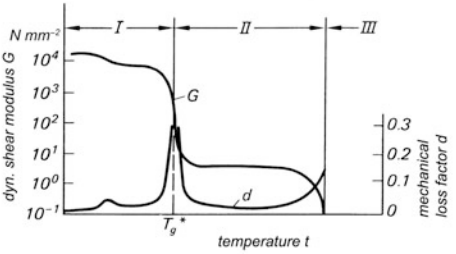
Impact strength can be increased by mixing plastics with higher glass transition temperatures and plastics with lower glass transition temperatures. The same thing applies to polymerization with suitable comonomers, see Sect. 1.1.

The energy elastic range and glass transition point are succeeded, as the temperature rises, by the entropy elastic (soft or viscoelastic) range, i.e., the application range for polyolefins.

For comparison with the shear modulus curves in Fig. 13 for plastics, Fig. 14 shows the temperature-dependence of the modulus of elasticity of some metallic materials [91]. The properties also show pronounced temperature-dependent changes, but only within the 1,000–1,500 °C range. The data for iron (Fe) reflect

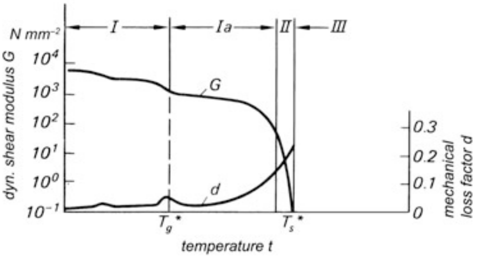
Amorphous thermoplastics, example PVC, PS, PMMA, PC

Range I:	Energy elastic behaviour (glass state). Application range of the plastic
T^*_g:	Glass transition temperature, phase transition point. Transition to thermoelastic range.
Range II:	Entropy elastic behaviour (quasi rubber elastic). Range of hot secondary forming.
Range III:	Viscous flow behaviour. Range of thermoplasticity: Primary forming and welding. Transition II-III gradual.



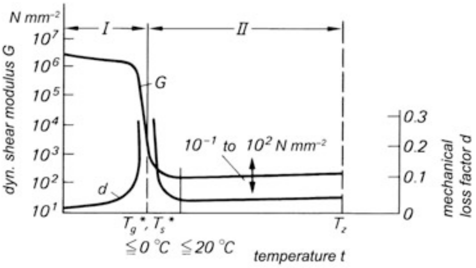
Semicrystalline thermoplastics, examples: PE, PP, PA, POM, PET, PBP, FEP

Range I:	Glass state, amorphous ranges frozen, plastic brittle.
T^*_g:	Glass transition temperature for amorphous portions.
Range Ia:	Amorphous portions thermoelastic. Crystalline portions solidified. Normal application range.
T^*_g:	Crystallite melting temperature.
Range II:	Range of melting crystallites, plastic enters range of hot secondary formability (narrow temperature range).
Range III:	Viscous flow behaviour. Range of thermoplasticity: Primary forming and welding.



Elastomers, examples: soft rubber, soft PUR

Range I:	Frozen state. Material is brittle. Temperature <20°C
T^*_g, T^*_m:	Glass transition temperature or crystallite melting temperature.
Range II:	Rubber elastic behaviour (entropy elasticity). Application range of (loosely) crosslinked materials.
T^*_g:	Disintegration temperature (incipient)



Duroplastics, examples: PF, UF, MF, UP, EP

Range I:	Energy elastic behaviour. Application range. Materials hard and brittle (no internal sliding)
T^*_g:	Glass transition tempreature
Range II:	Non-crosslinked portions "softened", flexible. Material possibly somewhat more amenable to secondary forming. No flow.
T^*_g:	Disintegration temperature

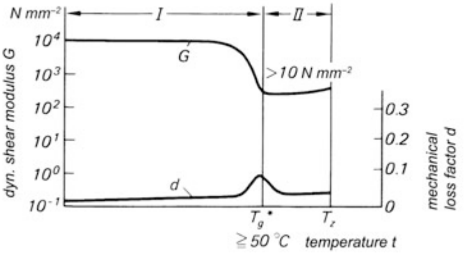


Fig. 13 Temperature-dependence of the dynamic shear modulus G′ and mechanical loss factor *d* of different groups of plastics [9]

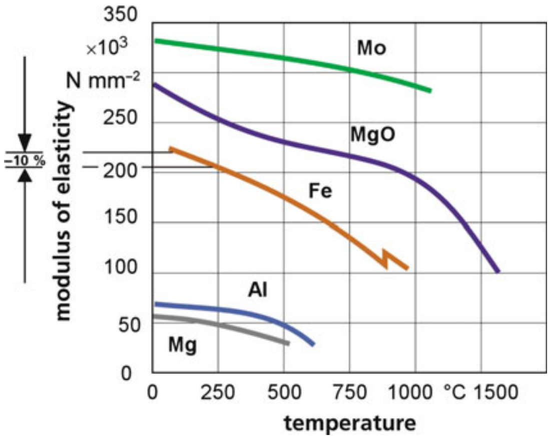


Fig. 14 Temperature-dependence of the modulus of elasticity of some metallic and ceramic materials

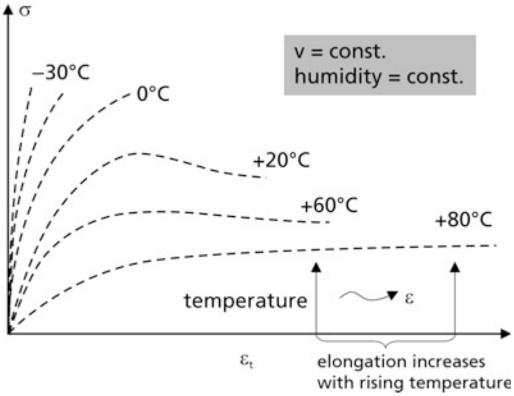


Fig. 15 Influence of temperature ϑ on $\sigma_n = f(\varepsilon_t)$ (qualitative) [4]: $\uparrow \rightsquigarrow \varepsilon \uparrow$ means: Elongation increases with increasing temperature (decreasing modulus of elasticity or tensile stress with increasing temperature)

the familiar fact that the modulus of elasticity falls by only ~10 % up to 250 °C, so that the properties of steels can be expected to remain constant within this temperature range.

The deformation behavior of metals is mainly elastic up to ~250 °C. The linear relation of rupture stress and elongation posited by Hooke's law applies.

In plastics, as in many solids, increasing temperature at constant elongation results in a strain level drop. To phrase this differently, the amount of force required to elongate these materials decreases, Fig. 15. This reduction in elasticity does not, however, follow a uniform curve. On the other hand, nor are the sudden changes in state in evidence that are observed when low molecular substances change from one state of aggregation to another.

Only brittle plastics go through all of the steps along the temperature-elasticity curve. Some states of plastics are determined by the crystallites, others by the amorphous regions. The properties of these two phases are additive.

Figures 23 and 15 characterize the connection between elongation and strain in the different temperature ranges. Brittle plastics show behavior similar to that of metals. They cannot be stretched very far before they break. Elastic elongations are reversible. Viscous plastics also have a reversible elongation range like brittle plastics, although less force is required to stretch them. Above the tensile strain at yield range (cf. Fig. 20), viscous plastics have a plastic formability range. Elastic plastics, and especially rubber elastic plastics, can be stretched at very low tensile strain levels and, as long as the tensile strain at yield range is not exceeded, will then return to their original state.

Polymers are no different to any other group of substances in that their physical properties are temperature-dependent. Plotting the properties of polymers (e.g., the modulus of elasticity) against a temperature gradient does not generally result in a linear or simple curve as with low molecular substances, in which aggregate state transitions are indicated by sudden changes. The modulus of elasticity of steel at first decreases at a constant rate as the temperature rises. When the melting point is reached, however, it drops to zero all at once. Liquid steel is absolutely formable. The transition from a liquid to a gaseous state is accompanied by sharp changes in other physical parameters. For example, the material's viscosity completely disappears at this point. Sudden drastic changes in elasticity are also observed in solid-state steel at certain temperatures, indicative of shifts in the crystalline form assumed by the iron.

Temperature-related behavior in plastics is also uniquely characteristic. No sudden transitions between different aggregate states are observed. Changes of state occur over a fairly wide temperature range. Further changes of state are observed at the transition from solid to liquid. Figure 13 shows this very clearly for the parameter shear modulus. As an example, the transition from the viscous to the elastic state corresponds to the "melting" of the crystalline regions. At higher temperatures, all polymers assume coiled forms. In the rubber elastic state, these coils can be stretched more and more by application of relatively little force. Relaxation of the force then results in contraction of the workpiece. Extreme stretching of the material causes the molecules to slide against one another, after which the workpiece can no longer return to its original form. The transition of plastics into the gaseous state corresponds to their decomposition range.

Figure 16 shows the influence of the rate of load application in the tensile test in qualitative terms. Section 2.5 describes the time-dependence of the material properties in detail.

The behavior observed in steel is similar in principle, the difference being the higher temperatures involved.

3.2 Deformation Behavior of Plastics

As described above, the deformation of plastics compared to metal is viscoelastic and viscous. The temperature-time dependence of the properties of plastics (and

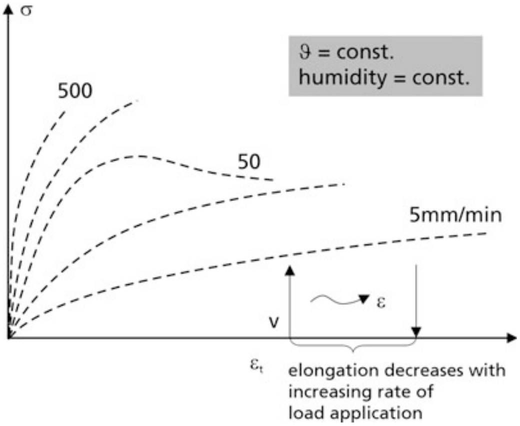


Fig. 16 Influence of rate of load application v on $\sigma_n = f(\varepsilon_t)$ (qualitative) [4]: ↑ $\rightsquigarrow$ ε ↓ means: Rate of load application increases, elongation decreases (increasing modulus of elasticity or tensile stress with increasing rate of load application)

metals at higher temperatures) can be described over time using the following simplified models (see also [11]):

3.2.1 Voigt–Kelvin Model

Spring and damper are arranged in a parallel fashion, Fig. 17.

Viscoelastic deformation results from the parallel overlapping of spring and damper deformation: Elongation is delayed, but completely reversible upon relaxation. This is called entropy or rubber elasticity.

3.2.2 Maxwell Model

Spring and damper are arranged successively (in series), see Fig. 18.

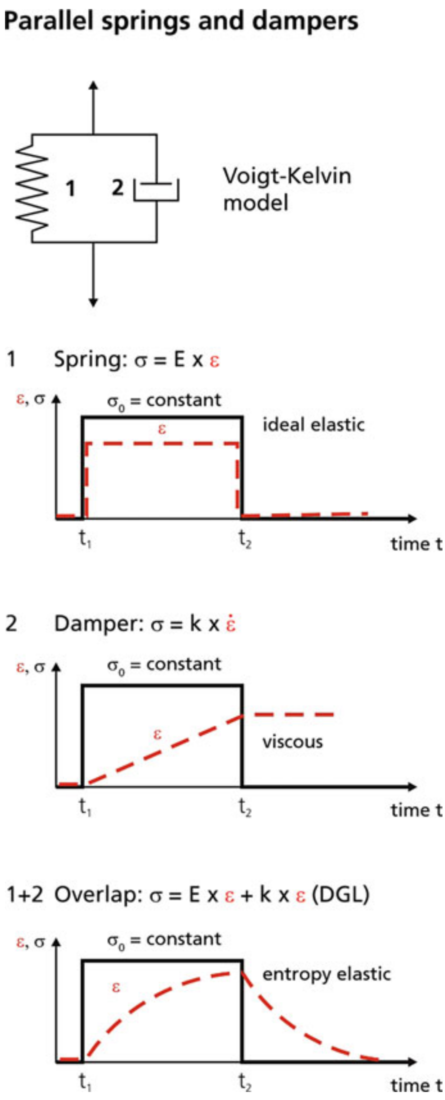
Spontaneous elastic deformations result from the successive overlapping of spring and damper deformation in response to load application and relaxation, there is residual deformation due to the damper.

3.2.3 Four-Parameter or Burger Model

Voigt–Kelvin series arrangement with Maxwell model, see Fig. 19.

The Burger model provides a correct graphic description of the elongation-time behavior of most plastics in a first approximation. The spring 1 results in spontaneous elastic load application and relaxation elongation, 1 + 2 in parallel cause creep during load application and creep recovery (delayed viscoelastic reverse deformation) after relaxation, damper 2 results in residual elongation.

Fig. 17 Simplified model with elongation-time behavior (two-parameter Voigt–Kelvin model)



3.3 Behavior Under Tensile Stress

In technical terms, the behavior of a material under tensile stress is of primary importance, leading to early experimental and theoretical investigation. The investigation of stress–strain behavior is particularly important. It is analyzed in tensile tests in which a test object is elongated to the point of breakage (or tearing) at a certain rate. The maximal tensile stress level reached is the material's tensile strength.

Fig. 18 Simplified model with elongation-time behavior (Maxwell model)

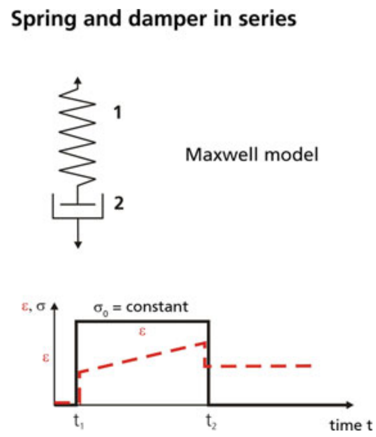


Fig. 19 Extended, more realistic model (four-parameter or Burger model) and its elongation-time behavior

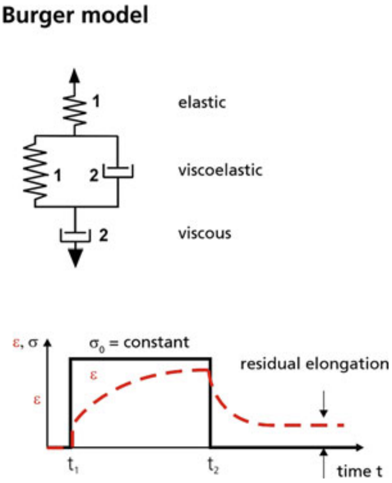
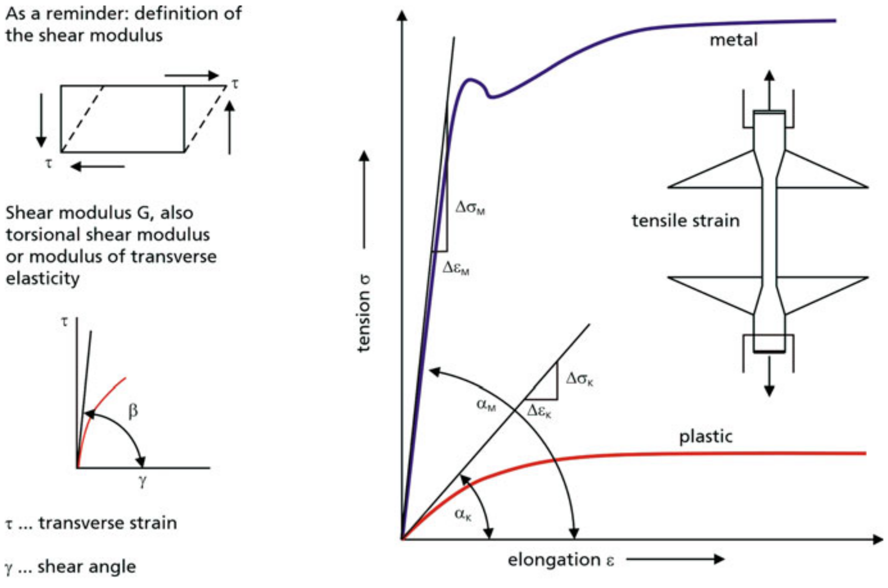


Figure 20 shows the stress curve as a function of deformation of metal and plastics for a basic comparison.

For the most part, plastics do not exhibit Hooke's linear elastic region in the stress–strain diagram as metals do, so that tangents are defined at given points on the stress–strain curve such as origin (elongation 0) or a given elongation ε_T or the secant gradient between origin and elongation ε_S, Fig. 21. In fiber-reinforced plastics and duroplastics Hooke's region is still approximately defined – at low temperatures more than at high temperatures and less so in the case of thermoplastics. Elastomers show no linear elastic region in the form of a straight line through the origin in the σ-ε diagram.

Figure 22 shows stress–strain curves at room temperature for comparison of different materials.



In linear elastic region: plastics $E_P = \frac{\Delta\sigma_P}{\Delta\varepsilon_P}$ ~ tan α_P (origin tangent)

metals $E_M = \frac{\Delta\sigma_M}{\Delta\varepsilon_M}$ ~ tan α_M (Hooke´s region)

Fig. 20 Definition of the modulus of elasticity *E* (original modulus) (ε close to 0 % corresponds to the original gradient) [4]

Figure 23 shows typical stress–strain curves for plastics and explains the various types of curves. In particular, the linear elastic region (Hooke's line) is clearly defined for the materials with a very high modulus of elasticity (gradient of straight line through origin) such as ceramics, cast iron, steel, Cu, Al, and PMMA (brittle).

Also, the AUC (area under curve) of the different materials represents their resilience. Cast iron and ceramics are very brittle; steel, copper, and aluminum, as well as the thermoplastics PA and PP, are highly deformable and can therefore absorb large amounts of energy, for example from (impact) load application. It must be remembered here that the deformation behavior of plastics is highly dependent on time and temperature factors (see Fig. 15). Simplified explanations of deformation terminology follow.

3.3.1 Energy Elasticity

Purely energy elastic bodies are deformed in response to force application *with absolutely no time delay* by a certain amount that is independent of the

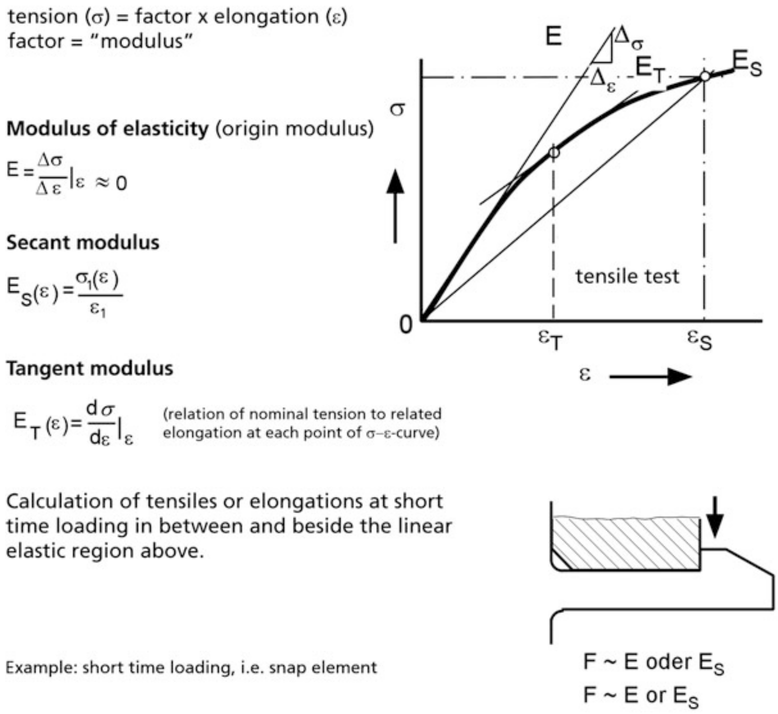


Fig. 21 Modulus of elasticity/secant modulus/tangent modulus [10]

duration of application of the force. The deformation is completely reversible upon relaxation.

The *work of deformation* is stored as *potential energy* in the form of changes in the atomic distances and bonding angles brought about by the deformation. The connection between force (stress) and deformation (elongation) is described in a good approximation by Hooke's law for small elongations in many materials.

3.3.2 Entropy Elasticity

Under force application, the deformation of purely entropy elastic bodies shows a delayed increase. The delay factor may be tiny (in the µs range). Such deformations are also completely reversible.

The force moves the molecules (or atoms) out of their positions of equilibrium (which requires a certain amount of time) in the direction of the application of force. The result is a higher order of the molecules (corresponding to a lower entropy factor). Because of their thermal motion, the molecules strive to attain a state of greatest disorder (coil form) and hence greatest entropy, since this is statistically the

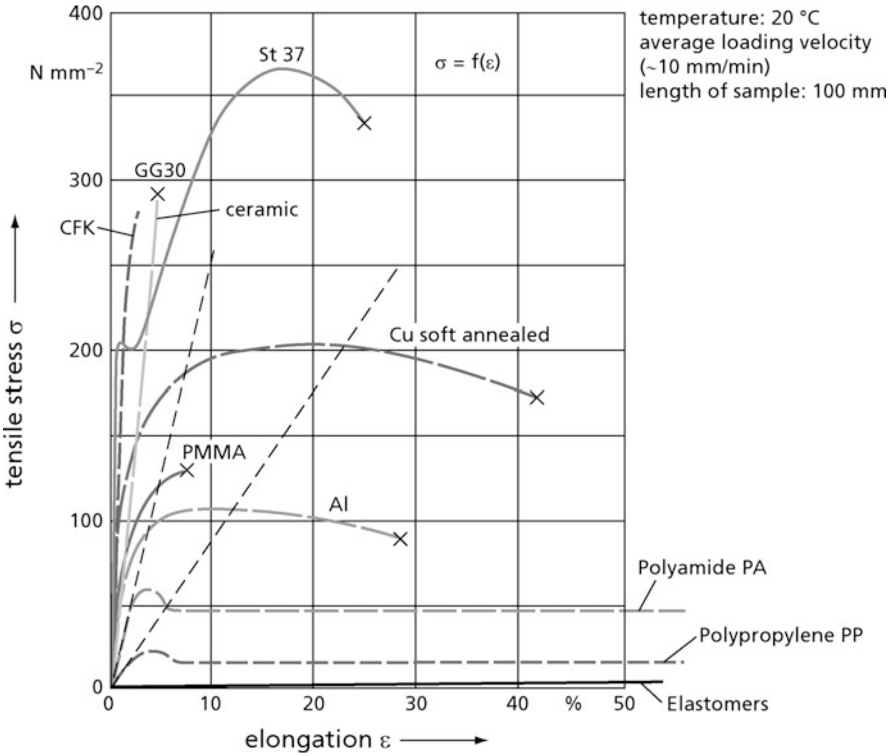


Fig. 22 Stress–strain diagram for different materials at RT; see also Fig. 23 [4]

most likely state. The result is an elasticity resulting solely from the change in entropy level during the deformation.

The *work of deformation* is stored, in this case, as *heat energy*.

Compared to energy elasticity, much greater elongations are sustained without damage, but the modulus of elasticity is lower by several orders of magnitude. Hooke's law is also closely approximated for smaller elongations.

3.3.3 Hyperelasticity

Various material models describe the deformation behavior of elastomers, for example Neo-Hooke, Mooney–Rivlin, etc.

All of these material models are so-called "hyperelasticity models." The stress in the material is clearly a function of the elongation, i.e., each defined deformation state in a structural material component has exactly one correlative load application state [12].

In tensile tests of elastomers, the stress–strain behavior between successive load application cycles deviates from the first cycle (post prestressing).

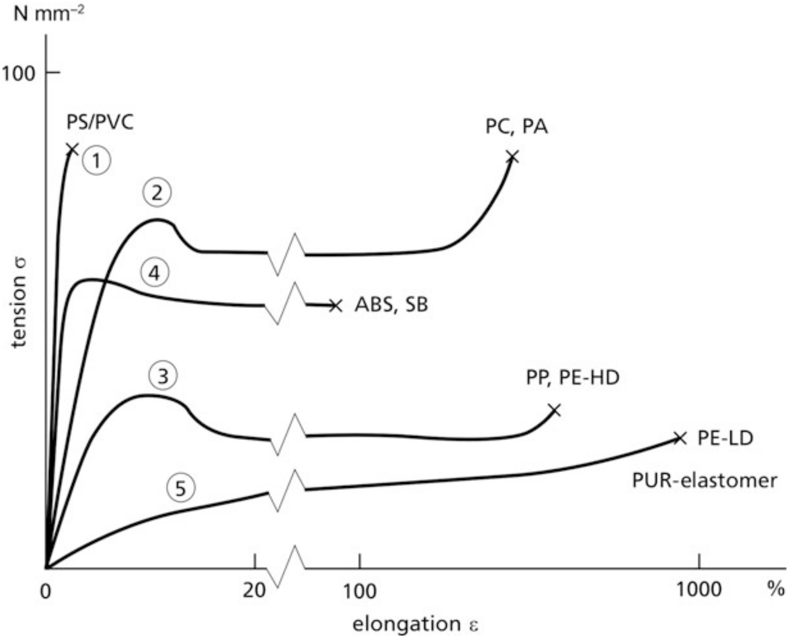


Fig. 23 Typical stress–strain curves for plastics (U. Delpy, IKP) [10]

This stress softening is known as the Mullins effect [13] and is observed in particular in active filled elastomers.

The elastomer–filler composite is partly destroyed during deformation, then partly restored. This results in a change in the stress–strain curve and depends on the prestressing level. Relaxation leaves a residual deformation. Under dynamic load applications, the shear modulus depends on the stress amplitude [14, 15].

It is important to note in this connection that the resilience of plastics – as with metals – is reduced over time due to aging and embrittlement.

3.4 Mechanical Damping

Vibration forces applying a *dynamic stress load* to viscoelastic materials results in a phase shift by the phase angle δ between stress σ and elongation ε. The tangent of δ is called the mechanical loss factor d or: mechanical damping. Damping is thus a measure of the heat produced by application of dynamic loads as a result of "internal friction" (dissipation) (Fig. 24).

The conceptual overlapping of the two "ideal" damping curves to obtain the real curve for a semicrystalline plastic clearly shows the two-phase nature of semicrystalline thermoplastics.

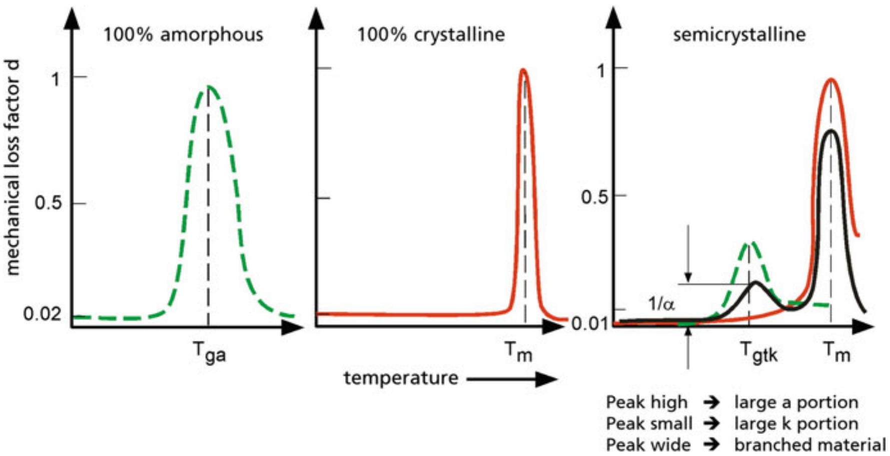


Fig. 24 The temperature-dependent mechanical loss factor *d* [4]: a … amorphous; t_k … semi-crystalline; k … crystalline

Table 12 Connection between temperature and mobility of macromolecules regarding the course of mechanical damping in the main softening range [4]

Operating temperature T_O	Mobility		
	Macromolecules (state)	Chain slipping	Mechanical damping "internal friction"
$T_O < T_g$	Interlocked (energy elastic)	Not possible	Very low
$T_O > T_g$	Macromolecules shift easily against one another (entropy elastic to viscous)	Readily possible	Very low
$T_O \approx T_g$	Macromolecules shift sparingly against one another; transition (from energy to entropy elastic)	Possible	High

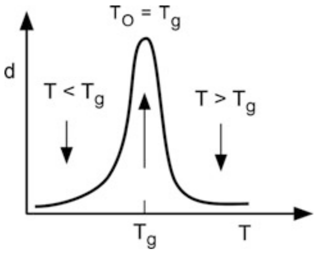
The larger the amorphous moieties, the higher the damping peak at the glass transition temperature T_{gtk}, and analogously for crystalline moieties, at melting temperature T_m.

Table 12 and the corresponding Fig. 25 will help readers grasp the molecular processes in the main softening range.

3.5 Time-Dependence of Mechanical Properties

All thermoplastics flow at room temperature under load stresses far below the yield point, cross-linked plastics at higher temperatures. This clearly demonstrates why it is not permissible to use tensile and breaking strength or the tensile, bending,

Fig. 25 Mechanical loss factor (qualitative) plotted against temperature



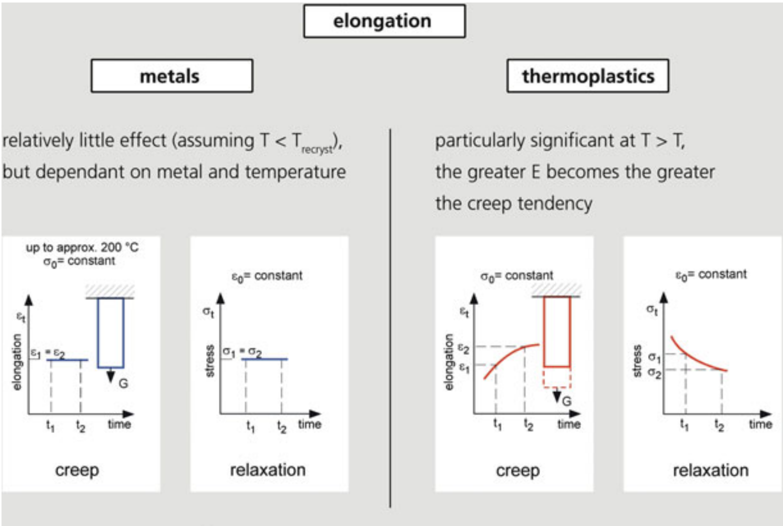


Fig. 26 Influence of time on elongation and stress in metals and thermoplastics [4]

pressure or shear modulus in calculations for structural components according to the formulae of material strength science in the sense of the one-point values usually listed in the material tables of raw materials producers. Any description of material properties must include the time factor. The short-time rupture test is not sufficient for this purpose. Instead of the single table values normally listed for metal materials, thermoplastics require a presentation of the continuous dependence of the mechanical properties on the time factor (and temperature over time).

The long-term behavior of plastics must, in other words, be investigated using static methods. The best-known method is the time-to-rupture or creep test, whereby a workpiece is subjected to stress σ_0 at time $t = 0$ and the stress parameter is maintained at a constant level for the entire duration of the test. Time-dependent deformation is then measured, Fig. 26. If the elongation is constant, the stress parameter drops off in time with plastics. This is known as relaxation. This knowledge has applications related, for instance, to screw connections (plastic screw and/or plastic gasket) and rubber radial shaft gaskets that lose their sealing properties over time.

Creep curves or lines are determined in so-called time-tensile tests for extensive deformations, i.e., far beyond the range of linearity. Instead of maintaining a constant stress level, the simpler mode of load application is used, namely constant initial stress, Fig. 27.

Figure 28 shows the creep lines resulting from such a test, for example carried out on test rods made of HDPE at different load levels and constant temperature.

The many creep lines for the parameter stress can be recalculated for a specific test temperature to obtain the creep modulus $E_c(t)$, entered as a function of time.

$$E_c(t) = \frac{\sigma}{\varepsilon(t)}.$$

Theoretically permissible stress levels, for example, can be derived from such creep line diagrams for each material (assuming an elongation of 1 % as is frequently done for calculations). The actual stress levels that can be used for

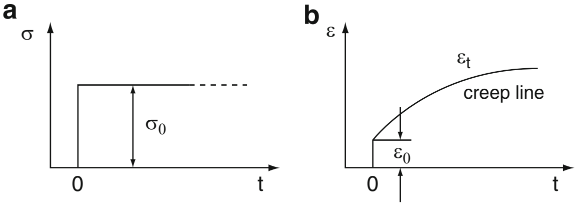


Fig. 27 Time curve for σ and ε in time-to-rupture test (creep test)

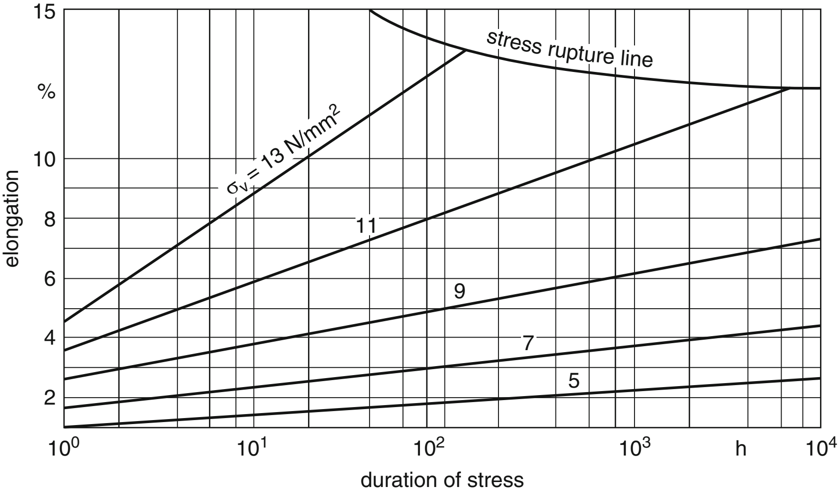


Fig. 28 Creep lines for HDPE at a temperature of 20 °C

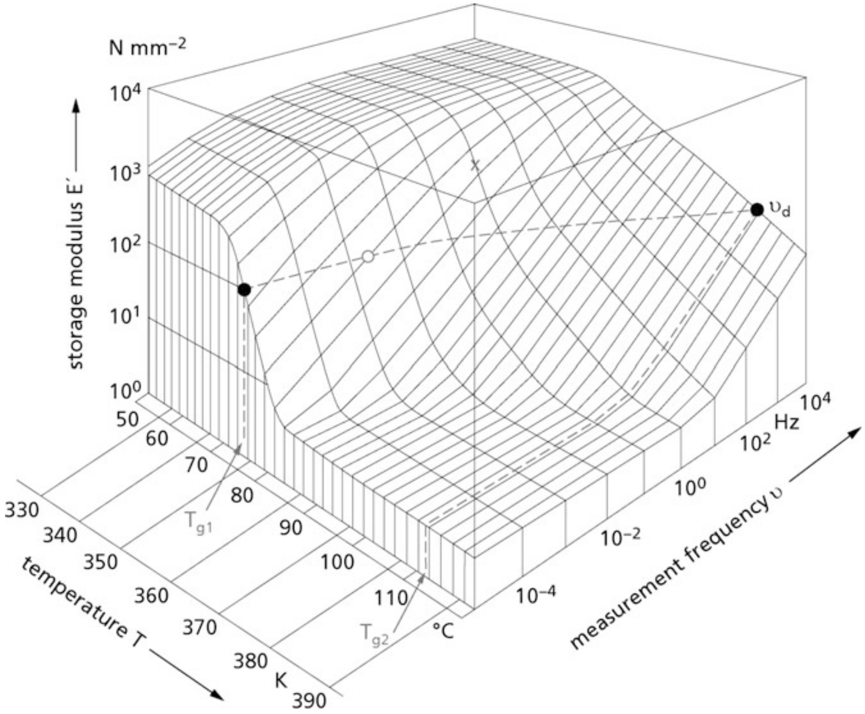


Fig. 29 Storage modulus (real component of the modulus of elasticity) E' of PVC as a function of measurement frequency ν and temperature T [16, 17]. Measured results from W. Sommer [18]. From *lower left to upper right*: Isotherms (T = const.): Increasing modulus of elasticity with increasing frequency (rate of load application). From *upper left to lower right*: Isochrones (n = const.): Decreasing modulus of elasticity with increasing temperature. (*Dashed Lines*) Connecting lines, dynamic glass transition points close to $E = 10^2$ N mm^{-2}. (*Open Circle*) Increasing glass transition temperature with increasing frequency. ("Static" glass transitions with coordinates $T_g = 352$ K (79 °C), $E_g = 10^2$ N mm^{-2}, $\upsilon_g = 2{,}5 + 10^{-3}$ Hz at turning point of dotted line. X Glass transition temperature T_g at 1 Hz isochrone of the torsional vibration test. $E_h > 10^3$ N mm^{-2} in upper part of figure: hard elastic (energy elastic) region; $E_W < 10$ N mm^{-2} in lower part: soft elastic (rubber elastic, entropy elastic) region

dimensioning results from division by the safety factor. The curves are used directly for calculation of the expected deformation of a finished construction.

To conclude this section on mechanical and thermal properties, the connection between the parameters stress, elongation and time and modulus of elasticity, temperature and measuring frequency (rate of load application, i.e., time) (Fig. 29) are clarified.

Figure 29 also shows, in addition to the familiar temperature-dependence of the properties, and here using the example of modulus of elasticity, time-dependence in the form of measuring frequency. A low measuring frequency results in a low glass transition temperature T_g, whereas a high measuring frequency shifts the glass transition temperature in the example in Fig. 29 about 40 °C higher. What this

Table 13 Recommended safety coefficients S

Type of failure	Safety coefficients S		
	Static stress load	Intermittent stress load	Vibrating stress load
Rupture	2...3	2...3	1.5...2
Impermissible deformation	1, 2	1, 2	1, 2
Instability	3	3	3

means is that an impact-type stress load allows little time for deformation of the macromolecules (derivative processes), and the plastic reacts with rigidity (energy elastic). On the other hand, the macromolecules react to low rates of load application (in Fig. 29 characterized by low testing frequencies) by slipping, entropy elastic, in the same test.

3.6 Safety Coefficients

It is a well-known fact that process conditions, for instance those involved in injection molding, extrusion, pressing, grain effects, and cooling conditions, have significant effects on the mechanical properties of plastic parts. Then there are the frequent effects of the technical environment, for example moisture, aging, and stress cracking. Because these individual factors remain hidden from the view of the designer of machine and apparatus components, he/she must take safety factors into account in each individual case – similar to those applying to metallic materials – to obtain standardized test workpiece data on which the stresses for dimensioning can be based.

Table 13 below presents a summary of safety coefficients recommended for the different stress loads. The permissible stress load is calculated – taking stress concentration data into account – as follows:

$$\sigma_{perm.} = \frac{K}{S \cdot \alpha_K}\ \mathrm{N/mm^2}$$

K Stress value N mm^{-2}; S Safety coefficient; α_K Form factor

Otherwise, the safety coefficients are not selected only on the basis of stress load type, form and processing conditions, but also depend on the plastic material itself. A notch-sensitive plastic that is hard and brittle requires higher safety coefficients than one that is hard and tenacious. Within this framework, the semicrystalline thermoplastics generally show a more favorable behavior than the amorphous ones.

4 Physical Properties

In addition to the mechanical properties with their temperature and time dependence, other properties can have decisive roles as well [2, 3]: *Thermal properties* (insulating foams for refrigerators, buildings, window frames, protective shields in

Table 14 Comparative guideline values for metals and plastics

Metals (conductors)	Plastics (nonconductors)	
Coefficient of linear thermal expansion α [10^{-6}/K] St: 10	T: ≈ 100 D: ≈ 30 E: ≈ 200 see Fig. 10 in Chapter "Processing (Primary Forming) of Plastics Into Structural Components"	$\times 10^{-6}$/K
Thermal conductivity λ [W/mK] Cu: 380; Fe: 76; St: 50	T: 0.2 D: 0.3 E: 0.1 glass 0.7 foam materials: 0.015–0.9 see Table 20	W/mK
Density ρ [g/cm^3] Fe: 7.8; Al: 2.7 heavy + precious metals 10–18	Plastics 0.9–1.8 unfilled Silicates: 2.7 PTFE: 2.3	gcm^{-3}
Opaque	Transparent/translucent/opaque see Figs. 13 and 14 in Chapter "Processing (Primary Forming) of Plastics Into Structural Components"	
Electr. volume resistance [Ωcm] Fe: 10^{-5}	Plastics: 10^{10}–10^{18} K with metal powder: ~1	Ωcm
Low mechanical damping	High mechanical damping	

T thermoplastics, *D* duroplastics, *E* elastomers, *K* plastics [4])

aerospace applications, protective clothing for firefighters, etc.), and of course the coefficient of linear thermal expansion. *Optical properties* (headlight mirrors and lenses, windshields, helmet visors, lenses, greenhouses, packaging materials, surface-effect foils, etc.) [1–3]. *Electrical properties* (cable insulation, PCB, insulation housings, safety components for mining applications, bipolar boards and membranes in fuel cells, etc.) [1–3]. *Acoustic properties* (musical instrument bodies, loudspeakers, engine compartment insulation, noise barriers, vibration dampers, etc.). *Substance transport properties* (diffusion, permeation) (barrier properties in packaging, fuel tanks, waste dump foils, medicinal membranes, open-pored clothing, etc.) [2, 3].

Table 14 compares the guideline values for metals and plastics for a number of these properties.

The following figures supplement and add details to the presentation in Table 14 [20].

Plastics expand when heated much more than other materials because their utility temperatures are not far below their melting temperatures. To compensate for this disadvantage, plastics can be filled, for example with fibers, etc.

Thermal expansion is described by the coefficient of thermal expansion α.

5 Chemical Properties

5.1 *Resistance to Chemicals/Media*

Whereas the physical properties of plastics are determined mainly by their morphological structure, their chemical behavior depends mainly on the chemical structure of their macromolecules. Thermoplastics are in most cases resistant to acids and lyes and duroplastics to organic solvents. Resistance to chemicals is a decisive factor determining general usefulness in all applications, for instance in the packaging industry, medicine and automobile production. An initial assessment can often be done based on the principle that “like attacks like in chemistry.” Polar plastics are attacked by polar aqueous solutions and polar organic liquids. Polar plastics include for instance PMMA, PC, and PA. Nonpolar plastics, on the other hand, are attacked by nonpolar liquids. For example, PE (nonpolar) swells in contact with benzine and PS is completely dissolved by benzole and toluene [3].

Table 15 provides a comparative summary of resistances in metals and plastics.

5.1.1 Transport Mechanisms in Reaction to Chemical Actions (Permeation)

When low molecular substance or solvent molecules migrate through solid plastics this process is called permeation. Basically, substance transport in permeation takes place in three steps: *adsorption*, *diffusion*, and *desorption* of the migrating molecule [3, 21, 22]. Figure 30 provides a schematic presentation of the transport mechanism involved in permeation.

At first, the low molecular molecule attaches to the surface of the plastic (step 1: adsorption). If the molecule is then unable to penetrate into the plastic, no further

Table 15 Comparative resistances of metals and polymers [4]

Metals	Plastics
Chemical properties	
Resistant to organic solvents, oils, fats, surfactants	Relatively resistant to electrolytes (acids)
Not resistant to electrolytes Corrosion! (Qualification of above: formation of strongly adhesive protective layers and precious metals)	Show little resistance to organic solvents, oils, fats, surfactants (depends largely on type of plastic!), particularly sensitive to chlorinated HC)
Effect: depends on specific metal	Effect: depends on specific plastic
– Dissolution or swelling	– Dissolution or swelling
– Stress cracking corrosion	– Stress cracking

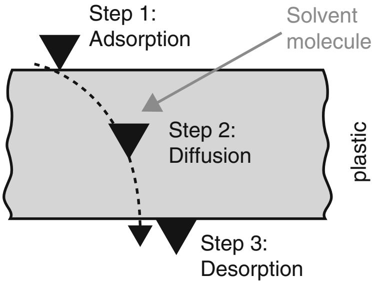


Fig. 30 Steps in the permeation process

substance transport occurs besides the purely physical attachment to the surface and the material parameters of the plastic remain practically unchanged [22]. However, if attachment is followed by diffusion of the polymer (step 2), pronounced changes in the properties of the plastic can be expected. The rate of diffusion, which depends on temperature, polymer structure, and the size of the diffusing molecules, is the decisive factor. Once diffusion through the plastic material is complete, the molecule returns to the surface, where it finally leaves the material (step 3: desorption).

5.1.2 Influence of Aggressive Media on Mechanical Properties

The chemical resistance of plastics is frequently illustrated in so-called resistance tables (e.g., with the classifications "resistant," "moderately resistant," "nonresistant") [3, 17, 21, 23]. The evaluation criterion is the change in mass caused by swelling (increase) or solution (reduction).

Considering the mechanical stress loads acting upon the plastic in addition to the attacking medium, it is apparent that they would further exacerbate the damaging effects. Therefore, the chemical resistance of different plastics, a factor that must be known for pipelines in particular, can be determined in time tests.

The practical example of a fuel container made of plastic emphasizes the important influence of dipole moments in molecules on the solubility behavior of plastics. The influence of ordered (crystalline) regions and unordered (amorphous) structures in the polymer is shown in Fig. 10.

In addition to structural characteristics, the degree of cross-linking naturally has a decisive effect on the solubility of polymers.

Densely cross-linked plastics (duroplastics) show little or no swelling, depending on their cross-linking density.

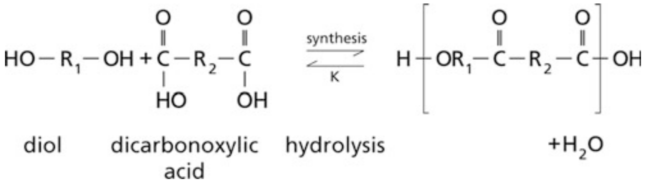
Plastics featuring wide-meshed cross-linking (elastomers) do swell, since their cross-linking bridges prevent complete dissolution. Swelling capacity is reduced as the degree of cross-linking increases.

Uncross-linked plastics (thermoplastics, thermoplastic elastomers) may either swell or dissolve in a given medium.

In the swelled state, the physical properties of the polymers are altered. For example, their volume increases, the cooling rate is increased, transition intervals are reduced (plasticization), and the modulus of elasticity and modulus of torsion are changed.

5.1.3 Effect of Water (Hydrolysis)

In polymers containing ester, amide, or similar functional groups in the main chain, it is possible in principle to split the chain by means of a reaction with water (hydrolysis). Acids and lyes may act as catalysts, whereby chain splitting may be encouraged in hot water in particular, which thus represents the reverse reaction of polymer synthesis. The relevant basic reaction equation for the class of polyesters is as follows (see also Table 16)



$$HO-R_1-OH+\underset{HO}{\overset{O}{C}}-R_2-\underset{OH}{\overset{O}{C}}\ \underset{K}{\overset{\text{synthesis}}{\rightleftharpoons}}\ H\left[OR_1-\overset{O}{C}-R_2-\overset{O}{C}\right]OH+H_2O$$

The reaction equation <polyester synthesis> makes it clear that these are basically balanced reactions. To maintain the forward reaction (polymer synthesis), the low molecular components of the reaction products (H_2O) must be removed from the balance. When such a plastic is then exposed to aqueous acids or lyes, it is always a possibility that the reverse reaction will occur, leading in the end to mass molecular disintegration.

Aromatic polyesters have hydrophobic phenyl groups that allow them to take up only very small amounts of aqueous solvents, so that hydrolysis is only observed at raised temperatures and the materials generally show a good level of resistance to cold water.

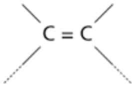
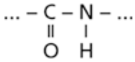
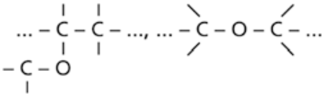
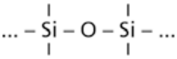
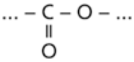
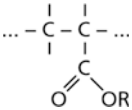
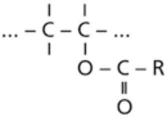
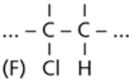
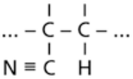
Physicochemical processes in connection with hydrolysis may include, for example, (local) changes in crystallinity, elution of additives, or softening as a result of water uptake.

Typical *mechanical processes* include development of internal stress due to local variation in swelling processes or abrasive damage to plastic surfaces exposed to aqueous solutions at high impact rates (e.g., in natural weather exposure).

5.1.4 Resistance to Stress Cracking

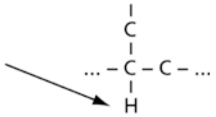
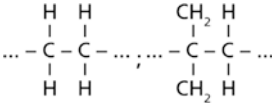
This phenomenon is observed in metals (stress cracking corrosion) as well as in plastics (stress cracking) and comprises a physicochemical process observed to occur between certain plastic–medium pairs. In many cases, moisture contacting the surface of the polymer suffices as an attacking chemical agent. The precondition is tensile stress, either production-related internal stress or external stresses more or less below the normal tensile strength levels. The cracking normally occurs at right angles to the acting tensile stress forces. Stress cracks occur in many plastics in response to surface-active attacking mediums. Presumably, the effect of these mediums is based on elution of low molecular components or contaminants from the plastic and occurrence of slipping processes caused by swelling in the stressed zones, resulting in cracks. The stress cracking is accelerated to a considerable degree by a rise in temperature. The agents that have penetrated by means of diffusion at first cause fine hairline cracks, reminiscent of plastic crazing. Longer exposure to surface-active substances, possibly also in combination with internal or external tensile stresses, causes the hairline cracks to penetrate the walls and break the molding.

Table 16 Resistance of plastics [17]

Weak point in macromolecule	Hydrolysis in particular against			Heat	Ozone weathering (UV + O_2)	Plastics () in parentheses do not show all resistance characteristics listed due to other sensitive groups in molecule
	Hot water	Acid	Base			
 − C = C − double bond (unsaturated) in main chain	r	r	r	(u)	u	SBR, BR, ABS, S/B, S/B/R, B/S, S/I/S, IR=NR, NBR, IIR is more resistant; CR resists weathering more effectively, but hydrolysis less effectively
Carbonate (urethane or amide group in main chain) 	(u)	(r)	(u)	(u)		PUR
	u	u	(u)	(u)	u	PA, UF
 Ether–oxygen in pendant group or main chain	(u)	u	(r)	r	(r)	POM, (polyether PUR), PPE, EP, PVB, PFA shows more resistance
	u	u	u	r	r	SI, SIR, FSIR
Ester group in main chain 	(u)	(r)	u	(r)	r	PET, (polyester PUR), PBT, PC, UP
Ester groups as pendant group 	(r)	(r)	(u)	(r)	r	PMMA, polyacrylic ester, ACM
	(r)	(r)	(u)	(u)	r	PVAC, VC/VAC, E/VA
Halogen as pendant group 	(u)	r	(r)	(u)	(r)	chlorinated: PV, PVDC, CR, PE-C, CSM resistance somewhat better in: PVF, PVDF (fluorinated)
	(r)	r	(r)	(u)	r	PAN (SAN) (NBR)

(*continued*)

Table 16 (continued)

Weak point in macromolecule	Hydrolysis in particular against			Heat	Ozone weathering (UV + O_2)	Plastics () in parentheses do not show all resistance characteristics listed due to other sensitive groups in molecule
	Hot water	Acid	Base			
H-atom on tertiary C atom 	r	r	r	(r)	(r)	PP, PP-LD, PE-LLD, PB, SAN, PS, EMP, EPDM, PE-V
	r	r	r	(r) to r		PE, esp. HDPE, PIB, (IIR) the most chemically stable hydrocarbon plastics
(Nearly) completely fluorinated carbon chain	r	r	r	r	r	PTFC, FEP, FCM, the most chemically stable of all plastics

——— bond to another atom, usually H or C, -------- main chain, r resistant, (r) conditionally resistant, (u) reduced resistance, u very little resistant against hot water, acid or base, heat or ozone weathering

The following measures may contribute to avoidance of stress cracking:

- Appropriate form design with regard to material and article.
- Selection of the most resistant plastic type and proper plastic type (as high molecular as possible).
- Selection of optimum processing conditions (for instance for injection-molded parts the type and location of the sprue). Internal stresses in the molding can in some cases be reduced by tempering.

As a *concrete example in industrial practice*, let us consider the case of damage caused in a lamp housing made of polycarbonate (PC) [4].

Previous history: Glass housings on lamps were replaced by plastic housings in the pedestrian zone of a large city in southern Germany. The new housings fell to the pavement after a few weeks for no apparent reason.

Cause of damage: DOP[3] plasticizer, which evaporates out of the soft PVC cable insulation material under the influence of the raised temperature caused by the burning lamps, in combination with mechanical tensile stresses in the lamp housings caused by screwing the lamp housings into the brackets, results in stress cracking (the lamp housing is suspended downwards, resulting in tensile stress on the threaded neck of the housing).

Remedy: Use of a different cable insulation material (e.g., made of polysiloxane).

Figure 31 shows a simple experiment for demonstration of the principle of stress crack development. It can generally be expected that pairing unstable plastic (in this

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[3] DOP . . . dioctyl phthalate.

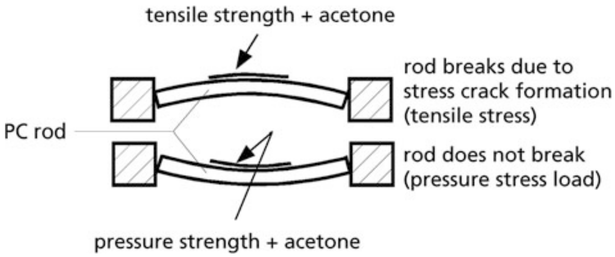


Fig. 31 Stress cracking resulting from the effects of acetone on polycarbonate [4]

case: PC) with an active solvent (acetone), will result in stress cracking in combination with tensile forces.

"Due to their corrosion-resistant qualities, plastics are widely used in the area of *environmental protection technology*. Examples include waste gas stack made of GFP, scrubbing towers made of GFP with plastic packing, coverings for water purification plants, culvert pipeline made of PE, waste dump sealing foils made of PE, reverse osmosis membranes, tree irrigation with PE pipes, heat insulation with EPS or PUR foam, solar heating, garbage bins, garbage sacks, greening of roofs or wasteland following soil treatment with UF foam.

Reverse osmosis is used in treatment of drinking and utility water. This method is used to pretreat gravitational water from dumps and other problematic waste water. Membranes made of PEI (Table 5) have proven themselves in these application due to their chemical resistance and dimensional stability.

Poly(3-hydroxybutyrate) (PHB) is a biochemically produced, biocompatible polyester that is degraded by microorganisms in PHB-moist soil into biocompatible low molecular substances. Moisture alone will not hydrolyze it. Its mechanical property profile is similar to that of PP. In drinking water purification systems it can be used as a colonization nucleus for denitrifying bacteria that use the plastic as a nutrient substrate. Instead of air oxygen, they reduce the nitrate ions in the drinking water to harmless elemental nitrogen (Institut for Siedlungswasserbau, University of Stuttgart). Application of pure PHB for medicinal implants, pharmaceutical applications.

Copolymers with 3-hydroxyvalerate (HV) with lower crystallinity and melting temperature as well as higher impact strength levels: 5 % HV for relatively rigid injection-molded parts, 10 % HV for injection molding, extrusion, injection-blow molding of packaging material, 20 % HV for veterinary/medical applications with controlled active substance release.

Manufacturer: GB ICI.

The biodegradability of a plastic is useful, except in medical applications, when it is beneficial to growing plants. It is not a feasible solution of the waste problem since it requires expensive dump volume. In the waste dump, the plastic continues to be converted into the greenhouse gas carbon dioxide by the bacteria, just as it would if incinerated, but without utilization of its energy content.

Halogen-free, flame-resistant, electronic printed circuit boards are made of EP with phosphorus compounds and heterocyclic nitrogen compounds in the macromolecular framework." (A. Franck [17]).

5.2 Aging and Stability of Plastics

Compared to metals [2], plastics are frequently considered to be "corrosion-resistant" materials [3]. However, in practical applications, there are a great many problems involving the stability and permanence of polymer materials. Aging is a much bigger problem with plastics than with metals or ceramics. The reasons for this lie in the lower bonding energy levels and lower packing densities of the macromolecules, facilitating the diffusion of low molecular substances. Also, metals and ceramics show much lower levels of sensitivity to electromagnetic radiation [2]. It has proven difficult to date to formulate a generalized theoretical description of the aging process in polymers [24]. The reasons for this lie in the complexity of the aging processes, which are also difficult to simulate in experiments. It is above all the long testing periods required that makes this testing so difficult. Rapid testing methods emulate reality in a limited way only and cannot be considered a full substitute for long-term real time testing [3].

In general, the term *aging* is defined acc. to DIN 50035 as follows: "The totality of all irreversible chemical and physical processes that occur in the course of time in a material."

Generally speaking, aging processes change the properties and the appearance of polymers over a certain period of time, in most cases leading to a degradation of the material parameters.

Typical examples of such aging processes are the embrittlement of PP and PVC when exposed out-of-doors (e.g., garden furniture, beverage crates, and pipes), aging of bicycle tires that are used regularly, the development of leaks in gaskets, reduced effectiveness of gas-filled foam insulating material, the embrittlement of surface foils in vehicle interiors, and the aging (degradation) of polyethylene joint prostheses.

The terms "cause of aging," "aging process," and "sign of aging" are explained as per DIN 50035 in detail below.

To start with, the *internal and external causes of aging* are differentiated [25].

The internal causes of aging based on the thermodynamic instability states of the material include the following:

- Incomplete polymer synthesis
- Internal stress
- Orientation stresses
- Limited miscibility of additives and polymer material

The external causes of aging, on the other hand, originate with chemical and physical effects of the environment on the material:

- Energy input via heat or radiation
- Temperature changes
- Chemical influences
- Mechanical stress loads
- Combination stress loads (energy input, chemical influences) under outdoor exposure

The causes of aging listed here result in *aging processes*, which can in turn be divided up into chemical and physical processes, which in practice frequently occur together.

The chemical aging processes always involve a change in the composition or molecular structure of the polymer. These processes include:

- Corrosion
- Postpolycondensation
- Postpolymerization
- Degradation reactions or cycling
- Auto-oxidation

Physical aging processes involve changes in the structure or molecular order state:

- Relaxation, stress degradation
- After-crystallization
- Unmixing
- Loss of plasticizer
- Migration of plasticizer
- Extraction of plasticizer
- Agglomeration

Signs of aging are therefore to be understood as visible or measurable effects of the causes of aging. They include:

- Faults, cracking (e.g., stress cracking, stress cracking corrosion)
- Swelling
- Aftershrinkage
- Exudations
- Rupturing (local embrittlement, fatigue)
- Discoloration
- Change in surface gloss
- Measurable change in material properties (e.g., mechanical)
- Change in chemical behavior

5.2.1 Aging Due to Mechanical Stress

The best-known effect of a long-term mechanical stress load is *creep*. Relaxation (reduction of stress at constant elongation) is differentiated from retardation (increase of elongation at constant stress load) [25]. These are processes that do not normally involve chemical reactions. The molecular chains slip apart in the course of time as a result of the mechanical load. Aging under exposure to mechanical load is also termed fatiguing. Polymers can fatigue in response to either static or dynamic stress loads. The dynamic stress forces necessary to damage the plastic are in most cases of lesser magnitude than the static stress forces that would be required to cause the same amount of damage.

5.2.2 Aging Due to Thermal Stress

Raising the temperature generally results in increased mobility of the molecules and molecular aggregates in polymers. Continued exposure to increasing temperature can result in both reversible and irreversible changes in the polymer, including for example the volatization of low molecular components (e.g. additives), the splitting off of specific atoms and molecular segments, chain ruptures, postpolymerization reactions, or accelerated chemical degradation due to oxidation. These chemical changes involve bond breakage and are thus irreversible.

Besides constant high temperatures, temperature changes have a pronounced aging effect. In addition to the mechanisms described above, this factor introduces alternating mechanical stresses into the plastic structural component, possibly resulting in fatigue of composites in particular (e.g. by way of delamination at the interfaces) [3].

5.2.3 Aging Caused by High-Energy Radiation (Photodegradation)

The following forms of high-energy radiation cause damage to plastics:

α *radiation*: Rays consisting of helium nuclei
β *radiation*: Electron radiation
γ *radiation*: Short electromagnetic waves

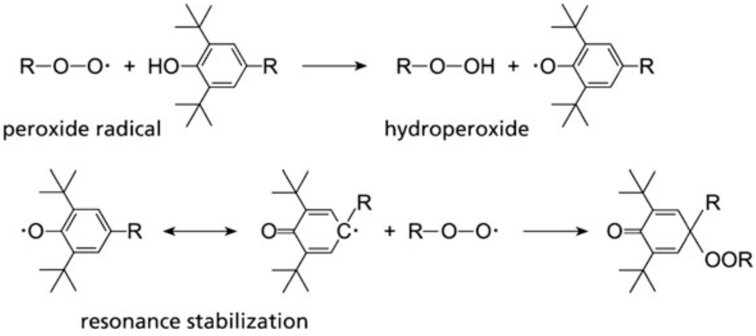
In principle, high-energy radiation causes aging when the polymer material can absorb the energy and the absorbed energy is sufficient to split chemical bonds (radiation-induced degradation) [17].

In terms of natural outdoor exposure, UV light (λ = 280–400 nm) is of particular importance due to its capacity to change polymers. The basic process involved in photodegradation depends on energy density, light wavelength, and duration of radiation exposure [26, 27]. In principle, light can be reflected, scattered, allowed to pass through or absorbed by plastic surfaces. It is above all the absorbed component that causes photochemical changes such as chain splitting, postcross-linking, and changes in existing functional groups or formation of new ones in the molecule. These processes usually involve reactive intermediate steps (e.g. radicals). That is why the photochemical reaction is described as comprising primary processes (UV radiation causes formation of intermediate products) and secondary processes (intermediate products react to produce stable end products) [28].

A valency line was only drawn in each case for the bond the dissociation energy of which can be read off the nomogram at the relevant point. The dissociation energies were in most cases measured in gaseous compounds, whereby however the abbreviations of plastics containing similar bonds were added in brackets.

5.2.4 Effect of Oxygen (Oxidation)

In so-called thermooxidative degradation, primary radicals are produced in the presence of oxygen due to the effects of heat, possibly coupled with mechanical stressing of the plastic. Certain substances like sterically inhibited phenols or amines can trap (*scavenge*) these radicals. For example, di-tert-butylphenols act as radical scavengers (antioxidants). The reaction scheme described below makes it clear that the oxidation inhibitor is consumed in the process. Thermooxidation can therefore be delayed until the radical scavenger is completely used up.



For the radical scavenger function of di-tert-butylphenol see the depiction above.

The combined effects of heat and oxygen characterize thermooxidative degradation, which changes the chemical composition of the polymer. In most cases, a reaction acceleration follows a rise in temperature [25]. Metallic impurities or additives (e.g. copper) may catalytically accelerate the thermooxidative degradation. The oxidation phenomena observed after thermooxidative degradation include for example changes in viscosity, elongation capacity, impact and tensile strength, and surfacing cracking.

Other atmospheric factors such as gaseous impurities in the air (e.g. sulfur dioxide, ammonia, carbon monoxide, ozone, carbon dioxide, halogen compounds, or formaldehyde) and solid impurities in the atmosphere (airborne dust, sand, and soot) result in an acceleration of aging processes in polymers. Whereas the effects of the gaseous impurities on polymers are mainly chemical in nature, the solid particles mostly cause abrasive damage to the plastic surface.

5.3 Protective Measures Against Aging Processes

Suitable antioxidants (stabilizers) are used to protect plastics against the effects of air oxygen, heat, and sunlight. The stabilizers exert an inhibitive effect on the aging process [25]. This results in a significant improvement in the utility of the material or structural components and longer useful product life.

Stabilizers are among the group of additives mixed into polymers during production or in structural component production to control and adjust their processing or utility properties. Basically, stabilizers can be categorized in groups as follows:

5.3.1 Radical Scavengers (Primary Antioxidants)

They provide protection during manufacture, molding, and use against the oxidative effect of oxygen and other oxidants. These are for the most part molecules that stop the chain reaction of the auto-oxidation process and are capable of forming highly stable, mesomerically stabilized, radicals. Without further additions, these stabilizers are consumed irreversibly in the course of the reaction.

5.3.2 Costabilizers (Secondary Antioxidants)

These additives significantly improve the efficacy of primary stabilizers on the basis of synergetic effects. Costabilizers reduce the hydroperoxides to take them out of the auto-oxidation process. These stabilizers (e.g. organic phosphites) are also irreversibly consumed depending on stress load levels.

5.3.3 Photoprotectants

These stabilizers are used to increase the light resistance of plastics so they can be exposed to outdoor weather conditions during use. Two types of photoprotectants are used: UV absorbers and quenchers.

UV absorbers transform high-energy UV radiation into comparatively harmless heat. Examples of UV absorbers include hydroxybenzophenones, hydroxybenzotriazoles, and cinnamic acid ester.

Quenchers are capable of taking up the photon energy already absorbed by a macromolecule by means of energy transfer and changing it into heat. The energy of the photons is thus prevented from splitting bonds in the polymer. Organometallic nickel compounds are often used as quenchers [28]. Both UV absorbers and quenchers are not destroyed by the light, i.e., their function is maintained throughout the entire period of utilization.

6 Additives for Plastics

Only very few polymers (thermoplastics, duroplastics, elastomers, converted natural products) can be processed and used as synthesized. The effects of heat and oxygen would damage them before they could even be processed. Then there are the environmental conditions applied during storage and use of the semifinished goods and finished products, including among the ambient liquid and gaseous mediums above all air oxygen – often in combination with sunlight UV radiation – and raised temperatures.

Besides the necessary protection against these damaging effects, use of these materials demands a considerable number of additive substances that influence the properties, processability, or appearance of the polymer materials [29, 30]. The result is a large number of irreplaceable additives that make processable resins, molding compounds and top-grade molding materials, i.e., technical materials, out of the primary products.

To obtain an overview of the great variety of additives, they can be arranged in three types according to their purpose and function [31, 32].

- Functional additives (processing agents, property enhancers, modifiers)
- Fillers and pigments (performance additives)
- Reinforcing materials (property enhancers)

A general statement that should be kept in mind before the individual additives are described is as follows: Common to all additives is the fact that their effects depend on their solubility in the specific polymer [29, 30, 33]. The relative parameters are their chemical structure, the temperature, and the crystallinity of the matrix. Additives can only be dissolved, for instance, in the amorphous phase of semicrystalline thermoplastics, in which the additive concentration is increased during cooling from the molten state [33]. This is advantageous in terms of stabilization, since oxygen and solvent atoms are only capable of permeation through the increased lattice vacancies of the amorphous phase with its many defects.

Once the solubility limit of an additive is exceeded in the plastic at a given temperature, blooming occurs. This results in surface blooms that cause problems with coating, painting, and printing. In injection molding, overdosing of mold release agents typically causes surface defects and adhesion problems [33].

Bottle caps are a good example of a process requiring precise dosing of lubricants. Underdosing results in increased torque and poor sealing during mold closing. Overdosing results in the printing problems mentioned above [33].

6.1 Functional Additives

An annual overview of the current status of additives is provided by W. Hohenberger [34] in the journal *Plastics*. Here are some consumption figures from 2001 (Table 17):

The functional additives below are listed alphabetically [35], which of course does not reflect any ordering of their applications or economic significance.

Here is a selective list:

- Antioxidants
- Antistatic agents [92, 93]
- Accelerators, promoters

Table 17 Worldwide consumption of some additives in millions of tons. According to [34])

Fillers	10	~60 % of which amount goes for PVC
Plasticizers	4	
Pigments	2	
Flameproofing agents	0.9	
Stabilizers	0.4	

Europe consumes about one quarter of these volumes

- Fire protection agents
- Emulsifiers
- Colorants
- Solid lubricants
- Flow aids
- Lubricants, slipping agents, antislipping agents, antiblocking agents, and mold release agents
- Curing agents
- Adhesion promoters
- Inhibitors
- Nucleation agent
- Kickers
- LP additives
- Metals and metal oxides
- Microbicidal additives
- Phlegmatizers
- Photoinitiators
- Impact strength improvers
- Blowing agents
- UV stabilizers
- Heat stabilizers
- Plasticizers

A smaller selection is described below.

6.1.1 Antioxidants

The antioxidants (AOs) [30–32] extend or maintain the useful life of a plastic part by slowing or even preventing oxidative degradation. Heat, UV radiation, shearing forces during processing, metallic impurities, or traces of hydroperoxides from the synthetic process may initiate polymer degradation by means of production of free radicals and/or peroxidic oxidation. The subsequent complex chemical reactions change the molar masses of the polymers by means of splitting or cross-linking. The sensitivity of individual plastic types to oxidation varies greatly. PTFE and PMMA are very stable, whereas the polyolefins and all unsaturated polymers would have very short useful lives indeed without protection from AOs.

Differences in the efficacy of AOs derive from the specific polymer involved, processing and utilization temperature, the use to which the part is put and the chemical and physical properties of the AO itself. A high molar mass reduces the volatility and extractability of the substance. An AO must never stain the polymers or react with other additives. The specifications of food laws must be complied with if there is contact with foods and other foodstuff products.

AOs are categorized into two groups: Primary AOs (which form terminal groups), react with chain-forming radicals to inhibit oxidation (e.g., substituted phenols and aromatic amines) and secondary AOs (peroxide decomposers), which convert peroxides and hydroperoxides into nonradical, stable compounds. These preventive AOs include phosphites, phosphonates, and thio compounds. The metal-catalyzed thermal oxidation of polyolefins, in particular of polypropylene, is not sufficiently inhibited by addition of sterically inhibited phenols and aromatic diamines. Sheathing of copper tubing and contact with copper alloys requires the addition of metal deactivators (MD) such as hydrazides or hydrazones. The MD forms a complex with the catalytically active metal compound, a complex that has only a minimal catalytic effect. The additive amounts are 0.05–0.5 %. Filling and reinforcing additives such as slate flour, chalk or talcum, may make it necessary to add MDs because of the metal moieties they contain, for example iron or manganese [36].

A great many polymers can be better stabilized by combined use of two or more AOs than with one alone. The most effective AO mixtures are those in which one component acts as a radical scavenger and the other as a peroxide decomposer. When the two components regenerate each other, this is termed synergism. Although AOs are required in the formulae of nearly all polymers, only about 85 % of consumption is attributed to ABS, PP, LDPE, HDPE, and PS.

The ABS and SB polymers require AOs due to the unsaturated double bonds during the rubber phase. Heat and UV radiation accelerate the oxidation. Because of the high processing temperatures, combination systems (hindered phenols and phosphites) are usually preferred. The additive amount is 0.25–2.5 %. The tertiary C atoms of the polypropylene and propylene copolymer, as well as the relatively high processing temperatures, require the use of higher molecular phenols and phosphites as well as synergetic thioesters. The additive amounts total 0.25–1.5 %. Dust-free products are the state of the art [37].

LDPE requires a smaller amount of AO than HDPE, mainly because the foils made from most of the LDPE produced have short product lives. Low molecular phenols or phosphite combinations in concentrations of 50–500 ppm are preferred. HDPE requires higher concentrations of higher molecular polyphenols. Thioesters often serve as the synergist. Phosphites prevent the discolorations that may be caused by catalytic residues. In the types used in wires and cable sheathing, metal deactivators provide protection from the effects of copper.

PS exhibits a natural thermostability. Antioxidants are only added to it if low damage levels due to use of recycling material is an important issue. Phosphites and polyphenols of medium molar mass in additive amounts of 0.1–0.4 % are usually selected. PS is sensitive to photooxidation. Yellowing and embrittlement can only be prevented by UV stabilization.

Both thermal and oxidative degradation are possible in polyacetalene (POM). The thermal degradation is prevented by stabilizing the end groups with amines and amides or copolymerization with methylene groups in the main chain. Substituted phenols are proven AOs. PA, PC, UP, and PUR do not show a tendency for rapid oxidative degradation. They show little yellowing and property changes. Suitable thermostabilizers include mainly the phosphite esters; often in combination with substituted phenols. The thermal degradation of PVC is delayed by heat stabilizers (stearates, laurates, ricinoleates of calcium, barium and strontium) and organic tin compounds. The synergetic effects of metal compounds are also used, for example Ba/Zn.

Recent developments in the field of AOs include improvements in effectiveness at higher temperatures, lower levels of volatility and extractability as well as improved handling and processing. The newer AOs are higher molecular and contain additional multifunctional groups that enhance the synergetic effect (antioxidants: see also under stabilizers).

6.1.2 Accelerators, Promoters

For example, if peroxide fragmentation cannot be realized with heat in UP resin curing, accelerators, and possibly promoters as supporting agents, must be used. The accelerators reduce the energy level required for peroxide fragmentation. This makes more rapid peroxide fragmentation possible, either at a lower temperature, for example room temperature, or at a higher temperature. Mainly cobalt, vanadium, and amine accelerators are used with UP resins. The vanadium accelerators show limited storage stability and are sensitive to oxidation, reducing their range of application [38].

The effect of peroxide accelerators [32] can be supported by so-called promoters (activators), which do not act as accelerators when used alone.

For example, dimethylaniline has no accelerating effect on methylethylketone peroxide, but it can have a significant influence on the system MEK peroxide/cobalt accelerator, whose effect is frequently made use of for processing purposes.

In the vulcanization of elastomers, metal oxides in combination with fatty acids activate the sulfur accelerator systems.

Zinc oxide, as well as lead and magnesium oxides, are used. Lead oxides activate water-resistant vulcanizates, whereas magnesium oxides neutralize acidic reaction products such as rubbers that contain halogens.

The effects of zinc oxide, fatty acids, and peroxides is described in more detail by Röthemeyer and Sommer [32].

6.1.3 Fire Protection Agents

Plastics are protected from fire by application of flame retardants [95–98]. These additives serve to reduce decomposition, burning rate, flame spread, and smoke production; they are also self-extinguishing and act to prevent dripping.

Flameproofing Agents

Chlorinated or brominated hydrocarbon compounds are used as organic flame retardants. Flame retardants containing phosphorus with either organic or purely inorganic structures are now produced – with few exceptions – free of halogens. Inorganic flame retardants include hydroxides and boron compounds with different metals, in particular aluminum, magnesium, and zinc. Antimony oxide is used above all as a synergist in flameproofing products containing halogens by extending the temperature range in which halogenated flameproofing agents are effective.

Halogen-containing compounds are chemical flame inhibitors that act by releasing halogen radicals in the gaseous phase that form hydrogen halide. The halogen halide neutralizes high-energy radicals produced by combustion, thus interrupting the radical chain mechanisms. Disadvantages of halogenated flameproofing agents include pronounced production of smoke gas, corrosive smoke gasses in particular. Certain halogenated flameproofing agents such as polybrominated diphenyls may form dioxins or furans. Efforts are therefore made to find substitutes for halogenated flameproofing agents. Some countries began prohibiting certain halogen-containing flame retardants. The EU bans the use of polybrominated diphenyl ethers (PBDE) and diphenyls (PBB) except for DecaDBE for electronic devices. Since 2006 several US states have started to outlaw some of these products.

Flame retardants that contain phosphorous release “polyphosphoric acid” and are effective in the condensed phase. These agents form a protective layer. The polyphosphoric acid also splits water out of organic plastics, resulting in formation of an additional protective carbon layer.

Boron compounds form vitreous crusts that prevent air oxygen from passing through. The crystal water also has a cooling effect.

Nitrogen compounds have been developed for special applications, and halogen-free flameproofing in particular. Melamine products have proven particularly useful. They form inert decomposition (NH_3, H_2O, CO_2, N_2) and condensation products under thermal effects.

Aluminum hydroxide ($Al[OH]_3$) and magnesium hydroxide ($Mg[OH]_2$) decompose above 200 °C, whereby they consume energy and release water. This cools the polymer, while the vapor displaces oxygen like a protective gas and dilutes the conflagration gasses.

Intumescent flameproofing systems form a voluminous, insulating protective layer by means of carbonization and foaming. These systems comprise a “coal” donator, an acid donator, and a blowing agent. When the polymer softens, an inorganic acid is released, for example from ammonium polyphosphate, which causes the carbonization of, for example, polyalcohol. At the same time, gas production by a blowing agent (e.g. melamine) foams the mixture, after which a protective layer can be formed by means of cross-linking reactions.

Reactive flame retardants can be integrated in plastics by way of reactions. For instance, tetrabromobisphenol A (TBBA) and reactive phosphoric flameproofing agents with P-OH or PH groups can be integrated into epoxy resins. HET acid and tetrabromophthalic acid anhydride in combination with antimony trioxide are used as reactive halogenated flameproofing agents in unsaturated polyester resins. Phosphoric polyols can be integrated into the polymer matrix of PU. The advantage is that the flame retardant is integrated in the resin by a reaction instead of as a filler. The disadvantage is the higher price.

Of the flame retardants named above, bromated compounds (consumption ~23 %[4]) are the most effective, generally useful and reasonably priced. However, physiological considerations and the desire to avoid corrosive smoke gasses have encouraged a greater demand for alternatives, above all phosphoric compounds (consumption ~11 %[4]). Use of aluminum hydroxide (consumption ~40 %[4]) in combination with magnesium hydroxide is limited to plastics in which a high filling level and changes in the mechanical properties are of little significance. Melamine derivatives, which still play only a minor role at present, are likely to become more important in the future.

To sum up, each particular polymer and application requires specific flameproofing, whereby the advantages and disadvantages of the different flame retardants must be balanced out.

Serious recent accidental fires in tunnels, airports, ships, underground railway stations, some of them caused by, and nearly all of them accompanied by, burning plastics, have raised the level of awareness and increased the demand for flame-resistant plastics with low smoke gas and toxicity levels.

In 2007, over a million metric tons of flame retardants were sold on the world market, ~40 % of which was for aluminum trihydrate (ATH).

Bromated flame retardants account for about 23 % of the volume, but for about 39 % of the expenditure in 2000.

At any rate, the current general trend is towards halogen-free or at least halogen-reduced products.

Melamine cyanurate in combination with magnesium hydroxide ($Mg(OH)_2$ or MH) or even with talcum (Japanese patents), melamine polyphosphate (DSM, type Melapur 200), also suitable for PA 6.6 GF, are two examples of more recent developments. Zinc sulfide can replace antimony trioxide in some cases.

Red phosphorus dosed at 50 %, provides very effective flameproofing for polyamides.

Expanded graphite [39, 40] is the best-suited of all halogen-free flame retardants in terms of combustion rate (self-extinguishing, 0 s). This means the required mass percentages of expanded graphite are lower, resulting in improved mechanical properties [40].

Smoke Density Reducers

A number of fire catastrophes involving plastics have demonstrated that not only the combustibility of the products made from a plastic determines how the material

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[4] Applies to 2007, source: SRI International Consulting: Flame Retardants Market Study.

behaves in a fire. Smoke gas development is just as important, i.e., its density, toxicity, and corrosive effects. The call for reduced combustibility and smoke development are mutually exclusive, making it difficult to develop substances that perform both tasks. Soot is the main contributor to higher smoke gas densities, which is why the density of the smoke is much greater when aromatic structures are involved, for example with PS, than when PA, PE, PP, or POM burn.

The toxicity of the smoke gasses results mainly from incomplete combustion of the carbon to carbon monoxide.

Smoke suppressants effectively reduce the amount of aromatic species released as smoke by promoting char development during a fire.

The duroplastics, which are cross-linked, always produce less combustion smoke than most other thermoplastics. They tend to carbonize more and therefore produce smaller volumes of combustion gasses. Highly heat-resistant polymers are made up mainly of aromatic or heterocyclic rings. Their structure is retained for the most part when it burns and carbonizes into graphite-like networks [41]. A lot of work has been done with many different polymers to develop products that produce less smoke gas, and these efforts have been most successful with the widely used standard plastic PVC. Whereas HCl formation is significantly reduced by addition of chalk and other carbonates, the best-known smoke gas reducing agents are molybdenum trioxide and ferrodicyclopentadienyl (ferrocene). Ferrocene is not suitable for chemical treatment of PVC-P. Another drawback to this substance is its high vapor pressure and yellow color. Ferroacetonyl acetonate and heavy metal salts (Fe, Mn, Cr) of the 8-hydroxyquinolines are suitable for use with PS and its modifications. In unsaturated polyester resins, the synergetic effect of MoO_3 and halogenated compounds such as dibromoneopentyl glycol result in reduced combustibility and smoke development. UP–GF contains the additive $MoO_3 + Sb_2O_3 + Al(OH)_3$. The green color of the molybdenum trioxide can be avoided by substituting ammonium octamolybdate [42].

In polyolefins and epoxy resins melamine octamolybdate reduces the smoke development during the process of carbonization of aromatic compounds. Other known smoke inhibitors are zinc borate, zinc stannate, and zinc hydroxystannate.

Features of the new, inherent, flame-resistant active polymers such as PSU (polysulfone), PES (polyether sulfone), and PAEK (polyarylether ketone) include high levels of temperature resistance and very low smoke gas densities.

6.1.4 Colorants

Titanium dioxide and carbon blacks account for most of the ~750,000 t of colorants consumed in Europe.

Current trends in technical developments [34]:

- Improved, environment-friendly production methods
- Easier handling and dispersion
- Low-cost substitutes for heavy metals, in particular pigments containing cadmium

- Reduction of migration and delay
- Special-effect colorants

Colorants [43] are classified as either pigments or dyes [44]. Dyes are soluble in plastics, whereas pigments are practically insoluble. The term pigment designates a particle size of about 0.01–1 μm. Particle structures are differentiated according to primary particles, aggregates, and agglomerates. The primary particles as manufactured have a pronounced tendency to form aggregates, i.e., superstructures that are in most cases divided up when the colorants are incorporated in the plastic material, so that the main parameters determining the coloring properties of specific pigments are grain size and grain size distribution. The dividing up, distribution, and wetting of pigments is termed dispersion, whereas dyes are dissolved in the plastic. Colorants [31] may be inorganic or organic. Inorganic pigments are insoluble, but low molecular organic pigments in particular may be soluble.

Of course the chemical structure of the binder and the processing temperature influence the solubility of these materials. Pigments with the same chemical composition can be manufactured in various different crystalline modifications with quite different coloristics and application characteristics, for example in titanium dioxide and phthalocyanine blue. Manufacturers can improve the application and utilization properties of given pigments by means of aftertreatment (coating), resulting in enhanced dispersibility as well as improved resistance to UV, weather, and chemicals. To reduce the high levels of expenditure in terms of engineering and energy, so-called pigment preparations are used, in which a solid pigment concentrate is used in the form of a readily dispersible paste, either in combination with the plastic to be processed or as a pourable ground mixture, i.e., a combination of readily dispersible organic pigments and/or fillers and sparingly dispersible organic pigments [45].

Color impressions as perceived by the human eye are the result of selective absorption and reflection. They can be elicited by additive and subtractive color mixing. An example of additive color mixing is color television technology, whereby tiny blue-green-red dots are stimulated to give off light. White daylight is also an additive color mixture as perceived by the human eye. However, color impressions result most frequently from subtractive color mixing, that is when certain segments of the spectrum are absorbed and the rest of the visible spectrum is reflected and perceived by the eye. This perception is inconceivable without light [46]. A further precondition for the perception of color, besides the absorption of certain wavelengths, is the scattering of the reflected light. Particles with a generally higher refractive index than the surrounding plastic material diffuse light in all directions. In principle, white pigments scatter nearly all of the light, inorganic color pigments absorb little and scatter a lot, organic color pigments absorb a lot and scatter only a little, solute dyes absorb most light and black absorbs just about all of the incident light. The covering capacity (opacity) of a pigment is determined by the particle size and by the difference between the refractive indices of the pigment and binder. Relative color intensity is based on the capacity to lend color to light-scattering materials thanks to a light-absorbent quality. Color perception differentiates between tone, brightness (in colors and white), and saturation (pure, cloudy or dirty in colors and black) [47].

The following factors, in combination with the plastic to be colored, are decisive in determining the suitability of a colorant for a particular application: nature, thermal load capacity (level and duration), light fastness, weather resistance, migration tendency (solvent and contact bleeding, blooming), plateout (deposits on metal surfaces in contact with melt) and influence on flow behavior [45].

Figures 32 and 33 show how many different areas of application there are for inorganic [30] and organic pigments.

Pigments always have advantages over dyes when, besides coverage, a specific application specifies insolubility of the colorant in the application medium (for example good overpainting qualities *and* good coverage) [44] [99–103].

In recent years, direct coloring of plastics from colorant master batches, economically gauged for specific batch sizes, has become more and more important.

When working with smaller batch volumes, the colorant master batches can be made more economically from predispersed monocomponents. The state of the art to date:

Pigments	Paints and lacquers	Printing inks	Plastics	Rubber	Building materials	Paper	Enamels and ceramics	Fibers	Pharmaceuticals and cosmetics
Titanium oxides	●	◓	◓	◓	◓	◓	◓	◓	◓
Iron oxides	●	–	◓	◓	●	–	◓	–	○
Pigment carbon blacks	◓	●	●	◓	◓	◓	–	◓	○
Chrome yellow pigments	●	○	◓	○	–	–	–	–	–
Molybdate red pigments	●	●	–	–	–	–	–	–	–
Zinc pigments	●	–	◓	◓	–	◓	–	–	○
Cadmium pigments	○	–	●	◓	–	–	–	–	–
Chromium oxide pigments	●	–	–	◓	–	–	●	–	–
Ultramarine blue	◓	–	●	◓	–	–	–	–	–
Cyanotype blue	◓	●	–	–	–	○	–	–	–
Special-effect pigments	●	◓	◓	–	–	–	○	–	◓

Fig. 32 Areas of application of inorganic pigments [44]. (*filled circle*) Significant application volume. (*half filled circle*) Moderately significant. (*open circle*) Low application volume. (*dashed line*) Not used

Fig. 33 Areas of application of organic pigments [44]. (*filled circle*) Significant application volume. (*half filled circle*) Moderately significant. (*open circle*) Low application volume. (*dashed line*) Not used

Pigments	Printing inks	Paints	Plastics
Azo pigments	●	●	○
Paint azo pigments	●	–	○
®Naphtol AS	◓	◓	–
Phthalocyanine	●	◓	●
Quinacridone	–	●	◓
Perylene	–	◓	●
Anthraquinone	–	●	◓

The pigments required for a specific color tone are intensively mixed with powdered plastic using dispersants (waxes), then dispersed in a twin-screw extruder (high energy consumption) and thereby embedded in the plastic. Laboratory mixtures and production often show different results.

The monocomponents are prepared in the initial step, followed by the master batches.

Currently, organic pigments can be mixed into plastics in concentrations of 40–50 %, and inorganic pigments up to 75 %, with good dispersing quality by means of single-screw extrusion [48].

Table 18 [48] provides an overview of monocomponent manufacturers from which processors can prepare master batches so as to avoid production differences and defective batches.

Inorganic Pigments

Inorganic pigments [30] are categorized as oxides, sulfides, chromates, and carbon. The oxides are, with the exception of thermal stability in some pigments, basically the stablest pigments, for example TiO_2, black rouge, and cobalt blue. Zinc and cadmium sulfide are not weather-resistant, ultramarine decomposes when exposed to acids. Chromate pigments are not alkali-stable, with heat resistance hardly exceeding 180 °C. Carbon pigments are stable up to 300 °C.

Organic Colored Pigments

Organic colored pigments differ from inorganic pigments in their high levels of light absorption and low levels of scattering power, for which reason they are often

Table 18 Manufacturers of monocomponents

Manufacturer		PE	PP	PS	Technical thermoplastics
Basell Polyolefine GmbH	Wesseling; D	X	X		
BASF AG	Ludwighafen; D			ASA/SAN	X
Dow Deutschland	Schwalmbach/Ts.; D	X	X	X	X
Borealis AG	Vienna, A	X	X		
Eastman Chemical B.V.	Capelle aan den IJssel; NL				X
Sabic Europe	Geleen; UK	X	X	X	X
Lanxess AG	Leverkusen; D				X
Arkema	Colombes Cedex, FR				X
DSM Engineering Plastics	KR Sittard; NL				X
DuPont Germany	Bad Homburg; D	X	X		X
ExxonMobile Chemical Deutschland	Köln; D	X	X		
Total Petrochemicals	Brussels, B	X	X	X	
Ticona Engineering Polymers Deutschland	Kelsterbach; D	UHMW-PE			X

used in combinations with light-scattering white or colored pigments. With glazing (transparent) pigments, the substrate (white paper, metallic foil) scatters the light. Color tone purity, brilliance, and tone quality are in most cases superior to those of inorganic pigments. Light-fastness and weather resistance decrease with the degree of whitening, for example with TiO_2. Chemical constitution, particle size, and grain size distribution determine the application properties. Color intensity, transparency, brilliance, and viscosity of the binding agent increase as the particle size grows smaller, whereas coverage, light-fastness and weather, migration and solvent resistance are all reduced. It is a well-known fact that no organic white pigments are available. The organic black pigments are rarely used since their light-fastness is inferior to that of carbon blacks.

Recently, pigment manufacturers such as Holliday Pigments, UK, have marketed colorants with extremely high levels of color intensity [e.g. ultramarine pigment type Premier XS or red (XSR) or greenish (XSG)]. These products can be used to reduce pigment concentration while maintaining the same coverage in existing formulas.

For odor-sensitive applications or use in moisture-sensitive polymers such as PET or PC, highly concentrated master batches of special pigments with extremely low moisture content levels are the most suitable choice (type DXS von Holliday Pigments).

The Cromophtal product assortment from Ciba Spezialitätenchemie (Switzerland) is particularly low-warping in polyolefins and vinyl polymers.

Monoconcentrates, the use of which is becoming more and more widespread, facilitate handling and dosing while maintaining property levels. Ciba Spezialitätenchemie is contributing to the SpecialChem platform at (www.specialchem.com), whereby technical knowledge and customer support are provided via the internet [34].

6.1.5 Lubricant, Slip, Antislip, Antiblock, and Mold Release Agents

Lubricants are added to thermoplastic and duroplastic molding compounds to increase internal and external lubrication during thermoforming. These agents not only reduce the internal and external coefficient of friction, they may also have positive effects on mold removal, blocking, and surface gloss. They are differentiated in terms of internal and external lubrication. Chemical composition, polarity, melting behavior, and additive volumes are the determinants for the effectiveness of any lubricant [31]. The internal lubricants usually have a low molecular mass, the external lubricants a higher molecular mass. Most internal lubricants are polar, most external lubricants nonpolar. The polar groups usually contain oxygen, oxygen + metal, oxygen + nitrogen or halogens. Lubricants can thus be categorized as HC, alcohols, carbonic acid esters, ketones, metallic salts of carbonic acids, amides, and halogen hydrocarbons [49]. Silicones reduce melt viscosities and therefore function as internal lubricants; between melt and metal they function as external lubricants; they suppress squeaking when plastic rubs against plastic.

Most lubricants are made from natural raw materials: paraffins from petroleum residues, lignite carbonization, or bituminous shales; the natural fatty acids (C_{16} to C_{18} acids and mixtures of same), vegetable and animal fats. Further hydration of the fatty acids results in fatty alcohols. The most effective lubricants in technical terms, as well as the most expensive lubricants, are refined montanic waxes (C_{28}–C_{32}). Semisynthetic lubricants are based on the conversion of alcohols to esters, metal oxides or hydroxides to salts or amines to amides. Fully synthetic waxes include low molecular PE and PP waxes or copolymers made from ethylene, VAC, acrylic, or crotonic acid.

PVC remains the largest consumer of lubricants. More recent developments are moving in the direction of lubricant compounds and mixtures. For filler coating, special products are required that allow higher filler concentrations. Foil manufacturers would like to avoid plateout and injection molders would like to prevent fittings exfoliation [50].

For processing aids for Wood Plastic Composites (WPC), see [51, 52].

Slip, *antislip*, *and antiblock agents* [30, 31] do not facilitate molding or semifinished product manufacture as do lubricants. What they do is to simplify further processing – of foils in particular. Foil bags that have been stored in stacks cannot be readily picked up or opened, problems that are particularly noted with LDPE and PP. An effective *slip agent* with LDPE is addition of 0.05 % oleic acid amide and with PP the same amount of eruca acid amide. Additive manufacturers supply concentrates of these compounds in granulate form for addition to molding compounds [50].

Antislip agents prevent, for instance, filled foil bags from slipping in stacks or on pallets. The agents can be worked into the material or sprayed on to give the products a low level of adhesion that still permits easy separation. Materials used as antislip agents include aqueous PVAC dispersions or benzine solutions of amorphous PP still containing small amounts of wax to give them favorable adhesion properties.

Antiblock agents prevent foils from melting together under the influence of pressure and heat and resemble, to this extent, slip agents. They are also used in combinations in some cases. Blocking occurs mainly on rolls or in stacks. Suitable antiblock agents, which are worked into the molding compound, include chalk, siliceous earths, and synthetic silicic acid. The concentration level is about 0.1 %. The ~20 μm particles act as spacers. Amide wax is also suitable for finishing soft PVC foils. It is also a good antiblock and slip agent in additive amounts of 1 %.

Liquid and powder *release agents* such as waxes, polyethylene glycols, polyvinyl alcohol and silicones, metal stearates and polytetrafluoroethylene are sprayed or dusted onto the mold cavity walls of pressure and injection molds. Mica is often sprayed onto them for foam moldings. Whereas mold release agents are required for processing of many duroplastics and thermoplastics, they cause weak joint lines in polyolefins, rendering welding, gluing, and printing difficult.

So-called internal mold release agents, for example calcium and zinc stearates, have established a predominant position in polyurethane RIM/RRIM production over the last 15 years. They are added to the molding compound or polyol in PUR in amounts of ~0.5–1 % by mass and prevent the molding from sticking when it is released from the mold.

Potential migration of the mold release agents during raw material storage or in the hot mold during cross-linking/crystallization necessitates intensive washing procedures for subsequent painting processes. Mass application of mold release agents also reduces mechanical properties such as the modulus of elasticity. The stearates may act as crack initiation centers under long-term stresses, for example in the ultrahigh molecular polyethylene (UHMW-PE) used for joint prostheses.

6.1.6 Curing Agents

Curing agents – also known as initiators – are substances that catalytically initiate the cross-linking process in resins (or linear polymers). Curing usually takes place under heat application. So-called cold curing, however, is even possible at room temperature. In phenolic, amino and furan resins, acidic curing agents initiate cross-linking during molding during heat application. The polymerization of unsaturated polyester and methacrylate resins, on the other hand, is initiated by peroxides, the effect of which can be enhanced by accelerators. The peroxide curing agents preferred for UP resins are hydro, alkyl, acryl, acetylbenzoyl, ketal, and ketone peroxides as well as the peresters [38].

Peroxide combinations can also be used to control certain curing properties, in particular the reaction rate. Peroxides [31] are available in liquid, paste, or solid form. The relatively low level of stability of peroxides makes it necessary to add so-called phlegmatizers, i.e., substances that neutralize. Curing agents also include

Table 19 Cross-linking reactions and cross-linking systems for rubber [32]

Cross-linking reaction	Cross-linking system	Rubber
Reaction of sulfur with rubber	Sulfur accelerator systems Sulfur donator systems	NR, BR, SBR, NBR, CR, IIR, CIIR, BIIR, EPDM, ETER, PNR, TOR
Reaction of radicals with rubber	Peroxide High-energy radiation	EPM, EPDM, EAM, HNBR, CM, CSM, Q, MVQ, AV, PE and all diene rubbers. Not suitable for IIR, CIIR, CO, ECO
Reaction of bifunctional compounds with reactive rubber groups	Polyvalent metal oxides	CR, BIIR, CIIR, CM, CSM
	Diisocyanates	AU, EV
	Phenolic resins	IIR, BIIR, CIIR
	Dioximes	IIR
	Bisphenols	FPM
	Diamines	CO, ECO, AEM, BIIR, CIIR, ACM, FPM
Reaction of bifunctional compounds with diene rubber	Diisocyanates	Diene rubbers
	Phenolic resins	Diene rubbers
Silane cross-linking	Multifunctional silanes	Silicone rubbers, PE

substances that bring about curing by polyaddition in thermosetting resins such as PUR and EP. Their reactions are not strictly speaking catalytic, rather they react as bifunctional or polyfunctional compounds, i.e., as cross-linking elements [53]. Among these substances are the polyisocyanates (PUR) as the polycarbonic acids, and polycarbonic anhydrides, polyamines, polyamides, and polyaminoamides (EP).

In elastomers, the cross-linking reactions are known by the term vulcanization, designating the production of elastomers from rubber by means of wide-meshed chemical cross-linking.

The covalent bridge formation between the rubber chains can be realized by means of a number of different chemical reactions. Table 19 [32] summarizes the most important cross-linking reactions and systems for rubber.

Different cross-linking systems influence selected properties of elastomers and duroplastics. So far the reaction kinetics influence the induction time, the activation energy, and the cross-linking rate. Cross-linking effects influence the density and the chemical structure. And the cross-linking system has an influence on the following properties: tension- and residential deformation, dynamic properties, thermal stability, and chemical resistance.

6.1.7 Adhesion Promoters

Adhesion promoters include the substances that create close physical and/or chemical bonds between two substrates [108]. The substrates to be connected are fibrous reinforcing or particulate fillers on the one hand and plastics or metals on the other. The adhesion promoters always form bridges between the interfaces of the two components. For example, adhesion promoter resins based on styrene/butadiene alloys serve as adhesive layers for laminating panels and coextrusion of foils made of styrene polymers with polyolefins, PC, PMMA, and PA [30].

When high cohesion strength levels are required of coated or laminated substrates made of polyester, polyamide, or aramide fibers bonded to soft PVC, adhesion promoters have to be used.

Which adhesion promoter system should be used depends above all on the specified performance of the articles to be manufactured, the working conditions influencing preparation of the priming coat paste, the type of coating system used, and the time spent in the gelling channel.

Typical applications for adhesion promoters today include truck tarpaulins and other coverings, air-inflated halls and other textile structures, flexible containers, tent roofs, marquees, protective clothing, conveyor belts, flocked carpeting, and foamed artificial leather.

Bayer [19] contains an overview of the different adhesion promoters. Single-component or two-component adhesion promoter systems, with and without solvents, are used. Tables 20, 21, and 22 show several substance classes suitable for soft PVC.

The bond between elastomers and rubber, textile or metallic reinforcing materials is also realized with adhesion promoters or intervening bonding agent layers.

Adhesion promoters for textile and metallic structural elements can include [32]:

1. Chemical bonding to structural elements with the bonding system, i.e.
    - Resorcin-formaldehyde-latex (RFL)
    - Isocyanate bonding systems
    - Resorcin-formaldehyde-silica (RFS)

Table 20 Single-component adhesion promoters. (Derived from [19])

Substance class	Remarks
Aromatic polyisocyanurate in DBP	Contains no solvents
Aromatic polyisocyanurate in butyl acetate	
Aromatic polyisocyanurate in DOP	Contains no solvents

Table 21 Two-component adhesion promoters. (Derived from [19])

Substance class	Remarks
Polyesters in ethyl acetate, containing hydroxyl groups	
Polyesters containing hydroxyl groups	Contains no solvents
Aliphatic polyisocyanate in MPA/X	
Aromatic diisocyanate	Powder
Aliphatic polyisocyanate	
Aromatic polyisocyanate in ethyl acetate	Contains no solvents

Table 22 Reaction retardants. (Derived from [19])

Substance class	Remarks
Organic acid chloride in butyl acetate	For long potlife

2. Chemical bonding to metals with the bonding system, i.e.
    - Brass or zinc coating
    - Resorcin-formaldehyde-silica (RFS)
    - Isocyanate adhesion promoter
    - Halogenated adhesion promoter

Common to all of these systems is that the adhesive bonds chemically to the substrate and reacts chemically with the rubber as well. Aqueous systems are preferred for adhesion between textile fibers and rubber.

RFL dip is known to possess the required properties; resorcin is precondensed in an alkaline medium, whereby monomethylol, dimethylol and trimethylol resorcins are formed.

The fibers are supplemented by the reaction product, coated with natural rubber or SBR and vinal pyridine latex. During the subsequent drying procedure at 150–230 °C, the methylol group reacts with both the fiber surface and the active molecule groups of the rubber. The rubber bonded to the fibers is also cross-linked in the subsequent vulcanization process.

Cross-linking is initiated by active hydrogen atoms in the methyl resorcin systems (Rayon or polyamides), epoxide predips or isocyanates in polyester and aramide fibers, and by silanes in glass fibers.

Adhesion promoters added to the mixture (so-called direct bonding systems such as resorcin-formaldehyde-silica), are advantageous because the dipping process is unnecessary. Disadvantages include the high resin consumption level and the potential elastomer property changes similar to the effects of mold release agents in the mixture [32].

Alpha brass coating is used on steel to improve the adhesion of rubber to the steel. It reacts both with sulfur, producing zinc sulfide, and with the rubber. Organic cobalt compounds catalyze the reaction and necessitate high sulfur dosing. Resorcin-formaldehyde-silica systems are an alternative. The brass layer is not needed if isocyanates are used as the adhesion promoter, although solvents are then required. Aqueous dispersions of chlorinated or sulfochlorinated polyethylenes cross-linked with polynitroso compounds offer an alternative [32].

For coupling agents for WPC, see [51].

The adhesion promoters known as coupling agents play a significant role in the filling and reinforcing of plastics – above all silanes, followed by titanates.

Silane-Based Adhesion Promoters

These are monomeric compounds with the general formula $(RO)_3SiR'X$, whereby X represents an organofunctional group, for instance amines, methacrylates, epoxides, and others. These groups are connected to the silicon by means of a stable carbon bond R′, usually a $–(CH_2)$ group. Hydrolyzed alkoxy or acetoxy groups (RO) are located at the organic end of the molecules. These groups hydrolyze in aqueous solution or under the influence of humidity into the reactive silanol group $Si(OH)_3$. The silanol group condenses with hydroxide groups at the surface of siliceous materials (glass, etc.) and forms a covalent bond. The organic group R′X reacts with the matrix, resulting in a better bond between it and the inorganic additives such as glass fibers or glass beads.

In filler coating, for example with synthetic silicic acid or ATH, a condensation reaction takes place between the reactive hydroxyl groups in the filler surface and the group $(RO)_3Si$. Adhesion promoter cross-linkages are also possible as a result of steric inhibition of the main reaction. The resulting Si–OH groups can form additional hydrogen bridges to the substrate with H_2O molecules. In nonsiliceous substances, the silanes react with oxides or surface moisture. A related variant is peroxidic grafting of vinyl siloxanes onto polyethylenes, followed by cross-linking initiated by water. Application areas include pipes, containers, and cable insulation.

Titanates

Inorganic materials treated with titanate are hydrophobic, organophilic, and organofunctional. In combination with polymers they improve impact strength, do not embrittle the material, and result in melt viscosities lower than that of most unfilled polymers even at filler ratios exceeding 50 % by mass [54]. Titanates react with chalk, heavy spar, carbon black, cellulose, peroxides, C and aramide fiber, and with plastics. The additive ratios are 0.1–0.5 %. Titanate adhesion promoters have a total of six functions, one of which is the chemical bonding of filling or reinforcing materials to the plastic matrix. Besides improving the mechanical properties of the molding materials, shortening cycle times in injection molding, reduction of injection pressure and a potential for a greater filler ratio, energy consumption is reduced for higher yields.

6.1.8 Impact Modifiers

Impact modifiers are homopolymers or copolymers that modify brittle polymers thanks to their low glass transition temperature so as to preserve high-impact characteristics even at low temperatures. A precondition for the combinatory characteristics of this polymer blend is the fact that the tolerance of the two ligands is conditional. This is therefore not a physical mixture, but rather a bulk blend, since only in such a constellation can the embedded elastifying component show its impact-absorbent quality. The percent by mass of this component usually exceeds 10 %.

Besides mixing different polymers, there are other possible ways to obtain high-impact plastics, for example copolymerization and graft polymerization or use of plasticizers in brittle polymers. These products will not be treated in this section. In the case of PVC-U, addition of ultrafine precipitated calcium carbonate (grain size 75 nm) has excellent impact conditioning and surface quality-enhancing effects.

Among the most important PP blends from the point of view of application engineering are the propylene homopolymers and copolymers modified with EPM or EPDM (polyolefin elastomers). Long-term UV stabilization makes these materials suitable for outdoor use. The painting qualities of these types have also been improved. In addition to the impact modifiers of PA that have been in use for years – ethylene/vinyl acetate (EVAC) copolymers and HDPE – there are also the new thermoplastic PO and PA elastomers. Molding compounds refined with these elastomers regain, by means of filling and reinforcing, the rigidity of the primary material without losing impact strength.

In addition to ABS, with polybutadiene as the elastifying component, there is another forerunner among the polymer products formulated for low-temperature impact resistance, PVC-U. Elastifying ligands include: EVAC, EVAC/VC graft polymer, PAE/VC (polyacrylic acid ester/vinyl chloride copolymer), ACE (acrylic ester/MMA graft polymer) as well as the chlorinated low-pressure polyethylene PE-C in use for over 35 years. All of the polymer blends listed here are suitable for outdoor applications since they contain no unsaturated components. Polybutadiene-modified products are better suited to interior applications, for example MBS, a methylmethacrylate/butadiene/styrene graft polymer [55].

Weather-resistant AXS polymers contain, in place of the UV-labile polybutadiene, a low-diene acryloic ester elastomer that is highly weather-resistant. Even polystyrene elastified with low-diene EPDM remains impact-resistant in outdoor applications. Transparent, high-impact polystyrene (SB) is obtained by embedding the – normally opacifying – rubber components in the form of ultrafine lamellae into the coherent PS phase instead of in bead-form particles. The transparency results from the equivalent refractive index of the materials.

Nitrile butadiene rubber (NBR), which is formaldehyde-resistant, is the predominantly used elastifying component for phenoplastics. The resin and rubber interreact during the curing process. Natural rubber is incompatible with phenolic resins. At a rubber content of 25 %, the modulus of elasticity, at 1,000 N mm^{-2}, has already fallen into the middle range of unreinforced thermoplastics. The impact strength reaches the values of type 74 (fabric chips, reinforced). Their form stability when exposed to heat is below that of type 31 at temperatures below 100 °C.

6.1.9 Blowing Agents

Foams can be manufactured using three different methods: injection foaming (in which the cell structure is obtained by injecting foam into the product), chemical blowing, and physical blowing. Among the blowing agents [30] with physical effects, those given off by soluble solids do not play a significant role. Among condensed inert gasses, the only possible alternative is nitrogen (in the US). Low-boiling liquids are of technical importance up to a boiling point of 110 °C [56]. Market acceptance of pentane is slow at best. Methylene chloride is used as the blowing agent for extrusion of PS foam. The fluorinated, aliphatic hydrocarbons (R 11, R 12, R 113, and R 114) come closest to meeting the specifications for physical blowing agents in that they are nonflammable, physiologically harmless, and thermally stable.

Table 23 Properties of chemical blowing agents in common use

Chemical designation	Disintegration range in air [°C]	Gas yield [ml g^{-1}]	Used preferably in
Azodicarbonamide	205–215	220	PVC, PE, PP, PS, ABS, PA
Modified azodicarbonamide	155–220	150–220	PVC, PE, PP, EVA, PS, ABS
4,4′-oxibis(benzole sulfohydrazide)	150–160	125	PE, PVC, EVA
Diphenyl sulfone-3,3′-disulfohydrazide	155	110	PVC, PE, EVA
Diphenyl sulfone-4,4′-disulfohydrazide	175–180	120	PE, EVA, PVC
Trihydrazinotriazine	275	225	ABS, PE, PP, PA
p-Toluylene sulfonyl semicarbazide	228–235	140	ABS, PE, PP, PA, PS
5-phenyltetrazole	240–250	190	ABS, PPE, PC, PA, PBT
Isatoic acid anhydride	210–225	115	PS, ABS, PA, PPE, PBT, PC

Use of FCHCs as blowing agents and refrigerants has been prohibited since the mid-1990s due to long-term damage done to the ozone layer protecting the earth. The substances now used instead are the less harmful HF(C)CH and/or the hydrocarbons (pentane, cyclopentane).

The best-known chemical blowing agent [31] for thermoplastics and EP resins is azodicarbonamide (ADC). With a gas yield of 220 g ml^{-1}, it is the most economical commercially available blowing agent. It complies with BGA and FDA recommendations. The decomposition temperature of 205–215 °C, which is quite high, can be reduced by additives known as kickers. The substances used as kickers include: polyols, urea, amines and zinc oxide, zinc stearate, calcium stearate, and others. Other chemical blowing agents include the hydrazine derivatives, semicarbacides, tetrazoles, and benoaxines, Table 23 [57]. Also worth mentioning is CO_2, which is released when water is present in polyol during synthesis of polyurethane with isocyanate, resulting in PUR foam (for instance in lecture demonstrations).

6.1.10 Stabilizers

The worldwide consumption of stabilizers in 2001 was 850,000 t/a. Seventy percent of this amount are used in PVC [34].

Restrictions against stabilizers containing heavy metals are resulting in a trend toward organic compounds. In combination with costabilizers and/or synergists, so-called multifunctional additives, for example processing agents with integrated light and oxidation protection, are being developed.

Use of stabilizers containing lead was discontinued in Scandinavia and the Benelux countries in 2001/2002. The automotive industry has been converting to lead-free cabling since 2003.

Stabilizers on a calcium-zinc basis are currently the best alternative, even though the systems are more complex, and in most cases also more expensive, because of the necessity of adding organic costabilizers (polyols and phosphites) [34].

In spite of these developments, lead stabilizers will continue to dominate the world market for some time, due for one thing to the unabated growth of the worldwide market for PVC (expected worldwide figure for 2010: 35 million t/a). The volumetric ratio of lead to alternative systems in current use is $\sim$4:1.

Multifunctional stabilizer systems with much-improved migration and coloration properties (one-packs) will finally replace the systems containing heavy metals. It is estimated that only 80,000 t/a of leaded stabilizers will be used in 2010.

For example, Crompton Corp. (www.cromton-corp.com) introduced an organic PVC stabilizer in 2002 (type: OBS) for PVC pipes.

Cognis (Netherlands) (a subsidiary of Henkel) supplies a Ca/Zn stabilizer (type: Stabilox CZ2913GN) for window casements that has the same properties as conventional Pb-stabilized systems at 10 % lower dosing levels.

Great Lakes, USA is offering an entire series of new stabilizers, including a liquid system (type: Anox 1315) for PVC ready-to-use preparations (one-packs) integrated with other components (type: NDB) [34].

Both natural and synthetic polymers oxidize. This damaging decomposition of plastics may result from the effects of heat during processing and use as well as from the influence of the UV portions of solar radiation. When the products are used outdoors, the combination of both of these influences may accelerate the rate of damage.

The most important oxidation stabilizers (antioxidants) for elastomers are listed in Table 24 [32].

The best protection is provided by the (heavily staining) p-phenyldiamines, which are however unsuitable for peroxide cross-linking. TMQ (Table 24) is a low-cost heat protection agent, which however provides no ozone protection.

The least favorable substances are the nonstaining, sterically inhibited phenols, which are however required for light-colored products and for food product contact [32].

Table 25 compares the efficacy of different antioxidants in natural rubber [58].

UV Stabilizers

In plastics exposed outdoors or exposed in closed rooms to fluorescent light, the high-energy UV portion of the radiation initiates physicochemical processes that may result in a reduction of the mechanical properties, a loss of gloss, and discoloration. The degree of damage depends on: the light sensitivity of the respective plastic, type of additive used, product wall thickness, and the intensity and wavelength range of the incident radiation. The most damaging effects are caused by the UV range (300–400 nm). In aerospace applications, radiation in the 200–300 nm range must also be taken into account. The protective effect of UV stabilizers [31] is due mainly to absorption of harmful UV radiation and its transformation into much less harmful heat energy, i.e., longwave radiation.

Table 24 Antioxidants for elastomers [32]

Antioxidant group	Chemical designation	Abbreviation	Properties
Substituted phenols	2.6-di-tert. butyl-4-methylphenol	BHT	nonstaining
Substituted bisphenols	2.2′-methylene-bis-(4-methyl-6-tert- butylphenol)	BPH	nonstaining
	2.2′-methylene-bis-(4-methyl-6-cyclo- hexylphenol)	CPH	nonstaining
Dihydroquinolines	2.2.4-trimethyl-1.2-dihydroquinoline, polymerized	TMQ	staining
Diphenylamines	Octylated diphenylamine	ODPA	staining
	Acetone/diphenylamine – condensation product	ADPA	staining
Phenylnaphthyl-amines	Phenyl-α-naphthylamine	PAN	staining
Paraphenylene diamines	N,N′-bis-(1.4-dimethylpentyl)-p-phenylene diamine	77PD	heavily staining
	N-isopropyl-N′-phenyl-p-phenylene diamine	IPPD	heavily staining
	N-(1.3-dimethylbutyl)-N′-phenyl-p-phenylene diamine	6PPD	heavily staining
	N,N′diphenyl-p-phenylene diamine	DPPD	heavily staining
	N,N′-ditolyl-p-phenylene diamine	DTPD	heavily staining
Benzimidazoles	2-mercaptobenzimidazole Methyl-2-mercaptobenzimidazole	MBIMMBI	nonstaining

Table 25 Comparison of efficacy of antioxidants against various influences in natural rubber

Antioxidants	Oxidation protection	Heat protection	Fatigue cracking	Ozone protection	Heavy metal stabilizer
Substituted phenols	3–4	4	5	5	4–5
Substituted bisphenols	2–3	3	5	5	4
Dihydroquin-olines	2	1–2	4	5	3
Diphenyl-amines	2–3	2	3–4	5	3
Acrylnaph-thylamines	2	2–3	2	5	2–3
Dialkyl-p-phenylene diamines	2–3	3	1–2	1	2
Alkyl-aryl-p-phenylene diamines	1–2	2	1	1–2	2
Diaryl-p-phenylene diamines	1–2	2	2	2–3	2

1 = very good, 5 = poor (no protective effect); [58])

Photochemical damage to plastics can be delayed by the following mediums: Protective coatings (lacquers, metal), UV absorbers, quenchers and radical scavengers/peroxide decomposers. The normally used concentrations of photoprotectants are 0.05–2 %. UV absorbers also include carbon blacks (usable only in black-colored products), above all the less volatile hydroxyphenylbenzotriazoles, some hydroxybenzophenones as well as formamidine, used to date in cosmetics, and the benzylidine camphors [57]. Cinnamic acid esters represent the transition phase between the UV absorbers and quenchers. The quenchers do not absorb the radiation to achieve their effect, rather they dissipate the energy stored in the chromophores. In this way, they prevent any further chemical reaction. Their effect is independent of wall thickness. The most important quenchers are the nickel chelates, which are highly effective with PP and HDPE. An additional property of nickel chelates is that they act as adhesion promoters for inks. Hydroperoxides play an important role in the photooxidative degradation of polymers. Radical scavengers, for instance phenolic antioxidants, inhibit degradation by transforming the radicals or breaking down the peroxides formed during degradation into less reactive substances. The best results are achieved by at the same time ensuring a high level of heat stabilization by application of antioxidants and/or heat stabilizers. Effective hydroperoxide decomposers include metal (Ni, Zn) complexes of sulfurous compounds. Radical scavengers include, for example, benzoates of the benzylidene camphor type.

The sterically inhibited amines (HALS) were the most important new development in the field of photoprotectants of the past 10 years. The low molecular types have now been supplemented by highly effective polymeric types. They are particularly effective with very oxidation-sensitive PPs and other polyolefins – even in products with minimum wall thicknesses (foils, fibers). The polymeric HALS types have proven highly resistant to extraction and migration.

Only a few of the large number of photoprotectants available produce optimum results with a wide range of plastics. Research and development efforts are therefore geared toward application-specific UV stabilizers for a number of different plastic types to facilitate plastic material applications for a market of growing variety. As a matter of course, photoprotectants are now also available in the form of nondusting, easy-handling master batches [59].

Heat Stabilizers

Whereas most polymers are protected from the damaging effects of heat during processing and product use by the presence of antioxidants and photoprotectants, PVC in particular requires additional heat stabilization. If the PVC macromolecule were made up only of methylene and CHCl groups it would be highly stable under normal processing conditions. Its instability is actually caused by certain groups of elements terminating the chain at both ends. Another possible source of weak points is the presence of tertiary Cl atoms in the polymer chain.

Considering the thermal instability of PVC, it becomes clear why the worldwide consumption volume of stabilizers required for this one type of plastic and its modifications exceeds 250,000 t/a to meet the constantly increasing consumption of PVC, now at 14 million t/a worldwide. Modern stabilizer selection is not based on application and economics only, but also on toxicological assessments, which may differ from country to country. The USA and France, for example, do not allow the use of lead compounds in drinking water pipelines, replacing them with tin-based stabilizers. In Europe, it is no longer permissible to use cadmium-based stabilizers for health-related reasons.

The purpose of heat stabilizers in PVC is to bind the hydrogen chloride released during decomposition, neutralize initiation points by means of substitution, and prevent auto-oxidation by means of the antioxidative properties of the stabilizer, possibly with contributory effects from phenolic antioxidants or phosphites.

The sulfurous tin compounds are suitable for stabilizing E, S and M-PVC, copolymers and graft polymers as well as PVC polymer blends. The glass-like product transparency achievable with tin-based stabilizers is highly valued. The sulfurous compounds require the presence of UV stabilizers to maintain material transparency [59]. The organotin stabilizers are highly resistant to migration. The butyl tin mercaptides are being increasingly used as substitutes for Ba/Cd stabilizers. Otherwise, they are generally used in production of technical products. The sulfur-free tin-based stabilizers, for example dialkyl tin maleates, are highly light-fast and odor-free in contrast to sulfurous tin-based stabilizers. As substitutes for Ba/Cd stabilizers, the barium/zinc and calcium/zinc stabilizers have been gaining ground. The combination of zinc carboxylate and Ba or Zn carboxylate results in a synergism. The color and long-term stability of these metal carboxylates is significantly enhanced by use of costabilizers (e.g., diketones, organic phosphites, polyols, epoxide compounds) [60]. Ba/Cd stabilizers are still preferred to stabilize hard PVC for outdoor applications. These stabilizers are processed in the form of dust-free concentrates in the interest of good industrial hygiene. The most important areas of application of *lead-stabilized* hard and soft PVC formulas are still wire and cable sheathing and pressurized pipeline production. The most important compounds are dibasic lead stearates. With these stabilizers as well, combinations with costabilizers and lubricants available in the form of concentrates have proven useful.

Time-Controlled Degradation

Whereas the purpose of the antimicrobial additives, heat and UV stabilizers treated in previous sections is to preserve valuable plastic products, other research and development efforts have been attempting to realize just the opposite, i.e., controlled degradability of certain semifinished and finished plastic products, mainly the standard plastics PE, PVC, and PS out of which packaging materials are made in large quantities. The aim of rationalized use of such products is to reduce plastic waste volume by means of time-controlled photochemical or biochemical degradation.

Readers are referred to “Degradable Polyethylene.” A number of other products of this type are mentioned briefly here.

According to G.C. Scott, controlled degradation of the above-mentioned polymers can be realized photochemically by incorporating radical-forming iron dialkyl thiocarbamate and exposing the materials to UV radiation [30]. According to Guilet, UV-sensitive ketones are polymerized by incorporation.

In the US, PE manufacturers can supply copolymers made of ethylene and carbon monoxide (E/CO) that begin to disintegrate after several hours of exposure to sunlight. Of course it must be ensured that these products are not recycled or compounded with normal PE.

Biochemical degradation of plastics is another possible approach. It is realized by addition of organometallic compounds or starch. Examples of applications include the mulch films widely used in agriculture, made of polyethylene or PVC. These films rot within one vegetation period and can be plowed under.

Other biodegradables include aliphatic polyesters, polycaprolactones, and thermoplastic starch [61].

Another successful method is processing of normal starch in twin-screw compounding machines, adding water and chemical additives with intensive mechanical shearing and thermal strain. The end product is thermoplastically processable starch. The granulate, which is produced on properly engineered systems, can be processed with standard extruders to make films and with injection molding machines to produce simple moldings.

6.1.11 Plasticizers

Plasticizers reduce the hardness and brittleness of polymers. They increase the distance between the molecular chains, thus reducing the secondary valence forces and shifting the transition interval to lower temperatures, see Sect. 1.1. There are two ways to reach these goals, internal and external plasticization.

- *Internal plasticization* is copolymerization of two compatible monomers with widely disparate glass transition temperatures.
- *External plasticization* is a solvation (swelling) process in which the low molecular plasticizer is bound to the polymer by secondary valence forces. The effectiveness of external plasticization, which only the processor can access, is particularly pronounced in polar polymers (for example the softening effect of moisture in hydrophilic polyamides). The solvation is not a chemical reaction, despite the strong dipolar forces involved.

Primary and secondary plasticizers [19] are differentiated – especially those used in PVC. Primary plasticizers must gel well and not exude. Secondary plasticizers are low-dipolar, moderate gellers used in combination with primary plasticizers. They contribute to reducing migration tendencies, to the cold strength of the material and to its extraction tolerance. Primary plasticizers are often replaced by extenders. They do not have a gelling effect, although they do influence viscosity, breaking strength, and surface adhesion. Formula economy is of course an important factor here. The so-called polymer plasticizers are particularly resistant to solvents and migration. They are nonvolatile and show good cold resistance, i.e., do not crystallize at low temperatures. The plasticizing effect depends to a considerable extent on the concentration. The oldest known plasticizer is camphor, in use since 1868 to improve the processability and flexibility of celluloid. The phthalic acid esters head the consumption lists, above all dioctyl phthalate (DOP), followed by diisooctyl phthalate and diisononyl phthalate as well as dibutyl phthalate (DBP). Use of phthalates from short-chained aliphatic alcohols, for example dimethyl phthalate (DMP), is limited to cellulose esters due to its extreme volatility. DOP is characterized by a high gelling capacity, good compatibility, photostability, a low level of volatility, good water resistance, and favorable electrical properties [30]. More recent developments have resulted in foodstuff and medical qualities in DIP [62].

The low-volatility, flame-resistant phosphoric acid esters have maintained their position in products subjected to high levels of mechanical strain such as conveyor belts. Triphenyl phosphate, used only for molding compounds made of cellulose esters, is a practically noncombustible product that is not soluble in benzine. Tricresyl phosphate (TCF) is a flame-retardant plasticizer for PVC products subjected to heavy mechanical stress. The esters of the aliphatic dicarboxylic acids (adipic, azelaic, and sebacic acid) are used as plasticizers for PVC and PVAC. These products are resistant to cold and light. The esters of higher fatty acids such as pelargonates, laurates, palmitates, stearates, and ricinoleates are, strictly speaking, not plasticizers, but are rather used as extenders, secondary plasticizers, or lubricants.

Epoxidized fatty acid esters are used in hard and soft PVC processing. Valuable synergetic effects are achieved in combination with metallic stabilizers such as Ca/Zn compounds. Epoxidized soybean and linseed oil are among the most important representatives of this group. The interest in citric acid esters is due to the favorable health-related assessments of these substances. Triethylene glycol-di-2-ethyl butyrate has become an irreplaceable plasticizer for production of polyvinylbutyral films for use in composite safety glass. It ensures good foil-splinter adhesion within a temperature range of −40 °C to +70 °C. Polyesters known as polymer plasticizers are available with a wide range of esterification components and molar masses. Propane and butandiol are the preferred diols. The dicarboxylic acids used include adipic, azelaic and sebacic acid.

Chloroparaffins with chlorine content levels of 30–40 % are used as secondary plasticizers. They may account for as much as 25 % of the volume of PVC pastes. With chlorine content levels of 50 %, chloroparaffins come very close to the primary plasticizers and can be used in semihard mixtures without addition of primary plasticizers.

Hydrocarbons such as dibenzyl toluene and products with an aliphatic-aromatic structure are used as extenders for immersion and rotation molding pastes. Polyamide flexibilizing with the help of plasticizers with comparable polar structures (e.g., Cetamoll in the sulfamide group), has receded into the background ever since the development of PA copolymers with elastomeric qualities that are for the most part resistant to low temperatures.

Phenolic resins can be plasticized by means of chemical integration of plasticizer groups such as bisphenols and polyphenols with elastic links. Monovalent or polyvalent alcohols, for example glycerol, as well as p-toluene sulfamide, can be used with MF molding compounds. Known plasticizer products for UP resins include DOP, TCF, Mesamoll, Chlophen, and Ultramoll. In applications in which a certain loss of mechanical and electrical properties is acceptable in UP resins, plasticizers such as DOP, BBP, or TCF can be used. Under certain circumstances these substances will exude, since they do not participate in the reaction. Proven flexibilizers include polysulfides and polyaminoamides.

Röthemeyer and Sommer [32] describe plasticizers for rubbers and elastomers.

Plasticizer Uptake

The ability of a PVC corpus to take up plasticizers is determined by grain size and grain structure, an aspect that is particularly important for soft processing. The uniformly highly porous grain of the types used for soft processing is very favorable, particularly with a view to the rate of uptake of the plasticizer during mixing (dryblend formation).

The method used to determine plasticizer uptake at room temperature (DIN 53417 T.1) is primarily an indicator of the porosity of the PVC brands. The determination of plasticizer uptake rate at higher temperatures (DIN 54802) provides a basis for conclusions concerning dryblend formation with higher plasticizer volumes [63].

- Nuclea agents see [30, 64])
- Antistatica see [30, 65])

6.2 Organic and Inorganic Fillers

Fillers are particulate, organic or, for the most part, inorganic substances in solid form. Their incompatibility with the basic material (matrix) results in a multiphase system, the compatibility of which can, however, be increased by means of coupling additives (coatings) – similarly to the process with reinforcing fibers leading, at the least, to bridge formation.

The fillers differ from one another in their chemical structures, granular form, grain size, and grain size distribution. Concerning the granular form, the ratio of length to thickness (l/t) is important. This ratio is 1 in spheres and cubes. In rectangular solids, this “aspect ratio” reaches values up to 4:1, in flakes from 5 to 100:1 and in fibers $>$ 4:1. Filler particles with values of 4:1 normally show a pronounced extending effect, i.e., they do not improve mechanical properties with the exception of stiffness; flakes have quite a different effect (mica, talcum, graphite, ATH), not to mention reinforcing fibers [66]. Grain size distribution is just as important as the l/t ratio. The “top cut,” i.e., the coarse grains – depending on content level and even at mean grain sizes of only a few μm – influences mainly the impact strength as well as the slipping and wearing properties of the molding materials. In critical cases it is therefore very important to sift out this top cut.

Basically, a large filler surface is desirable, but if it is too large it may result in agglomeration and will have a coarse-grained effect.

High surface energy levels are also basically desirable in fillers. Should they become too high, dispersion is rendered difficult. Coating is then the only productive solution. The many times greater specific heat capacity and much higher thermal conductivity levels have a favorable effect on the plasticizing and cooling times of the molding compounds, increasing process yield. Mohs hardness is an essential – if not the only – factor in the effect a filler has on wearing qualities. The different types of optimum surface coating (silanes, titanates, chromium complexes, fatty acids, lubricants) reflect the differences in behavior of the fillers in this respect and their structures. In the presence of fibrous reinforcing materials, fillers are also advantageous since they increase the stiffness of the molding materials, thus adapting their modulus of elasticity to that of the reinforcing fibers. This is a decisive advantage of so-called hybrid reinforcement [67]. The large consumption volumes involved underline the significance of this method from the point of view of application engineering: The consumption of fillers plus reinforcing materials worldwide in 2006 ~52 million t/a (Asia 19 million tons, Europe 15.5 million tons, North America 13.3 million tons). The expected amount in 2016 worldwide is estimated at 74 million tons, with a value of 48 billion Euro [68]. Annual rates of increase for the most important additives are ~10 %.

To sum up: The fillers increase the density, modulus of elasticity, compression and bending strength, hardness, form stability under heat exposure, surface finish as well as – depending on the filler type – antistatic properties and fire resistance. Shrinkage and elongation at rupture are reduced. Tensile and shearing strength, as well as creep stability under heat, can however only be increased by the addition of fibrous reinforcing materials. The medium permeation rate is usually greatly increased (depending on the adhesion of the polymeric matrix).

6.2.1 Organic Fillers

Among the particulate organic fillers, wood meal is the most important material for use in thermoplastics, in particular PP. For curable molding compounds, powdered cellulose is also in this category. These finely powdered materials are actually fibrous, finely ground and specially conditioned products based on spruce or beech wood or cotton. Others include wood granulate, sawdust, shell and seed meal and, already mentioned in relation to impact modifiers, natural rubber.

6.2.2 Inorganic Fillers

Approximately over 50 million tons of inorganic fillers were produced in 2006, dominated by a small number of major manufacturers such as Omya, Luzenac, Imerys, DAM, and Quarzwerke. Table 26 shows some of the details.

Table 26 Inorganic fillers and their use

Filler	2006 Share of world market volume in % (approx.)	Main application in plastics
Calcium carbonate	66	PVC, UP, PE + Paper
Talcum	6	PP
Kaolin	6	PA, elastomers
Wollastonite	3	PP, PA, PUR-RIM
Barium sulfate Mica Quartz, etc.	19	Significance still minor, but increasingly important

The price-performance ratio, purity, consistency of product quality, and availability determine the acceptance of a filler, whereby the mean aspect ratio characterizes most of its properties.

The trend is to micronized types (nanocomposites) with high aspect ratios up to 1,000. With a degree of filling of 5 % of these materials, the obtainable properties resemble those obtained with a 30 % degree of filling with conventional fillers, for example nanoclays. The challenge is to distribute the nanoparticles in the plastic matrix uniformly, finely, opened up and with a skeletonizing effect.

Inorganic fillers top the list of all additives, including fillers, in terms of variety, volume, and importance in terms of application engineering. They not only function as extenders but also, as shown above, as functional additives.

For a summary report on organic and inorganic fillers, see [69] as well as [68, 70, 71] at the end of Sect. 5.3.

6.3 Reinforcing Materials

Mineral, organic and metallic fibers, and the surfaced materials made from them such as fleece mats, textiles, and weaves, not only make possible economical manufacturing of materials with specifically targeted physical property improvements based on standard plastics and technical molding compounds, but also help manage high mechanical stress loads, which are often direction-dependent and show local variations, with anisotropic composite structures.

In view of the fact that no revolutionary new developments of economically and/or technically significant plastics are to be expected in the coming years, measures taken to improve existing plastics are still of decisive importance [72, 73]. The reinforcement, filling [94] and alloying of standard plastics and technical molding compounds to improve their properties also has an economic effect that should not be underestimated: The wealth of experience gained in recent decades in this field ensures the major raw material producers in the industrialized countries a position ahead of the pack of Near and Far Eastern countries looking to break into the market with mainly standard plastics. The composites comprise several phases, usually with widely differing properties, the combination of which results in an entirely new set of properties.

6.3.1 Composites

Composites are materials made up of a polymer matrix, as the continuous phase, and reinforcing fibers or fillings as an interstitial discontinuous phase. The transition between fiber-reinforced and filler-reinforced composites is fluid. The binder, the matrix, may be a duroplastic (for example PF, MF, UF, UP, or EP resins) or thermoplastic (for example PA, PC, POM; PET, PBT, PP, or ABS). Both natural and synthetic, organic and inorganic, fibers in the form of short, long and endless fibers as well as products made from them such as fleece textiles, mats, woven and knit fabrics and bands can be used as reinforcing materials. The reinforcing materials may be arranged in uniaxial or multiaxial, directional or undirectional patterns in the matrix. The reinforcing effect improves the closer the modulus of elasticity of the resin approaches that of the reinforcing fiber. C fibers are therefore more effective in EP resin than in PP.

Embedding the reinforcing materials in the polymer matrix improves mainly the mechanical and thermal properties of the basic material, for example the tensile and breaking strength, modulus of elasticity, heat resistance and dimensional stability, whereas the impact strength and notch impact strength are in most cases lower than in the unaltered basic materials. These parameters can, however, be raised again by adding elastifying components, for instance elastomers. The fibers orient during processing and increase the shrinkage difference between the lengthwise and crosswise dimensions; the difference can be compensated by adding fillers, for instance glass beads.

The extent to which properties can be improved depends on curing between the matrix and the additive, i.e., on the processes in the boundary layer. The elastic component (glass fibers, C, aramide, natural or chemical fibers) is embedded in a viscoelastic component (resin or thermoplastic). Tensile stress stretches the composite. In molding materials with uniaxial reinforcement, the fibers absorb these forces along their length until rupture. Material failure can be expected must faster across the longitudinal direction. For example, in UP laminates with uniaxial GF reinforcement, the critical elongation is 0.9 %, but crosswise it is 0.1 %. Therefore, resin molding materials subjected to multiaxial stress should have multilayer reinforcements along the lines of strain.

The adhesion promoters must be optimized for each specific additive/matrix combination. The forces acting in the boundary layer influence not only the mechanical properties strength and stiffness, but impact strength as well. Most wetting agents are hydrophilic, polar, and water-sensitive. What is needed, however, is a hydrophobic bonding agent that reacts with the reinforcing material (or the specific filler) and renders its surface free of air and water, i.e., coats it with a thin hydrophobic film. The functional films have proven to be the most effective adhesion promoters for glass fibers. They still maintain their predominant position among a number of competitive materials. The silane adhesion promoters are characterized by the structure R–Si–X_3. R is formed by an organic residue and X_3 by hydrolyzable groups. The X groups are first hydrolyzed, then condensed in a follow-up reaction into oligopolymers or polymeric silanols, which form the thin, water-insoluble film mentioned above. The bond is produced partly by hydrogen bridges, partly by covalent siloxane bonds. The organofunctional X_3 group of the ambivalent bonding agent molecule is geared to the specific matrix. In order to develop adhesion promoters that are as universally useful as possible, silane compounds with several functional groups are formulated that are also capable of coupling by means of ionic interaction [74].

In curable plastics, the functional groups react with the resin. For example, methacryl silanes are best for UP resin, epoxy silanes for EP resins, and amino silanes for nearly all other resins. The property enhancements possible with thermoplastics depend mainly on the polarity of the matrix polymer. Therefore, the reinforcing effect of glass fibers, given the same percentage by mass, is greater in polar polyamides and saturated polyesters than in the nonpolar polyolefins. However, for example, polypropylene grafted with unsaturated carboxylic acids contains polar carboxyl groups that react with the amino silane on the fiber, enhancing its strength property. The adhesion between fillers and polymers is based on principles similar to those that apply between fibrous inorganic reinforcing materials. For example, with the help of multifunctional silanes, pretreated fillers can increase the elongation at rupture of PA 6 up to tenfold compared to nonsilanized fillers, without reducing either strength or modulus of elasticity [74]. The silanes also maintain surface adhesion when attacked by water. Additives without hydroxyl groups require surface treatment with wetting agents before silanization; these agents form a hydrophic boundary layer with the filler.

The *sizing of the C fibers*, as opposed to glass fibers, consists of an EP resin containing no curing agent. An effective coupling of fiber and matrix is realized by means of an oxidative surface treatment before the sizing is applied, whereby covalently bonded carboxyl, carbonyl, hydroxyl, and lactone groups are formed. These react with the sizing and resin components and ensure a permanent covalent bond to the polymer matrix [74]. These sizings do not influence the properties of EP resin composites up to temperatures in use of 180 °C, but they may suffer damage at higher curing or application temperatures [75]. This has been observed above all in polyimide composites. The only effective remedy was a sizing not based on EP resin. Other preconditions included a high carbon content (99–100 %) and a very low content level in the C fibers of metals that promote aging such as potassium and sodium.

The *sizing of the aramide fibers* is a processing aid that does not influence the mechanical properties of the composites. This effect is clearly observed in the low tensile, compression and shearing strength levels measured at right angles to the fibers, and these strength parameters depend to a great extent on boundary layer adhesion. GF and CF-reinforced composites are naturally stronger in this respect.

The reinforcing fibers are stronger and more rigid than the polymer matrix itself. The mechanical strain absorbed by the fibers in the composite depends on the percent by volume content of the components, their modulus of elasticity ratio, boundary layer adhesion, fiber lengths, and fiber orientation. Under tensile strain, tensile stress builds up beginning at the ends of the fibers, assuming a constant level in long fibers in the middle. The longer the fibers, the less effect the drop in tension at the ends will have. What then remains is only a reduction in strength due to the concentration of stress at the ends of the fibers. The shorter the fiber length, the greater the effects of the parameter-reducing factors. At fiber lengths below a critical point (<10 d), complete stress relief is no longer achieved in the fiber. The high shearing stress levels then cause the polymer matrix to flow or detach from the ends of the fibers, depending on the adhesion. Fibers below the critical length are no longer loaded to rupture point, but are detached and disembedded from the matrix before this point is reached. This so-called pull-out effect is characteristic of thermoplastics reinforced with short fibers with subcritical lengths of 0.2–0.4 mm. The processes involved in rupture of long-fiber-reinforced composites take place in this order: matrix deformation, boundary layer detachment, boundary layer sliding, fiber rupture or pull-out. With short fibers, rupture is more immediate and takes the form of a pull-out [74].

Figure 34 presents the example of a modern civilian jumbo aircraft, the Airbus A380, in which a wide variety of structurally relevant components and composites are used [76]. Figure 35 illustrates impressively how metals and fiber composites have competed, leading to mutual improvements [76]. These developments were made possible to a great extent by price reductions for the carbon fiber prepregs, which are down 50 % since 1990.

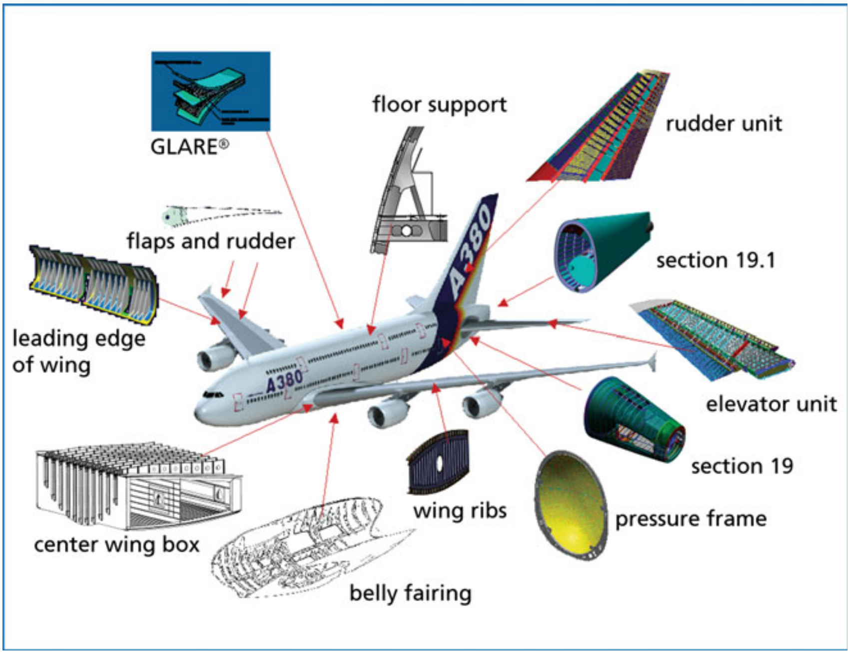

Fig. 34 The most important composite applications in the A380 [76]

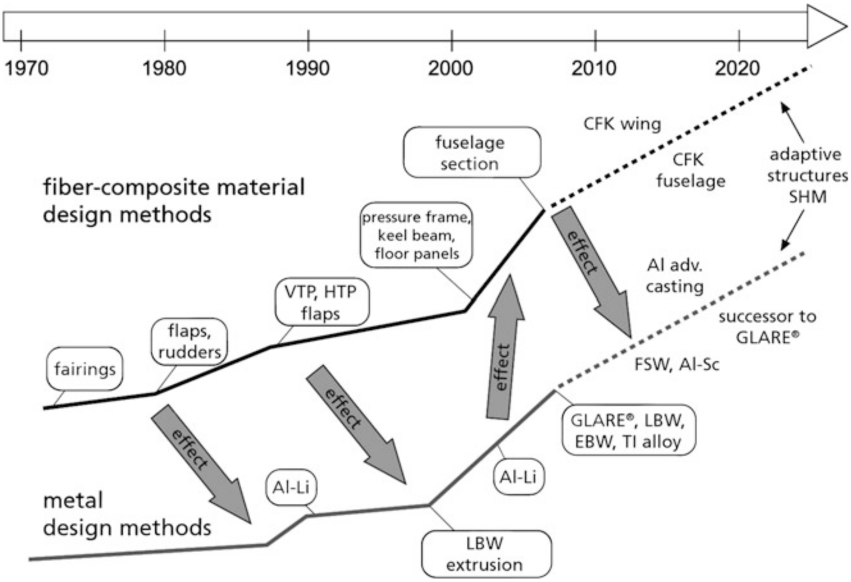

Fig. 35 Competition between materials and methods: metal and fiber composite design construction in Airbus aircraft [76]

6.3.2 Nanocomposites [77]

"New families of nanofillers and nanocomposites are opening up performance reserves of plastics, rubbers and dispersions. Even very low nanofiller % by volume can suffice to alter the property profiles of polymeric materials and functional additives in significant ways. The application spectrum extends from new construction materials to a diversity of functional polymers" [77, 106].

Homogeneous dispersion of nanoparticles of nanofibers in plastic – a problem yet to be solved satisfactorily – results, assuming equal parts by volume of nanoparticles and microparticles, in a significantly larger number of particles (10^7 with 1 μm to 1 nm particles), producing a polymer entity based entirely on interfacial interactions. Mülhaupt et al. [77] have called these materials "interfacial polymers." This approach opens up new opportunities to modify the properties of older plastic types with low volumes of reinforcing nanomaterials.

Nanofillers have actually been around for decades (the oldest for over a century): carbon blacks, pigments, precipitated silicic acid (Ultrasil, Degussa-Hüls), pyrogenic silicic acids (Aerosile, Degussa-Hüls), phyllosilicates, nucleation agents, reactive silicone nanoparticles for epoxy resins, ceramic materials and inorganic–organic hybrid particles from sol-gel transformations, for example synthetic, dispersible aluminate (boehmite) powder.

New developments in recent years have included inorganic and organic molecules with nanodimensions and freely variable surface functionalities that dissolve in the plastic matrix, in which they can then be coupled to form complex nanoarchitectures [77]. This is the answer to the problem of achieving the finest possible distribution of nanoparticles in the plastic matrix, at least for these newly developed materials. Examples include silsesquioxanes (Hybrid Plastics, Fountain Valley, CA, USA: POSS, polyhedral oligomeric silsesquioxane). POSS monomers are also found in the form of oils, waxes, and powders. Processing of this material may require melt compounding, polymerization/grafting, or coating. Silsesquioxanes have been attached to nearly all functional groups: acrylates, silanes, silanols, olefins, epoxides, amines, esters, phenols, styrenes, and thiols.

Cascade-branched polymers (branched dendrimers), with their variable end groups and nanometric dimensions, have been known to research for about 15 years now. Raw materials manufacturers have found ways of producing highly branched polyethylenimines (BASF) (less perfect branching, but more economical) for paper finishing and, in a direct single-pot reaction involving anhydrides and diisopropanolamine in intermediate oxazoline stages, highly branched polyesteramide polyols (Hybrane, from DSM) as well.

The spectrum of applications is broad, including raw substances for lacquers and adhesives, pigment and filler dispersants, ink additives, detergents, and cosmetics [77].

Polyesterpolyols (Boltorn from Perstop, Sweden) – highly branched nanopolymers – allow for tailor-made duroplastic chemistry. Small amounts of epoxide-functionalized, hyperbranched polyesters increase the impact strength of epoxy resins without reducing rigidity.

With hyperbranched polyesterpolyols and polyesteramides, molecular nanosystems have now reached the cost-performance threshold for use in plastics and composites along a broad front.

Anisotropic nanoparticles that do not form or set in the polymer matrix until the processing run are now being developed (no health risk). Hyperion Catalysis International (nanotube technology company) has produced electrically conductive carbon nanotubes by means of gas phase synthesis and is now selling master batches (FibrilR). Plastic fuel tanks (cars) and chip packagings (no electrostatic charging) are among the applications.

A further group of nanocomposites are the well-known bentonites, revitalized at the end of the 1980s by Toyota Research. Bentonites are swellable, three-layer silicates consisting mainly of montmorillonite. The new organophilic bentonite Nanofil product family from Süd Chemie AG is based partly on the Bavarian calcium bentonites, which are activated by acid leaching [see Table 27 [77]], and do without cationic exchange. (Author's remark: With a mean particle size of 4 μm, these are by no means nanoparticles!).

Mülhaupt et al. [77] conclude their overview with a broad spectrum of potential applications:

"The versatility of nanocomposites and phyllosilicate nanofillers is apparent from the developments of Planomers technology in the TNO Research Institute in Eindhoven, The Netherlands. According to Hartmut Fischer, the Planomers technology makes use of organophilic phyllosilicate modifications to realize a number

Table 27 Nanofil fillers based on unmodified, acid-activated calcium bentonite (Süd Chemie AG)

Product		Nanofil EXM 1167	Nanofil EXM 1168	Nanofil EXM 1169	Nanofil EXM 1170
Acid activation	% HCl	None	Low	Medium	High
Color		Cement gray	Pearl white	Pure white	Vehicle white
Bulk weight	$g\,l^{-1}$	360	220	180	120
Average particle size	µm	4.5	3.5	3.5	3.5
BET surface	$m^2\,g^{-1}$	91	265	388	268
pH		7.6	3.5	3.6	4.6
Moisture	%	3.9	6.0	3.7	2.9
Loss on ignition at 1,000°C	%	8.7	7.6	7.6	5.5
Ion exchange capacity	mVal/100g	74	52	33	4

of applications. The addition of organophilic phyllosilicates to starch (*green nanocomposites*) renders starch materials and films resistant to water without hydrophobic agents. In paints, phyllosilicates are loaded with dyes that are then efficiently dispersed in the acrylate matrix with the phyllosilicates. The resulting nanoreinforced paints are highly transparent and more UV resistant.

The immobilization of dye molecules on the silicate layers, e.g., methylene blue, greatly improves the UV stability of the dyes and makes them highly solvent-resistant. In numerous working groups, phyllosilicates and nanocomposites are being used in production of functional materials. Phyllosilicate nanocomposites give the polymeric polyelectrolytes in batteries and fuel cells dimensional stability, rigidity, heat deflection temperature stability and barrier properties. A number of new approaches to future developments are inherent here. Nanocomposites based on phyllosilicates are establishing themselves as new additives for polymers that greatly enhance the material value yield."

Summary for chapter 5.2

Table 28 provides an overview of the effects of known fillers and reinforcing materials on the property profiles of plastics.

In view of the importance of functional materials, fillers, and reinforcing materials in modified technical plastics, special compounding facilities now offer up to one hundred special types. Depending on the intended purpose of the polymer material, they contain highly efficient heat stabilizers, various lubricants and reinforcing fibers that are opening up new applications in the areas of office and communications technologies, automotive engineering, and textile processing machines, especially for economically processable thermoplastic molding compounds. (A good example is the LUVOCOM product series from Lehmann and Voss, Hamburg.)

Table 28 Influence of fillers and reinforcing materials on the property profiles of plastics; see also [104, 109, 110, 111, 112, 113]

	Glass fibers	Wollastonite	C-fibers	Whiskers	Synthetic fibers	Cellulose	Mica	Talcum	Graphite	Sand/ quartz powder	Silica	Kaolin	Glass beads	Calcium carbonate	Metal oxides	Soot
Tensile strength	++		+	+−			+	0					+			
Compression strength	+							+		+			+	+		
E modulus	++	++	++	+			++	+		+	+		+	+	+	+
Impact strength	−+	−	−	−	++	+	−+	−		−	−	−	−	−+	−	+
Reduced thermic elongation	+			+			+	+		+	+	+			+	
Reduced shrinkage	+	+	+				+	+	+	+	+	+	+	+	+	+
Improved heat conduction		+	+					+	+	+	+			+		+
Improved thermal stability	++	+	++				+	+				+		+	+	
Electrical conductivity			+						+							+
Electrical resistance		+					++	+			+	++			+	
Heat resistance		+					+	+		+	+	+			+	+
Chemical resistance		+					+	0	+			+	+			
Improved abrasive behavior			+				+	+	+			+				
Extrusion rate	−+						+					+		+		
Abrasion in machines	−			0	0	0		0	0	−			0	0		0
Lower cost	+	+				+	+	+	+	++	+	+	+	++		
	Fibrous fillers and reinforcing materials						Platelet – form types			Spherical filling materials						

++ strong effect, + weaker effect, 0 without effect, − negative effect

6.4 Inorganic Reinforcing Fibers

The only inorganic fibers that occur in nature are the monocrystalline and polycrystalline asbestos and wollastonite fibers. Wollastonite with a length/diameter ratio of 3:1–10:1 is used as a filler, and as a reinforcing fiber with values from 10:1 to 20:1. Vitreous mineral fibers made from slag, stone, ceramic, quartz, silica glass and, above all, glass fibers, are among the amorphous fibers made from melt. Polycrystalline inorganic fibers and monocrystalline "whiskers" are made of boron, silicon carbide, boron nitride, boron carbide, aluminum oxide, and zirconium oxide. Polycrystalline structures are also found in steel, aluminum, and tungsten metal fibers as well as in carbon and graphite fibers. Monocrystalline fibers include corundum, silicon carbide, and potassium hexatitanate.

6.4.1 Natural Inorganic Fibers

Asbestos fibers are among the oldest known fibrous materials. They are still obtained exclusively from natural mineral substances. Asbestos is a collective term covering a number of fibrous, hydratized Mg and Na silicates. These naturally grown monocrystals (i.e., they grow under certain conditions of pressure and temperature) can also be termed natural whiskers. The long-fibered types are used in the form of fibers and yarns, the short-fibered types as fillers in curable molding compounds, extenders in floor coverings, or as viscosity regulators. Chrysotile (Canadian white asbestos) is the type of asbestos most commonly used. The fiber diameter is 30 nm, the strength parameter 500–1,000 N mm^{-2} and the Mohs hardness 2.5–1.0. The fibers are up to 50 mm long. Chrysotile is lye-resistant, while acids attack it. Crocidolite, or South African blue asbestos, is resistant to both acids and lyes and is, in this respect, superior to E glass. Used in specific molding materials, asbestos increases their rigidity, tensile strength, form stability under heat exposure, dimensional stability, and hardness. The electrical properties, as well as the flow and abrasion characteristics of the material, are however negatively influenced. Compared to glass fibers, the stronger bundling and interfibrillary bonding of asbestos fibers results in a more isotropic reinforcing effect.

Although the different types of asbestos do not contain any free silicic acid, asbestos dust – similar to SiO_2 dust – is the causative agent in a dust-related lung condition, which is however much less frequent than silicosis. Asbestosis may occur together with lung cancer. Fine dust, with fiber lengths under 5 μm, has turned out to be the most dangerous form.

For reasons related to industrial safety and environmental protection, considerable effort has been invested for decades now in replacing asbestos in such items as automobile brake and clutch plate linings with metal, glass, synthetic mineral and organic fiber materials. Asbestos-free disk brakes and clutch linings have now been on the market, and on original equipment lines, for some time. The phenolic resin

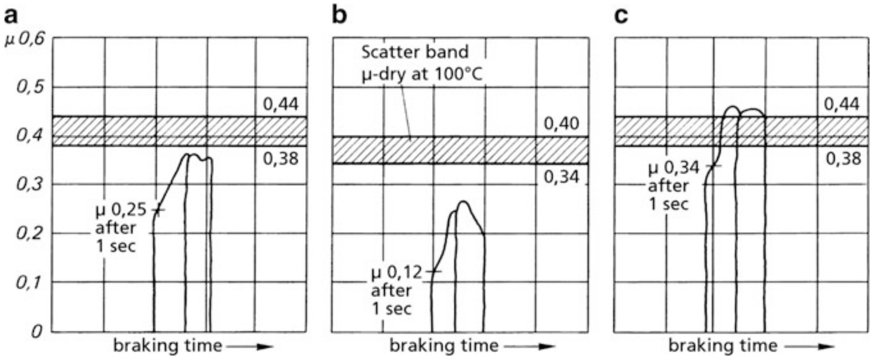

Fig. 36 Performance levels of disk brake systems, whereby: a = friction material containing asbestos; b = asbestos-free semimetallic friction material; c = asbestos-free ATE friction material (fiber substitute)

bonding agents, albeit with altered formulae, have been retained in all cases in which asbestos has been replaced by other reinforcing fibers [78].

The decisive factor in the performance of disk brake linings is their frictional behavior measured against time, especially under cold, wet weather conditions. Figure 36 compares three typical lining materials: The asbestos-free fiber substitute brake lining develops a frictional coefficient ($\mu = 0.34$) after only 1 s under cold, wet conditions that is much better than the value obtained with the semimetallic lining material ($\mu = 0.12$), even reaching the level of the conventional asbestos lining ($\mu = 0.25$).

A combination of fibers is the only effective replacement for asbestos. The sum of the properties obtained must make sense in terms of the material's price. The fibers must not exceed any critical load limits under the given conditions and must not form fibrils. The ATE substitute fiber lining obviously satisfies these standards. C and PAN fibers make suitable substitutes due to their capacity to stand up to the thermal stress loads involved [79].

In view of the hysterical reaction to products containing asbestos, readers should be reminded that about 30,000 smokers die of lung cancer every year in Germany, compared to fewer than 1,000 deaths from asbestosis. Furthermore, the explicit aim of a number of nanoengineering research projects funded by state, federal and EU ministries and other authorities is the development of nanocomposites, including fibers. Chrysotile asbestos fibers are nanofibers in this sense. Therefore, such fibers are already available in large volumes at low prices. The dimensions of the nanofibers (asbestos or others) are the factor that decides whether they can be exhaled from the lung alveoli or will remain caught in them. Lung cancer may then develop after two decades or more of exposure to nanofibers that remain in the lungs.

6.4.2 Synthetic Inorganic Fibers

Among synthetic inorganic fibers, glass fibers account for about 90% of those in use, easily occupying the top slot. C fibers are well-suited to applications requiring structural components characterized by high levels of rigidity and strength, combined with low composite density and a low thermal expansion coefficient. If, in addition to these properties, a high-viscosity molding material is required, aramide fibers may be preferable. Reinforcing materials used with them include boron fibers, beryllium fibers, silicon carbide fibers (SiC), and metallic fibers (aluminum and steel) [80].

Glass Fibers

Glass fibers consist of silicon, boron, and aluminum oxides. The term glass fiber (ISO) is used to designate all commercially available glass types (E, R, S, etc. glass) from which optical or *textile glass fibers* (ISO: textile glass) can be spun or which can be processed to produce *glass wool* or *glass bat* (wadding).

The E glass originally developed for purposes of electrical insulation is a borosilicate glass. The alkali-rich A glass type can be used to make textile products in combination with certain bonding agents. The chemically resistant C glass is used for applications requiring corrosion resistance.

Optically pure glass fibers are used as photoconductors; glass bat and glass wool are used as thermal and acoustic insulators. Textile glass is used to manufacture both filaments and staple fibers. Textile glass can also be spun. It is used to make household textiles, as a reinforcing or filling material in plastics and for electrical insulation applications. Glass fibers used for reinforcing and filling are generally *E glass* [81].

Glass filaments are endless threads drawn from the melt. 204 or more glass filaments are bundled into an untwisted *glass strand*, the basic commercial product. Glass strands are then used to make simple glass filament yarns, glass rovings, and textile glass mats (designations acc. to ISO):

- *Textile glass mats* are mats not produced by weaving, but rather either made directly from glass strands or using the intermediate step of glass rovings (to rove = stretch before spinning).
- *Glass rovings* (rovings, ends) consist of several parallel, untwisted glass strands laid together in a forming package. They are then either further processed to make *woven glass roving fabric*, roving cloth (USA) or ground into *milled glass fibers* or cut into chopped glass fibers (∼140–210 μm long).
- *Single glass filament yarns* are either laid up together as *multiple wound glass filament yarns* or twisted together in one or more steps to make *folded or cabled filament yarns*. Woven glass filament fabrics are then made out of the single or multiple yarns [81].

Glass staple fibers, 5–50 mm long and 5–15 μm in diameter, are produced either by drawing out glass rods or blowing air or steam into the melts through extrusion dies. The fibers are then either used directly to make *surfacing matting* in which the nonoriented filaments or staple fibers are fixed with bonding agents, or else a *roving* is first made as with organic split fibers consisting of practically parallel, slightly interwound staple fibers. After winding, the roving becomes a *single glass staple fiber yarn*. The yarns can then be mixed with filaments to produce *mixed glass fiber cloth* or *multiple wound glass staple fiber yarns* as with filaments, or *folded or cabled glass staple fiber yarns*. The different types of glass staple fiber textiles are then obtained using these wound, folded or cabled yarns, or made directly from simple glass staple fiber yarns (Table 29).

Glass mats are manufactured in the same basic types as organic fiber textiles. They are also manufactured in the same way. These basic types are known as biaxial or 0/90 textiles. In addition to biaxial textiles, there are also triaxial (0/45/90, 0/60/−60) and tetraaxial textiles on the market (0/45/90/−45) [81].

To protect these fibers from mechanical and chemical stress as well as against the effects of moisture, the glass fibers are treated with sizing and the staple fibers with spinning oil. Fibers, and the surfaced products made from them, that are used to reinforce plastics are desized and finished with a bonding agent finish or coupling agents (see Sect. 5.3.1).

The reinforcing effect is influenced by: the percent by mass of glass fibers, the ratio of length to diameter of the fibers (long fibers having more effect than short ones), the nature of the adhesion promoter, the orientation of the fibers in relation to the lines of applied force, and the degree of comminution during processing, for example injection molding of GF-reinforced molding compounds [108].

The maximum tensile strength of glass fibers is 2,500 N mm^{-2}. Yarns and twisted yarns reach strength levels of 1,300–1,500 N mm^{-2}. The relation between

Table 29 Properties of silicate and other mineral fibers at room temperature [18]

Property	RH (%)	Phys. unit	Quartz	E glass	S glass	Asbestos chrysotile	Al_2O_3	Al_2O_3 whiskers
Filament diameter	65	μm	10	10	7	10	20	–
Density	65	g cm^{-3}	2.2	2.54	2.48	2.55	3.1	3.96
Modulus of elasticity	65	GPa	69	72	86	80	345	2,100
Tensile strength	65	GPa	0.9	2.41	4.59	5.68	1.3	43
Elongation at rupture	65	%	1.3	3.5	2.8	11	0.8	–
Melting temperature	0	°C	1,650	1,260	–	1,520	2,045	–
Max. application temperature	0	°C	900	600	–	1,400	–	–
Hardness		Mohs		6.5				
		Vickers, 0.1 kg		620–640				
Coefficient of linear thermal expansion		10^{-6}K^{-1}		4.8				
Coefficient of thermal conduction		kJ/mK		3.71				

strength and deformation is linear up to rupture. No persistent elongation occurs. Elongation is the decisive factor in the reinforcing effect of a fiber material.

Possible relations between fiber and resin [82]:

- Glass fiber and resin show the same elongation at rupture (the tensile strength of both materials can be used to the full extent).
- The elongation at rupture of the resin is greater than that of the glass fibers (the tensile strength of the resin is only partly utilized, the glass determines the tensile strength of the composite).
- The elongation at rupture of the resin is less than that of the glass (the tensile strength of the glass fiber is not used and the resin fails at an early stage).

The second case is the target result. The elongation at rupture of the glass fiber is 1.5–3 %; the resins normally used reach 3–5 %. The elongation at rupture of GFP is determined by the glass fiber, which determines the strength of the material. The relation between strength and glass fiber content is only linear if reinforcement is unidirectional. A maximum strength parameter is exceeded in other reinforcing configurations. The breaking strength is also a function of glass fiber content.

Maximum glass content levels in GF-reinforced resins (GFP):

- Mats:
  - Hand lamination, 35 % by mass
  - Pressing, 50 % by mass
- Textile weave
  - Linen bonding, 66 % by mass
- Roving (uniaxial), 75 % by mass

A high modulus of elasticity in the resin and good adhesion between glass and resin improve the compression strength of the material. Maximum bending strength levels are obtained with GFP composites in which reinforcing glass textile is applied to the side of the structural component exposed to tensile strain. Impact force absorption in GFP is mainly elastic. Under exposure to vibration stress, the tolerable strain amplitude as the number of stress reversals increases. The behavior of GFP thus resembles that of light metals, whereas the Wöhler curves for steel approach a limit value – the fatigue strength under reversed stresses of GFP drops down permanently. The notch impact strength drops in GF-reinforced molding materials, although this effect is not as pronounced under exposure to cold as in unreinforced molding materials. Lower shrinkage and a lower coefficient of linear thermal expansion result in greater dimensional stability of the moldings. Sound damping is more pronounced under exposure to vibration stress. The lower enthalpy levels in reinforced molding compounds result in shortened processing cycles.

The erstwhile climax in the 50-year history of glass fiber technology is represented by a product [83] (type: Zen Tron, manufactured by Owens Corning) with a tensile strength 15–50 % greater than that of other high-strength glass fibers, both standard and other types. The composition of the glass, combined with optimized fiber orientation in the composite, also makes for a higher modulus of elasticity as well as an increase in impact strength of as much as 50 %. Impregnation adhesion, for example with epoxide or vinyl ester resins, is achieved by means of a special sizing compound that also increases the rate of production. This high-strength fiber can be processed by means of pultrusion and winding methods. Expected applications are in the fields of pressurized containers, shipbuilding, and the construction industry.

6.5 Organic Reinforcing Fibers

When an applications engineer thinks of typical reinforcing fibers for plastics the first thing that comes to mind will be glass fibers. In the actual history of this technology, however, the use of organic fibers began several decades earlier with the use of natural cellulose fibers to reinforce phenolic resins (Fig. 37).

Deformations in textile fibers are measured on force-elongation curves $F = f(\varepsilon)$, and not on stress–strain curves $\sigma = f(\varepsilon)$ as with technical fibers, plastics, and rubbers. The curves $F = f(\varepsilon)$ often show a weak maximum characterized by the *breaking force* F_{max} (or force at break) at the point of *elongation at break* ε_{max}. This point is sometimes followed by the somewhat lower value of the force at rupture F_{B} at the point of *elongation at rupture* ε_{B}.

F_{max} and F_{B} are not, however, indicated as such, but rather as force (e.g., in Newton N) per unit of linear density or titer (e.g., in tex), i.e., as the *count (or denier) breaking strength E/m* (or tenacity; no official ISO symbol), i.e., the specific (= mass-related) energy (e.g., 1 N/tex = 1 (J m^{-1})/(10^{-6} kg m^{-1}) = 1 10^6 J kg^{-1} = 1 MJ kg^{-1}). These values can be combined with the density for conversion into tension values, e.g., (value in N/tex) × (density in g cm^{-3}) = (tension in GPa). Older publications incorrectly use mass (as a measure of *weight*) instead of force, and also express the titer in terms of denier count; the conversion is as follows: (value in N/tex) × 11.33 = (value in gf/den or gpd) (gf = gram force; gpd = gram poid denier). The (textile) *moduli* are not derived from the initial rise of

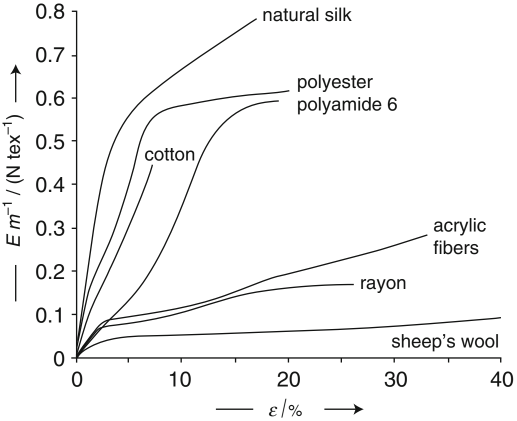

Fig. 37 Count or denier breaking strength of different fiber types as a function of elongation ε [81]

the curve $E/m = f(\varepsilon)$, but rather as the *tangent modulus* from the origin and as *secant modulus* from the origin to a given elongation value ε or as a chord modulus between two elongations ε_1 and ε_2 [81]

6.5.1 Natural Organic Reinforcing Fibers

The best-known renewable primary sources for natural fibers are wood and cotton. Both of these natural materials consist of basic fibrous units known as fibrils, the diameter of which is probably equivalent to that of the cellulose crystallites. Crystalline and amorphous regions alternate along the length of the fibrils. Several elementary fibrils may also be united in fibrillary structural units [84].

The importance of technically useful plant fibers has increased in recent years. Table 30 [81] compares some of their properties. Additional information is provided by, for instance, Elias [81, 109, 110, 111].

6.5.2 Synthetic Organic Reinforcing Fibers

Whereas natural fibers, mainly in the form of short fibers and fabric chips, have found application above all in the curable phenoplast and aminoplast molding compounds, it was more than anything else the development of the polyesters and epoxy resins that made it necessary to develop new kinds of reinforcing fibers to optimize the properties of these products as well. Modern, high-strength, synthetic organic fibers are the results of these efforts [112].

Polyacrylnitrile

The production of PAN fibers, which commenced around 1950 at about the same time in the USA and West Germany, now accounts for about 20% of worldwide chemical fiber production and 10 % of total fiber production (i.e., of chemical and natural fibers) – a production volume equivalent to that of worldwide wool production. A wool-like character and good coloring qualities have ensured these fibers a position next to the polyester and polyamide fibers. The substitution of asbestos starting around 1980 (because of the fine dust resulting from processing of this material) was the starting signal for further development of textile PAN fibers by means of chemical and physical modification. The resulting products are high-strength fibers (with about three times the breaking strength of textile types at 75 cN/tex) with kidney-shaped cross-sections, which have proven their worth as top-grade substitute materials in numerous asbestos cement products as well as phenolic resin-bonded frictional and brake liners [85]. See Elias [81] for more detailed descriptions of acrylic fibers.

Table 30 Properties (mean properties in some cases) of different technical plant fibers

Property	Rel. hum. (%)	Phys. unit	Hemp	Jute	Gambo	Sisal	Abaca	Hene-quen	Kapok	Coconut
Length	–	mm	5–55	0.7–6	1.5–11	0.8–8	2–12	1.5–4	15–30	0.2–1.0
Diameter	–	μm	10–51	25–200	12–36	50–200	6–46	8–33	10–30	100–450
Count (fineness)	65	km kg^{-1}	140	490	180	40	32	32	–	–
Density	65	g cm^{-3}	1.48	1.3–1.5	–	1.45	–	–	–	1.15
Module, textile[a]	65	N/tex	18–22	13–26	–	9–22	–	13	13	4–6
Breaking strength, text[a]	65	N/tex	0.57	0.38	–	0.40	0.64	0.39	0.24	–
Elongation at rupture	65	%	1.6	1.2–1.7	2.7	2–7	2–4.5	3.5–5	1.2	15–40
Moisture regain	65	%	12	14	–	–	–	–	–	–

[a] Reference value: The textile modulus of elasticity of cotton is 5.7 N/tex [18]

Polyester Fibers

Standard polyester fibers consist of poly(ethylene terephthalate). Fibers made of poly(trimethylene terephthalate), poly(butylene terephthalate), and poly(1.4-cyclohexane dimethylol terephthalate) are produced in smaller volumes.

Polyester fibers are the most universal chemical fibers, since they are most readily adaptable to changing fashions and applications by means of chemical, physical, and textile modifications (Table 31), which also explains their high production volumes. Filaments of polyester fiber are silk-like. Most polyesters, however, are used as cotton-like or wool-like staple fibers [81].

There has been recent success in the production of *superfils* from polyesters, polyamides, and other polymers using a variety of methods. These fibers include everything from fine fibers (1 dtex–0.1 dtex) to the actual *microfibers* (0.3 tex–0.1 dtex) and ultrafine fibers (10^{-3} dtex) and ultrasuperfine fibers (10^{-4} dtex). These fibers are much finer than natural silk thread (~1.3 dtex) [81].

Microfibers can be produced by the mechanical method using spinnerets (spinning nozzles) with many holes and lateral air jets. The pore width of the resulting knitted fabrics is ~1/3,000th the diameter of a raindrop, so that water droplets cannot penetrate into them, especially when poly(tetrafluorethylene) fibers are used (*Gore-Tex*®), but allowing water vapor to exit through them. Such fabrics made of microfilament yarns, with counts of 0.5 dtex, are free-breathing and watertight [81].

Other methods are based on polymer blends of two immiscible polymers, a water-soluble matrix [e.g., poly(vinyl alcohol)] and an insoluble fiber-forming component [e.g., poly(ethylene terephthalate)]. Upon extrusion, the streamlined flow characteristics produce a fibrillary morphology. The matrix is extracted after cold drawing. The resulting foamed slurry is then filtered off and spun into microfibers with a diameter of 0.1–10 µm. Using this method, ultrasuperfine fibers with counts of 10^{-4} dtex are obtained for use as filter material [81].

Table 31 Properties of polyester fibers at 21 °C and 65 % relative humidity [86]

Property	Phys. Unit	Filaments		Staple fibers	
		Regular	High breaking strength	Regular	High breaking strength
Applications		Weaves, knits	Tire cord fabric, industrial yarns	Mixtures with wool or cotton	Industrial fibers, sewing yarns
Density	$g\ cm^{-3}$	1.38	1.39	1.38	1.39
Module, textile	N/tex	6.6–6.8	10.2–10.6	2.2–3.5	4.0–4.9
Breaking strength, textile	N/tex	0.35–0.5	0.62–0.85	0.35–0.47	0.48–0.61
Elongation at rupture	%	24–50	10–20	35–65	17–40
Elast. recovery after 5% elongation	%	88–93	90	75–85	75–85
Moisture regain	%	0.4	0.4	0.4	0.4

Polyester fibers are frequently used in combination with cellulose fibers and fabric chips to produce impact-resistant PF molding compounds. In combination with glass fibers, they increase the impact strength of reinforced UP molding materials as required.

Polyamide Fibers

The most important polyamide fibers in technical terms are based on PA 6.6 and PA 6, and the latter at first accounted for only 10% of total PA fiber production but has seen this figure increase appreciably in recent years. Polyamide fibers are used to improve the elasticity and creep resistance of PF molding compounds.

"Polyamide 6 and 6.6 threads are characterized by high levels of breaking and bending strength and abrasion resistance, a broad range of elongation adaptability, good texturizing capacity and sufficient form stability to make them suitable for applications in heavy-wear textiles such as stockings, floor coverings and technical textiles. The coloration properties can be varied over a wide range by means of copolymerization with monomers including acidic or alkaline groups, variation of end groups or grafting of other monomers. In polyamide cord for tires, the relatively high modulus of elasticity is undesirable. It can, however, be reduced by melt blending of polyamides with polyesters, whereby however the end groups of the polyamides must be blocked to prevent them from catalyzing a chain termination in the polyesters [81]."

Table 32 shows properties of polyamide yarns.

Polyvinyl Alcohol and Polyolefin Fibers

Staple fibers made of PVAL are still produced in North Korea and China today (estimated production capacities 50,000 and 150,000 t/a, respectively).

Table 32 Textile properties of polyamide yarns [81]

Property	Phys. unit	Polyamide 6	Polyamide 6.6	Polyamide 4.6
Density	g cm^{-3}	–	–	–
Crystallinity	%	23	37	45
Melting temperature	°C	221	266	290
Ironing temperature, maximum	°C	150	180	–
Washing temperature, maximum	°C	60	71	–
Textile module 25 °C (conditioned)	cN/tex	279	360	324
120 °C	cN/tex	135	153	225
Breaking strength, textile	cN/tex	85	85	86
Elongation, conditioned	%	33	–	–
Shrinkage, 180 °C	%	12.0	7.8	5.3
Moisture regain, 65 % RH	%	7.5	7.5	–

Table 33 Mean properties of olefin and vinyl fibers (filaments)

Property	Rel. hum. %	Phys. unit	PP	HDPE[a]	PTFE	PVC	PS	PVAL
Density	65	g cm^{-3}	0.90	0.94	2.2	1.40	1.05	1.28
Textile module	65	N/tex	6.0	2.5	1.2	3.0	–	3.8
Breaking strength, textile	65	N/tex	0.62	0.27	0.13	0.25	0.48	0.66
	100	N/tex	0.62	0.27	0.13	0.24	0.50	0.50
Elongation at rupture	65	%	20	30	23	17	<10	16
	100	%	20	30	23	16	<10	21
Moisture regain	65	%	0	0	0	0.1	<0.1	4.2
Water retention capacity	100	%	0	0	–	5	–	30
Melting temperature	0	°C	165	125	325	–	–	250[b]
Glass transition temperature	0	°C	−14	−80	−52	68	100	81
Oxygen index (LOI-O)	0	%	17	18	95	32	18	22

PP it-poly(propylene), *HDPE* conventional fibers made of high-density poly(ethylene), *PTFE* poly(tetrafluoroethylene) (Teflon), *PVC* poly(vinyl chloride), *PS* atactic poly(styrene), *PVAL* poly (vinyl alcohol)

[a] Maximum values for high-modulus fibers: $\rho = 0.97$ g cm^{-3}; $E = 172$ GPa; $\sigma_B = 3.0$ GPa; [81]

[b] Disintegration value

"In Japan, dry-spun filaments are produced with considerably improved mechanical properties (1993: Production 36,000 t/a, capacity 80,000 t/a). Poly(vinyl alcohol) filaments have high breaking strengths (Table 33) and 90 % of them are therefore used for industrial purposes (fishnets, conveyor belts, etc.), as well as more recently as short-fibered additives in production of paper and textile composites [81]."

Table 33 also shows properties of other vinyl and olefin fibers for comparative purposes.

"The *poly(olefin) fibers* are manufactured in the largest volumes thanks to the low cost of the polymers and the simple melt-spinning production technology. Annual worldwide production of textile products based on poly(olefins) was ~1.7 10^6 t/a in 1985, ~90 % of which was isotactic poly(propylene) PP and ~10 % high-density poly(ethylene) HDPE [81]."

"About half of the fibrous poly(olefin) textile products are produced in the form of strips, split fibers or monofilaments, another third as staple fibers and the rest as filament yarns and textile composites. All poly(olefins) are characterized by excellent resistance to acids, alkalis and other chemicals. Due to this lack of affinity, on the other hand, all poly(olefin) fibers can only be colored by means of melt pigmentation [81]."

"*it-poly(propylene)* dominates the field because of its excellent breaking strength (Table 35). Although its theoretical modulus of elasticity is much lower than that of poly(ethylenes), it crystallizes more readily and thus has a higher technical modulus of elasticity than poly(ethylene) (Table 35). By gel-spinning *ultrahigh molecular poly(ethylenes)*, however, highly oriented (>95 %), highly crystalline (≈85 %)

fibers with densities of 0.97 g/cm^3, moduli of elasticity of 90 N/tex (∴ 87 GPa) and breaking strengths of 2.7 N/tex (∴ σ_b 2.6 GPa) (Dyneema®, Spectra®) [81] are obtained".

PVAL fibers are made water-insoluble by treating them with formaldehyde. They show good adhesive qualities with many plastics and result in greater impact strength. In the plastics industry they are also used as reinforcing mats in plastic laminates.

Elasthane Fibers

The second major group of elastic fibers are the elasthane fibers (US: Spandex), made from block copolymers with urethane and ether segments. They are produced by a reaction of diisocyanates with linear oligomeric polymers possessing hydroxyl end groups (macroglycols) and chain extenders (diamines or glycols). These polymers are processed by means of melt or solution spinning. In the case of elasthane fibers, the "hard" polyurethane segments serve as the physical cross-linkage segments for the rubber-like matrix made up of "soft" polyether segments. Elastomeric bicomponent fibers contain hard components made up of polyamides or polyesters and soft components comprising segmented polymers with hard polyurethane or polyester segments [81].

Aramide Fibers [see [81]]

Aramide fibers, according to a definition issued by the US Federal Trade Commission, consist of long-chained synthetic polyamides in which at least 85 % of the amide groups are bound directly to two aromatic rings. DIN specifies that such aramides can also contain imide groups. The worldwide production volume of aramide fibers is ~40,000 t/a.

These fibers are naturally flame-resistant. They neither melt nor shrink. The permissible temperature range for long-term use is −200 °C to +160 °C.

The tribological properties of thermoplastic bearing materials such as PA, POM, PBT, and PC can be improved considerably by reinforcing them with wear-resistant aramide fibers [87].

Depending on how much stress is applied to a particular molding, hybrid reinforcements consisting of AF and GF or AF and CF are used. Separation of cured laminates requires special tools [88, 89].

The aramide fibers include those made of poly(*m*-phenylene isophthalamide) (Nomex® types) and poly(*p*-phenylene terephthalamide) (Kevlar® types). The industrially produced aramide fiber Technora is a copolyamide.

The *polybenzimidazole fiber* PBI was originally developed as a flame-resistant textile fiber for the US aerospace program. Because of their high oxygen index, they are inflammable, do not melt, and also give off little or no toxic gasses, and no smoke, at temperatures below 550 °C. This material is also suitable for other applications, for example as a substitute for asbestos in protective gloves and in protective suits for workers at metal smelters and flue gas filters.

Poly(m-phenylene isophthalamide) forms lyotropic liquid crystals. Fibers can therefore be spun at lower concentration from isotropic solutions and at higher concentrations from nematic solutions. Because of their high degree of chain segment orientation, fibers spun from nematic solutions show, as expected, higher moduli of elasticity, tensile strengths and lower elongation at rupture values than those spun from isotropic solutions.

As the graphic structural formulae would lead one to expect, the chain segments of *poly(p-phenylene terephthalamide)* seem significantly more drawn than those of the poly(*m*-phenylene isophthalamides). Spinning poly(*p*-phenylene terephthalamide) out of nematic solutions in, for example, sulfuric acid, therefore results in improved moduli and tensile strengths under regular spinning and drawing conditions (Kevlar 29), and these properties can be further improved under certain conditions (Kevlar 49). Coloration of these fibers presents a difficulty, since they lack sufficient groups or an “open” fiber structure to take up the dyestuffs and spin dyeing with pigments generally disturbs the crystalline structure, resulting in poorer mechanical properties.

Kevlar fibers are temperature-resistant special fibers used, for instance, in bulletproof vests. The main application of Kevlar is, however, as a reinforcing fiber in composites. One drawback here is the lack of compression strength of the fibers, presumably due at least in part to the mantle–core structures produced by spinning from sulfuric acid solutions. Helical kink band defects appear when Kevlar is compressed. Composites with Kevlar as a reinforcing fiber therefore do not fail due to rupturing of the fibers or matrix, but rather due to an elastic fault caused by shearing forces.

Kevlar 49 has a high elasticity-to-shear modulus ratio accordingly – about 70. This ratio is much lower with other fibers, for example around 2.0 (glass fibers), 3.2 (sheep’s wool), 3.7 (cotton), or 5.8 (polyamide 6.6). A really high ratio is only found in flax – 19 [81].

PBO Fibers

P-phenylene-2.6-benzobisoxazole (PBO) is a semicrystalline polymer. The company Toyobo began production of this fiber in 1998 under the brand name Zylon®.

Next to plastic fibers made of PPS, polyester and PI, aramide fibers are among the most competitive.

There are two different Zylon® fiber types

- Zylon HM (high-modulus fiber)
- Zylon AS (spinnable fiber)

Their properties are as follows:
Advantages

- The modulus of elasticity of PBO fibers is higher than that of aramide fibers
- The heat resistance of Zylon® is greater than that of the other fibers
- High level of resistance during heatup
- High level of flame resistance when working with parting-off grinders and welding equipment
- Zylon® (PBO fiber) represents the next generation of fibers with strength and moduli nearly twice as high as those of p-aramide fibers
- The dissolution point of Zylon® is 100 °C higher than that of p-aramide fibers.

Disadvantages

- Considerably more expensive than aramide
- Zylon® cannot be cut, resulting in significant fabrication problems.

Table 34 compares the properties of PBO fibers (Zylon®) with those of other fiber types.

Applications of Zylon to date include

- Rubber reinforcement, for instance in tires
- Safety equipment such as safety belts, gloves, shoes, clothing items for police and firefighters
- Sports clothing, sports equipment such as sails, nonwearing textiles for racing drivers and riders, ski poles, bicycle rims.

Carbon Fibers

Until the early 1960s, glass and asbestos fibers were the most important high-strength inorganic reinforcing materials for thermosetting resins as well as for duroplastic and thermoplastic molding compounds. GF-reinforced molding resins

Table 34 Comparison of the properties of different fibers [90]

	Zylon HM	Zylon AS	p-Aramide	m-Aramide	Steel fibers	Carbon fibers	PBI	Poly-esters
Tensile strength [cN/dtex]	37	37	19	4.7	3.5	20	2.7	8
Tensile strength [GPA]	5.8	5.8	2.8	–	–	–	–	–
Elongation at rupture [%]	2.5	3.5	2.4	22	1.4	1.5	30	25
Density [g cm^{-3}]	1.56	1.54	1.45	1.38	7.8	1.76	1.4	1.38
Moisture content [%]	0.6	2.0	4.5	4.5	0	–	15	0.4
LOI	68	68	29	29	–	–	41	17
Thermal resistance in °C	650	650	550	400	–	–	550	260

do achieve more favorable strength: density (σ/ρ) ratios than metals, but their rigidity/density ratio (E/ρ) is less favorable. This places limitations on the technical applicability of GF-molding materials. Development research therefore focused on new reinforcing materials with higher rigidity/density ratios. The most promising materials of this type available today are the C and aramide fibers. Boron fibers, touted for a time in the US, have now receded into the background because they cannot be processed in textile forms. The price of C and A fibers is still high (although it is beginning to drop), forcing users to optimize their applications and designers to think "anisotropically."

The production process for C fibers, based mainly on polyacrylonitrile (PAN) fibers, comprises two steps (pyrolyzing at 300 °C and carbonizing at 1,600 °C) and results in so-called LS (low strength) and HS (high strength) fibers. The next processing step (graphitizing at 3,000 °C) produces the HM (high modulus) and UHM (ultrahigh modulus) fibers, Table 35 [82].

The fibers are naturally drawn during the production process. The LS and HS fibers serve as filter mediums, catalyst carriers, and reinforcing fibers in composites. They have excellent ablation properties. Their relatively low electrical resistance has led to their use in flexible heating elements and wherever a bendable, nonmetallic conductor is required.

The HM and UHM fibers, with their very high modulus of elasticity of 400 kN mm^{-2} (HS fibers 230 kN mm^{-2}) and resulting high rigidity/density ratio, make possible composite constructions that are three to nine times as rigid as with titanium, steel, or aluminum. C fibers are produced as rovings, with 1,000–1,500 individual threads, as staple fibers and in the form of greatest technical significance: the prepreg.

Ten years ago, most C fiber applications were still in sporting equipment. Now, consumption is moving into the fields of sailing and passenger ship construction (see under Composites) as well as combat aircraft, general construction, aerospace engineering, racing sports, running sports, and self-defense. Automotive engineering is a hopeful area for future applications (engine and body). However, series production with this material will require processing techniques that differ considerably from the methods used to date.

Table 35 Properties of carbon fibers based on pitch or poly(acrylonitrile) (PAN)

Property	Phys. unit	PAN HS	PAN HM	PAN UHM	Pitch HM	Pitch I
Filament diameter	μm	7.5	7.5	8.5	10	–
Density	g cm^{-3}	1.78	1.85	2.0	2.15	1.55
Modulus of elasticity	GPa	240	400	535	690	40
Tensile strength	GPa	3.75	2.45	1.85	2.24	0.9
Elongation at rupture	%	1.55	0.65	0.35	0.3	2.3
Viscosity	MPa	20	7.5	3	–	–
Linear coefficient of elongation	$10^{-6}K^{-1}$	−0.6	−1.0	−0.9	–	+3
Thermal conductivity	W m^{-1C-1}	15–20	60–100	–	–	15

HM high modulus, *UHM* ultrahigh modulus, *HS* high-strength, *I* made from isotropic liquid; [81]

The further development of the HS types based on PAN aims above all to increase elongation at rupture up to 2 % (heretofore: 1.0–1.4 %), at the same time increasing the modulus of elasticity and tensile strength. At $\varepsilon = 1.7$ %, instead of 1.2 %, and a modulus of elasticity of 250 kN mm^{-2}, the result would be a tensile strength of 4,250 N mm^{-2} on the basis of $\sigma = \varepsilon \cdot E$. In the HM types, a further increase in the modulus of elasticity combined with a rise in elongation at rupture is the target combination. A number of manufacturers are offering so-called intermediate types (IM). These materials combine a raised elongation at rupture and strength with a relatively high modulus of elasticity. Further developments in C fibers will have to take into account the fact that the elongation at rupture of the matrix material is 2–3 % at most. If the elongation of rupture of the fibers was at the same level they would be unable to bear any additional load.

More recent developments that will soon see series production in the automotive industry will facilitate low-cost placement of local structural component reinforcement with C fiber bundles combined with process engineering using a thermoplastic matrix (PP, PA, PET, PC) in 30-second cycles (see also under processing of thermoplastic fiber composites in the LFT-D process).

All of these fibers are used as reinforcing materials. The rigid carbon fibers do not, however, form loops well, making yarn knitting difficult. The problem is solved by knitting with precursor yarn materials (e.g., poly(acrylonitrile), which are then carbonized (CCPF = chemical conversion of precursor fiber) [81].

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Processing (Primary Forming) of Plastics into Structural Components

Peter Eyerer, Volker Gettwert, Axel Kauffman, and Michael Kroh

Abstract The next step in the engineering cycle after properies is processing. The different process techniques influence the design, properties, and life time of a component during use. Therefore, the opportunities and risks associated with the application of polymer components are also influenced by processing. This chapter summarizes a multitude of processing techniques for the very different kinds and structures of plastics, including rapid prototyping.

Keywords Additives, Compounding, Deformation of melts, Extrusion foaming, Flow properties, Influences of processing on properties, Injection molding, Plastic melts, Processing of elastomers and thermosets, Processing of fiber composites, Processing of thermoplastics

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P. Eyerer (ed.), *Polymers – Opportunities and Risks I: General and Environmental Aspects*,
Hdb Env Chem (2010) 11,
DOI 10.1007/978-3-540-88417-0_4,

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1 Introduction

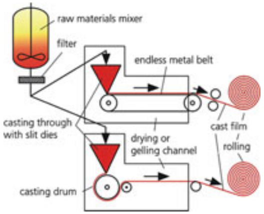
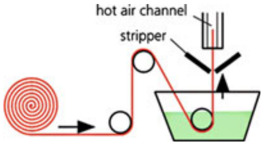
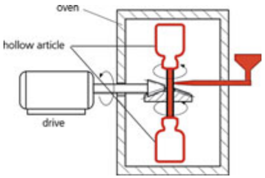
Most plastics are processed in a completely separate operation following synthesis by a raw materials manufacturer. The two processes are therefore separated by cooling, reheating, and in some cases multiple transport. Exceptions to date are the polyurethanes RIM, RRIM and SRIM and niche applications such as caprolactam synthesis in the mold, so-called cast PA. On the other hand, production of semifinished goods with glass mat-reinforced thermoplastics (GMT), in most cases with PP matrix, rod (or long fiber) granulates with long glass fibers or SMC, is now the state of the art. Changes are in sight, however, for some processing technologies. Complex intermediate steps will be eliminated, processors will increasingly concentrate on material design (compounding), with the raw materials manufacturer supplying the semifinished goods. On the other hand, no basic processing changes are on the near horizon for standard injection molding and extrusion processes.

Table 1 provides an overview and summary sketches of the frequently used plastic processing methods.

2 Compounding and Additives

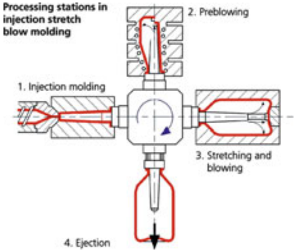
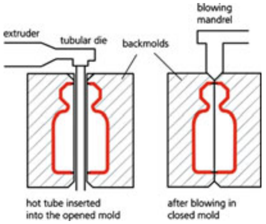
Compounding is the designation for all the process methods applied to render a plastic raw material into a processable molding compound. As a rule, various

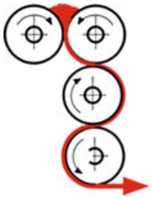
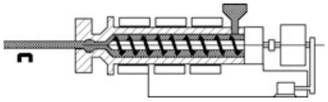
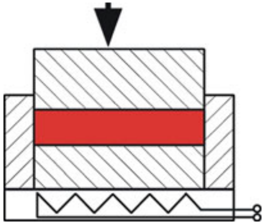
Table 1 Overview of plastic processing methods [1] (also using [2, 3])

Process	Process engineering	Preferred polymer material	Applications	Remarks
Polymerization in situ/in chambers	Monomer and initiator are filled into mold. Temporal and spatial control of polymerization process by means of introduction and dissipation of heat energy and variation of the initiator amount	PMMA	Wafers, blocks, tubes, optical lenses, bone cement	Good surfaces are obtained between glass plates; volume reduction can be compensated by elastic wires
Molding	Reaction injection molding (RIM)	PA 6 (in situ caprolactam synthesis)	Ship propellers, large-scale gears, cable pulleys, blocks, bearing casings	
Cast film extrusion	Casting of a polymer solution or paste through a slit die onto a rotating drum or endless belt, solvents, e.g., methylchloride, chloroform	CA, PTFE	Films, foils, (0.01–0.1 mm), photographic industry, packaging, electroengineering (condensers)	
		PVC pastes	Floor coverings	
Dipping	Dip coating of textiles or dipping of objects into polymeric solutions or dispersions followed by gelling or crosslinking in ovensDip molds: ceramics or metal	PVC PVAC PVAL	Textile coating, rubber finger gloves, protective boots, anti-corrosion immersion packaging	
Rotomolding	Stress-free hollow articles are produced at low rotation rates. Metered amounts of raw materials are applied to the interior wall of hollow articles rotated in two directions and heated externally in even layer thicknesses, then gelled, melted and polymerized to the surface	PE, PS, POM, PA 11, PA 12, cellulose ester, PVC pastes, PC	Balls, dolls, traffic warning units, arm supports, large containers, cable drums, sandwhich constructions, e.g., with foamed middle and cover layers made of other plastics are possible	

(*continued*)

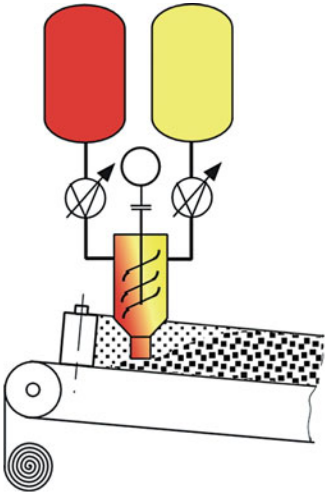
Table 1 (continued)

Process	Process engineering	Preferred polymer material	Applications	Remarks
Centrifugal casting	Rapidly rotating molds, plate casting machines, hollow cylinder centrifugal drums	PA 6, soft PVC, PMMA, PUR, (UP)	Toothed gears, rings, wafers	
Injection molding	Discontinuous process (piecewise), melting, mold filling, mold cooling while fluid melt is forced in at the same time, within the flow range, thermoplastics can be pressed into the hollow of a mold between ~150 and 300°C, where they then cool and solidify	Nearly all thermoplastics	Series moldings requiring no finishing (large series production)	
Injection blow molding	Injection molded preform is blow-expanded to form a larger hollow space in the entropy elastic state; biaxial stretching results in good strength qualities	PE, PO, PS, PVC, POM, PC, PETP	Household and beverage bottles, containers	
Extrusion	Continuous process (flow process), process steps, feeding and condensation, melting and mixing, pressurizing and pressure feeding, molding in extrusion mold, calibration and cooling	PVC, PE, PS, ABS, PA, PP, POM, CA	Wafers, tubes, profiles, flat films, cable jacketing, coating of supporting strips	
Extrusion blow molding	The (primary molding) tube exiting from the extruder is gripped by a two-part tool, severed and blow-expanded (primary molding). Cooling is also possible with CO_2 or direct filling with product to be packaged	PE, PP, PC, ABS, PVC, PE	Containers from 0.1 to 1,000 I, preferably made of PE	

Calendering	Forming of thermoplastic masses between two or more rollers with an endless beltProcess steps: Preprocessing with preplasticizing, film casting	PVC, PE, PP, PS, ABS	Films and foils in packaging, office applications	
Compression molding	Preferred with duroplastics and elastomers; with thermoplastic materials only good for structured surfaces and to make sample test articles. New: Long fiber-reinforced thermoplastics (LFT)	PVC, PMMA, etc. PVAC PVAL PE, MF, HF NBR, ACR, PP, PA	Optical items (lenses), phonograph records Automobile parts in large series	
Extrusion molding (ram extrusion with UHMW-PE)	Also for duroplastics; the ultra-high molecular polymers lack free-flowing characteristics: The powdered raw material, with lubricant is condensed and rammed through the heated profile mold	PTFE, UHMW-PE (ultra-high molecular weight polyethylene)		
Sintering	Powdered raw material is condensed in molds at a high temperature (190–350°C) and pressure of 10–80 N/mm^2 and sintered, sometimes for hours. Sintering occurs above the crystal melt temperature. The cooling time determines the degree of crystallinity and thus the material properties		Profiles, tubes, pipes, bands	
Laser Sintering	Powdered raw material is sintered under laser arrays	PEEK, PA	Rapid prototyping	

(*continued*)

Table 1 (continued)

Process	Process engineering	Preferred polymer material	Applications	Remarks
Foaming	Differentiation according to structure: (a) Foam materials with uniform density distribution – Thermoplastic melts (extrusion, calendering, compression molding) – Expandable individual particles, pastes – Reactive liquid primary components (continuous or discontinuous foaming in molds or on conveyor belts; also on site injection)	PS, SB, ABS, PVC, PE, PP, (EPP) PS, (EPS) PUR, PF, UF, UP	Foaming in place, e.g., steering wheel, floats (life jacket, surfboards, buoys), heat insulation elements, protective clothing, prostheses, seals, noise protection Styrofoam, packaging, inulation, agriculture Padding (PUR) (automobile seats, furnituremaking)	
	(b) Structural foams (foamed core, edge zone compact/foamed in place) Categories as with a). Further structural differentiation: open-cell, close-cell foams; technical differentiation between soft (DIN 53570/8) and hard foams (DIN 53220/30)	PS, SB, ABS, PVC, PE, PP, POM, PC, mod. PPO, PUR, PI, EP, UP	Exercise mats, protective helmets, structural elements (SMC-foamed) for interior and exterior constructions Armchair shells, joint foaming, shoes, embedding of electronic components	

additives are required [4] before a plastic can be processed (primary forming) after synthesis, for example:

Plasticizers
Adhesion promoters
Diluents
Lubricants
Reinforcing materials
Thixotroping agents

(e.g., paint is brushable, but does not run: A liquid is said to be thixotropic when its viscosity increases as the shear rate decreases).

In the compounding process [5–7] these additives (in mass percentiles of 0.01–60 %) are to be homogeneously distributed in the mass.

This is done by:

Comminution	In a rolling crusher, swing-hammer pulverizer, cutting mill, pinned disk mill, etc.
Mixing	In stirrers, drum mixers, paddle mixers, vortex mixers, screw mixers, etc.
Plasticizing	In kneading plasticizers, rolling mills, double screw extruders, in plasticizing, the dry plastic molding mass premix is melted and further homogenized, so that plasticizing is actually mixing in the plastic state
Pelletizing	Figure 1 shows a schematic presentation of a hot-die face pelletizing system

2.1 Influence of Moisture and Drying

Because of the importance of the moisture level in plastics processing, this parameter receives special attention within the compounding process. Table 2 illustrates a number of basic principles involving moisture in the melt and in the structural component. Table 3 shows examples of moisture sensitivity in some plastics, moisture regain and, using the example of polyamide 6, the influence of moisture on the material properties.

Processing operations have a choice of several systems for *drying of the granulates*, whereby the driers are often integrated in the material supply chain. Schroer and Wortberg [9] provide a summary report on this aspect.

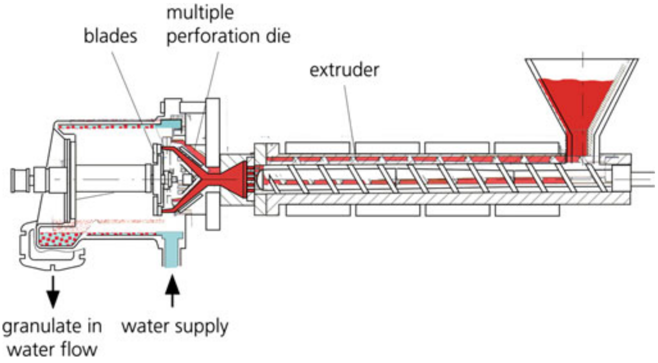


Fig. 1 Hot die face pelletizing [8]

Table 2 Influence of moisture on thermoplastics, basic principles

Cause	Effect	Remarks
Melt		
Plasticization	Enhanced flow properties	(Ir)reversible Often involves hydrolysis
Evaporation (due to pressure reduction)	Bubbles, streaks	
Injection-molded part		
Moisture uptake	Altered dimensions (swelling)	Reversible
Plasticization	Altered properties	
Hydrolysis (molar mass reduction)	Loss of properties	Irreversible; at RT very slow; at high temperatures rapid

Table 3 Influence of moisture on thermoplastics

Moisture sensitivity		
No hydrolysis	Absorption only	Hydrolysis
No drying required for:	Drying usually required for:	
Polyacetal (Delrin)	Acrylic resin plastics	Polycarbonate
Polyethylene	ABS	Cellulose butyrate
Polypropylene		Polyamide (Zytel, Minlon)
Polystyrene		Polyester (Rynite, Hytrel)
Polyvinyl chloride		Polyarylate (Arylon)
		Polyurethane

Moisture uptake (% by mass)	Room temperature		Max. moisture content for processing of melt	Hydrolysis rate at melt temperature
	50 %	100 % res. moisture	%	
Polyamide 6.6 (Zyl E101)	2.5	8.5	0.25	Slow
PET polyester (Rynite 530)	0.26	0.6	0.02	Rapid
Polyester elastomers (Hytrel 5556)	0.15	0.7	0.10	Medium
Polyarylate (Arylon 101)	0.35	0.9	0.02	Rapid
Polycarbonate		0.35	0.02	Rapid

Material properties – polyamide 6

Moisture content (%)	Change in linear dimension (%)	Flexural modulus *E* (N/mm^2)	Yield stress (N/mm^2)	Impact strength acc. to IZOD (J/m)
0.2	–	2,830	82.7	53.4
2.5	0.5–0.7	1,210	58.6	112.1

Raw material moisture influences the process reliability and product quality of high-grade plastics. Excessively high levels of processing moisture may result in foaming, ejection problems and process parameter scatter resulting from viscosity variations. The quality of the products may be influenced by occurrence of, for example, bubbles, waviness, and joint lines. Properties such as mechanical strength or elastic puncture strength may be negatively affected by moisture. In further processing, insufficient predrying of the granulate may result, for instance, in galvanizing or painting problems. Excessive drying of the material, on the other hand, can lead to discoloration, increases in viscosity, and a slacking off of physical properties. See [9] for further references.

3 Processing of Plastic Melts

The primary forming of plastics is generally a flow process. The individual macromolecules of thermoplastics, duroplastics, and elastomers must be mobile and capable of chain slipping. The duroplastics and elastomers do not crosslink or vulcanize until after forming, when they develop their characteristic crosslinked structure.

This gives duroplastics and elastomers, in contrast to thermoplastics, an inherent rigidity sufficient for mold ejection, even at high temperatures (above the main softening range). Amorphous thermoplastics, on the other hand cannot be ejected until temperatures below the main softening range are reached, and the different semicrystalline thermoplastics at ~50–100 °C below the crystallite melting temperature. Primary forming of all plastics, with the exception of some rolling and pressing processes, can be illustrated schematically as follows (Fig. 2):

The plastic mass is plasticized by the introduction of energy, then pressed into the desired form under pressure (injection molding, extrusion, blowing, etc.).

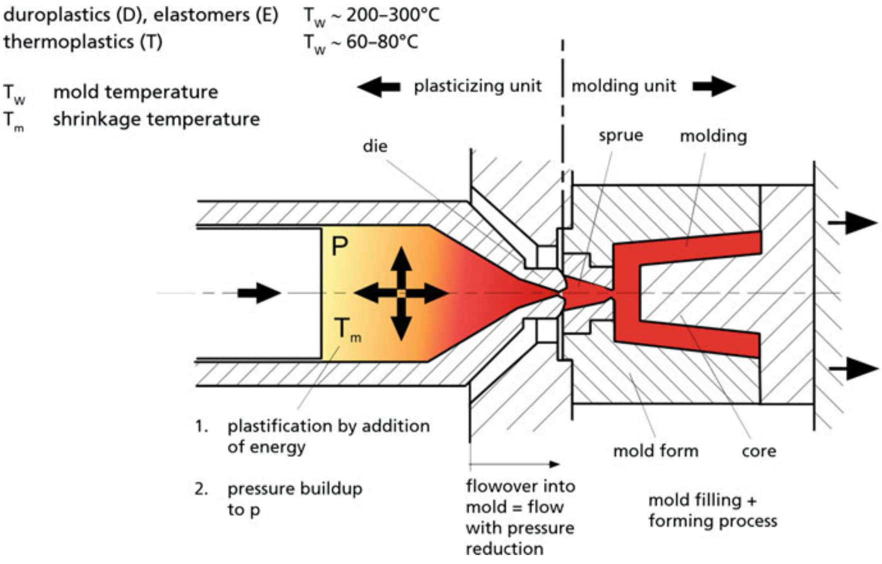


Fig. 2 Scheme showing primary forming of plastics (T, D, E)

The shearing forces deform, i.e. orient, the macromolecules. The degree of orientation reached in the molding depends on the magnitude of the shearing forces at work in the forming process, which are in turn influenced by the shear rate.

3.1 Flow Properties of Melts

The flowability of a plastic melt depends essentially on the mobility of the molecular segments (and therefore on the temperature), their form, their degree of entanglement and branching, their molar mass and their distribution.

3.1.1 Rheology of Plastic Melts

The description, explanation, and measurement of flow properties of materials (for example of plastics) is the main object of the "science of deformation and flowing of bodies" known as "rheology."

To be processed, plastics must generally be in a flowable state. In the case of thermoplastics, this state is reached by melting.

Viscosity is a measure of the internal resistance of the material to a constantly acting force applied during the flow process.

The forces acting on the melt in the flow process that occurs in plastic processing machinery are mainly shearing forces (IKV, Aachen) [6].

It is necessary to differentiate between *shear flow* (flowing through an extrusion die in primary forming processes) and *elongation flow* (change in cross-section, e.g., during drawing), whereby the two processes usually overlap in real situations. Whereas in shear flow the melt front moves in only one direction, Fig. 3a, an additional orientation effect due to elongation flow occurs in a two-dimensional melt front shift see Figure 3b.

It can be demonstrated in a quarter-circle graph, Fig. 3b, how in a volumetric element spreading concentrically about the sprue gate is elongated more and more in the cross-sectional direction. The elongation forces orient the macromolecules, and glass fibers, in the direction of the elongation flow and thus at right angles to the direction of flow. This also applies, for example, to plates injected from the center and to most injection-molded parts.

The liquid layers between the plates moving in opposite directions slide off on another – the liquid is sheared (Fig. 4).

The shearing stress deforms the cuboid at the shear rate $\dot{\gamma}$ (also known as the shear gradient), Fig. 5:

$$\frac{\mathrm{d}v}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\mathrm{d}s}{\mathrm{d}t}\right) = \left(\frac{\mathrm{d}s}{\mathrm{d}y}\right) = \frac{\mathrm{d}\gamma}{\mathrm{d}t} = \dot{\gamma}$$

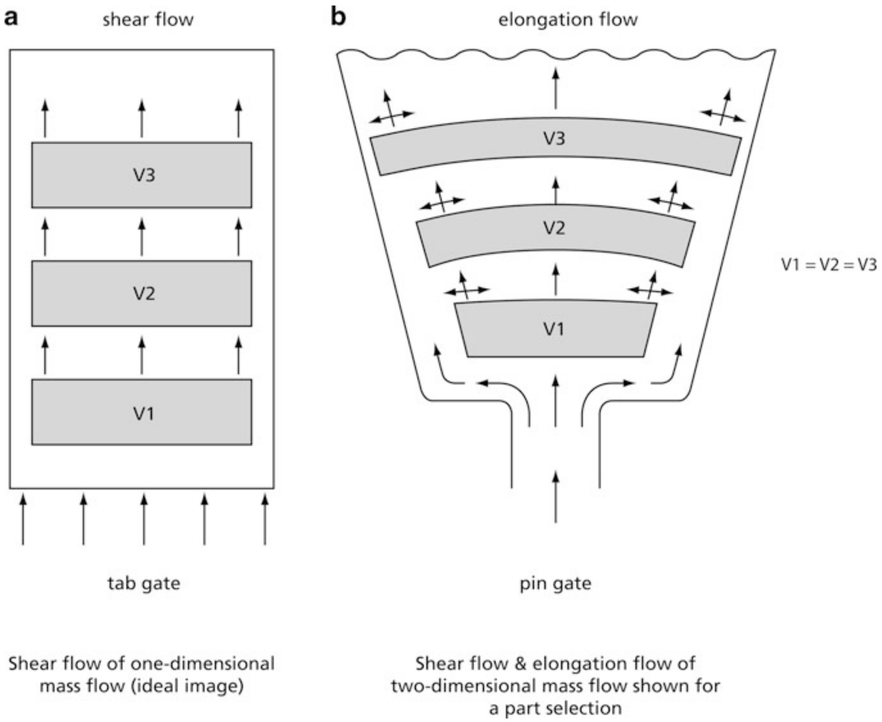


Fig. 3 Schematic illustration of shear flow and elongation flow (according to [10])

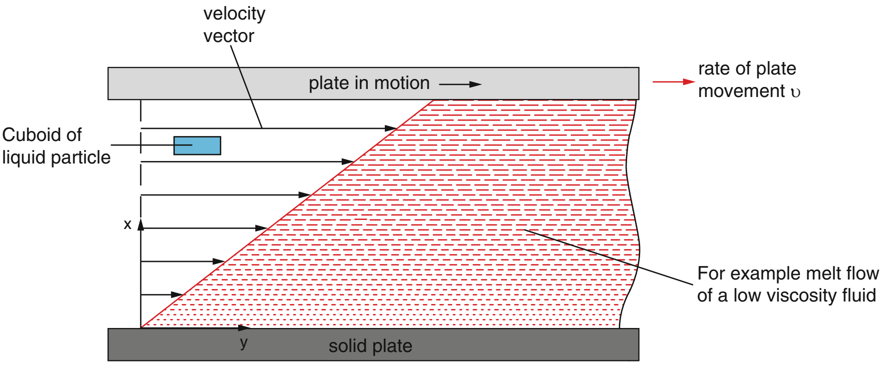


Fig. 4 Schematic illustration of shear flow in a laminar flow (rate distribution in two-plate model with wall adhesion) (according to [11])

The shear rate is the ratio of the rate difference Δv between two layers flowing past one another to their distance y (at right angles to the direction of flow).

It expresses how rapidly a particle lying between different layers changes its form while the layers move on at the flow rate.

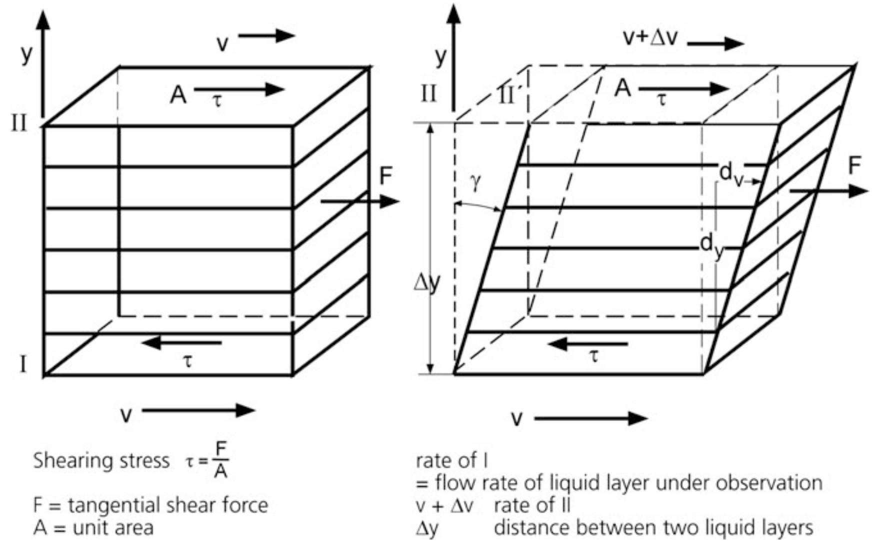


Fig. 5 Explanation of shearing stress and shear rate illustrated by a particle in the liquid [11]

In so-called Newtonian flow behavior (e.g., with water and oil), the shearing stress τ and deformation rate (shear rate) $\dot{\gamma}$ are proportional.

$$\tau = \eta \cdot \dot{\gamma}$$

The coefficient η is known as viscosity.[1]

Most liquids, including plastic melts, do not behave in accordance with Newtonian flow at medium and high shear rates. The simple viscosity datum will therefore not suffice as a characterization of such liquids, but rather the flow behavior is indicated by a curve, Fig. 6, plastic melts flow viscously.[2]

These non-Newtonian flow properties of the melts are designated by the term intrinsic viscosity.

Figure 6 illustrates, ignoring solidification on the wall, the influence of the flow behavior of plastic melts on rate profiles in tube flow.

In real situations, various different rate profiles will be established across the cross-section as per Fig. 7, depending on the continuation of the solidification process at the molding tool wall.

---

[1] More exactly: dynamic viscosity μ Nsm^2 $\triangleq$1 Pa sOlder dimension: 1 poise (P) $\triangleq$ 0.1 Pa s; 1 Centipoise (cP) $\triangleq$ 1 millipascal second (mPa s); also called kinematic viscosity

$$\upsilon = \frac{\eta}{\rho} : \upsilon..\mathrm{cm}^2\mathrm{s}^{-1} \overset{\wedge}{=} \mathrm{Stokes(st)}$$

[2] Plastic flow is the persistent deformation observed in solid bodies when a certain minimum strain level (flow point) is exceeded; viscous flow, on the other hand is the persistent deformation in the entropy elastic range as well as in the melt or flow range of plastics.

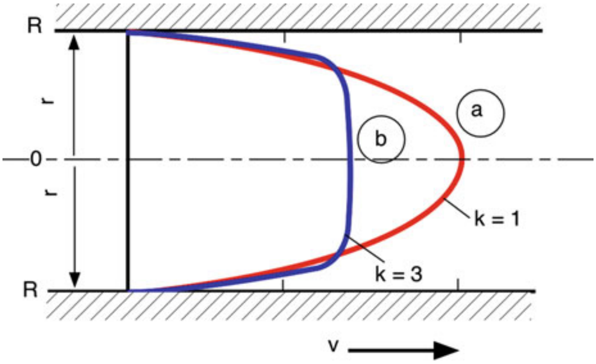


Fig. 6 Dependence of rate on radius *r* in tube flow [12] (**a**) Newtonian flow; $k = 1$. (**b**) Structurally viscous liquid; $k = 3$ plastic melts

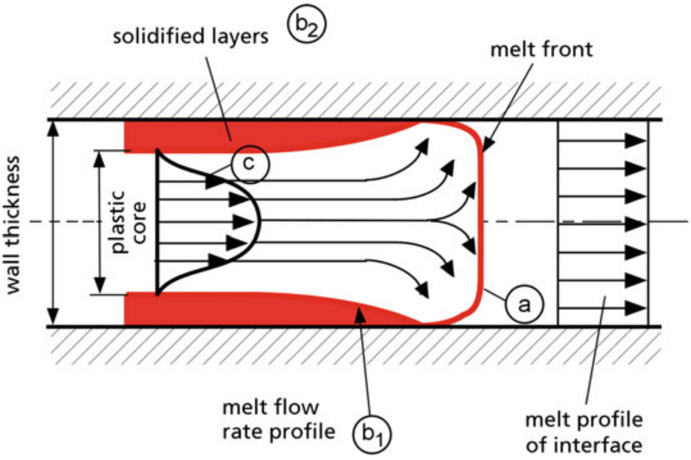


Fig. 7 Scheme of movement process during filling [13]. (**a**) Melt front. (**b**$_1$) Boundary layers begin to solidify. (**b**$_2$) Boundary layers already solidified. (**c**) Melt profile in "plastic core"

Figure 8 demonstrates that in plastic melts the shearing stress shows a degressive curve (intrinsically viscous) at higher shear rates, i.e. less force is required as the shear rate increases, a highly advantageous characteristic from the point of view of ease of processing.

Table 4 reflects the qualitative effects of different influences on the flow behavior of plastic melts.

Summary explanations of melt behavior terminology (Fig. 9) [12]:

1. Viscosity η changes with shearing load, i.e. shearing stress τ or shear rate γ
   a. η increases with *t*: dilatance
   b. η decreases as *t* increases: intrinsic viscosity (or "pseudoplasticity")

Fig. 8 Principal flow behavior of Newtonian, intrinsically viscous and dilatant liquids or melts

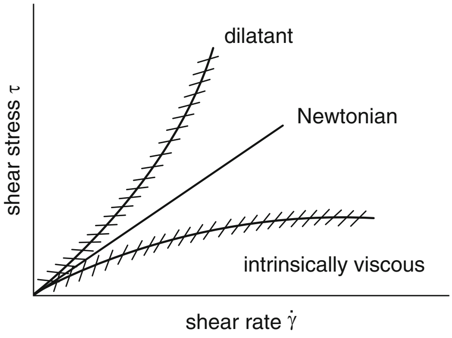


Table 4 Qualitative effects of different influences on the viscosity η of plastic melts

Influences on viscosity	η
Greater molar mass	↑
More long-chain branchings	↑
Increasing process pressure	↑
Higher proportion of fillers	↑
Higher temperature	↓
Addition of plasticizers (lubricants, blowing agents, etc.)	↓
Higher shear rate	↓
Aging (chain ruptures = lower molar mass)	↓

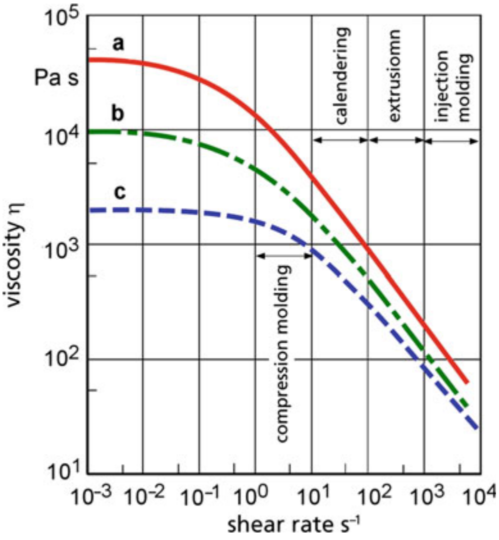


Fig. 9 Viscosity in its dependence on shear rate in three polyethylene types, temperature 150°C. The processing ranges are indicated at the upper right (BASF, Ludwigshafen)

2. Viscosity η changes under constant shearing load in the course of the testing time t:
   a. η increases with t: rheopexy
   b. η decreases with t: thixotropy
3. Rubber elastic deformations are coupled with viscous flow (and tend toward elastic reverse deformation when the flow ceases).

Elastic liquid: As a result of elasticity, normal stress also occurs during flow in addition to shearing stress: normal stress or Weißenberg effect.

3.1.2 Deformation Behavior of Melts (and Solids) – Viscoelasticity

When a plastic melt[3] is deformed, it shows a delayed and incomplete return to its original form once the deformative forces are no longer applied.

A partial irreversible deformation remains. Therefore, elastic properties independent of time and time-bound viscous properties act together. A number of phenomena can be described in simplified terms by combining the basic equations for elastic and viscous behavior of the materials in different ways.

Table 5 provides an overview of such basic equations for the deformation behavior of materials, including melts.

The deformation behavior of plastic melts, and therefore of plastics and materials in general can be described in simplified, clear terms by using spring and dampening elements.

An exemplary phenomenon of practical relevance in which the viscoelastic behavior of plastic melts plays a rheological role is expansion of the extruded mass (die swell) when melt flows freely out of an extrusion die (profile molding tool).

Contributing factors include molecular orientation, shearing forces, die length, relaxation, mass temperature, viscosity, and molecular form (constitution).

In Section “Influences of process and plastic on the structural component properties,” die swell is explained as one example of molecular orientation in the extrusion process.

4 Processing of Thermoplastics

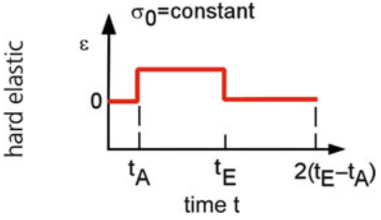
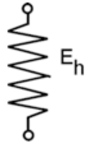
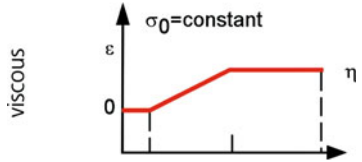
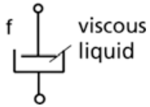
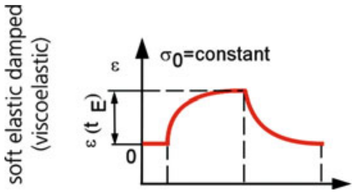
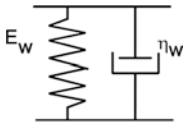
The primary forming of amorphous and semicrystalline thermoplastics is realized in the flow or melting range. Figure 10 shows once again that the individual states have no fixed temperature limits. The temperature-dependence of the processability of thermoplastics is shown clearly.

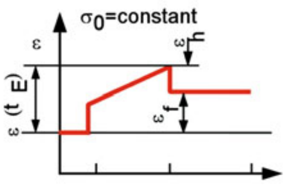
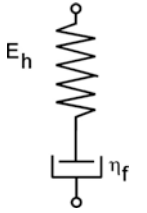
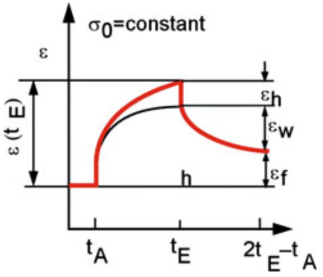
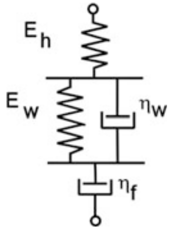
Table 3 provides a summary overview of the most important processing methods used for thermoplastic melts. For more information see also [2, 7, 14].

---

[3] In the widest sense, an amorphous thermoplastic is actually a melt at any temperature. Below flow temperature, the melt is more or less congealed. In semicrystalline thermoplastics this applies to the amorphous ranges, so that the above considerations apply to thermoplastics in general.

Table 5 Comparison of different models and equations describing the deformation behavior of materials

Deformation behavior in creep (schematic)	Model	Basic equations	Examples
		Hook's law of energy elastic bodies (elastic deformation) $\varepsilon = \frac{\sigma_0}{E_\mathrm{h}}$	Steel plastic below T_g at low elongation levels
		Newton's law of viscous fluid (viscous deformation) $\varepsilon = \frac{\sigma_0}{E_\mathrm{h}}.t$	Oil, ideal polymer melt
		Voigt–Kelvin model $\varepsilon = \frac{1}{E_\mathrm{w}}\left(1 - \mathrm{e}^{\frac{tE_\mathrm{w}}{\eta_\mathrm{w}}}\right).\sigma_0$	Ideal elastomers, in particular NR

hard elastic viscous (elastic + plastic)			Maxwell model $\varepsilon = \frac{\sigma_0}{E_\mathrm{h}} + \frac{\sigma_0}{\eta_\mathrm{f}}.t$	Polymer melt
hard elastic + soft elastic dampened + viscous			Burger four-parameter model (succession of Voigt–Kelvin and Maxwell models) $\varepsilon = \frac{\sigma_0}{E_\mathrm{h}} + \frac{1}{E_\mathrm{w}}\left(1 - \mathrm{e}^{\frac{tE_\mathrm{w}}{\eta_\mathrm{w}}}\right)\sigma_0 + \frac{\sigma_0}{\eta_\mathrm{f}}.t$	Real plastics

Schematic presentation valid

$t_\mathrm{E} >> \frac{\eta_\mathrm{w}}{E_\mathrm{w}} = \tau$

σ_0 constant tensile stress (creep test)

ε elongation

E_h E modulus in hard elastic range N/mm^2 time in s

E_w E modulus in soft elastic range N/mm^2

η_w viscosity in soft elastic range in N × s/mm^2

η_f viscosity of viscous flow in N × s/mm^2 time in s

t_A time at which stress s commences

t_E time of stress release

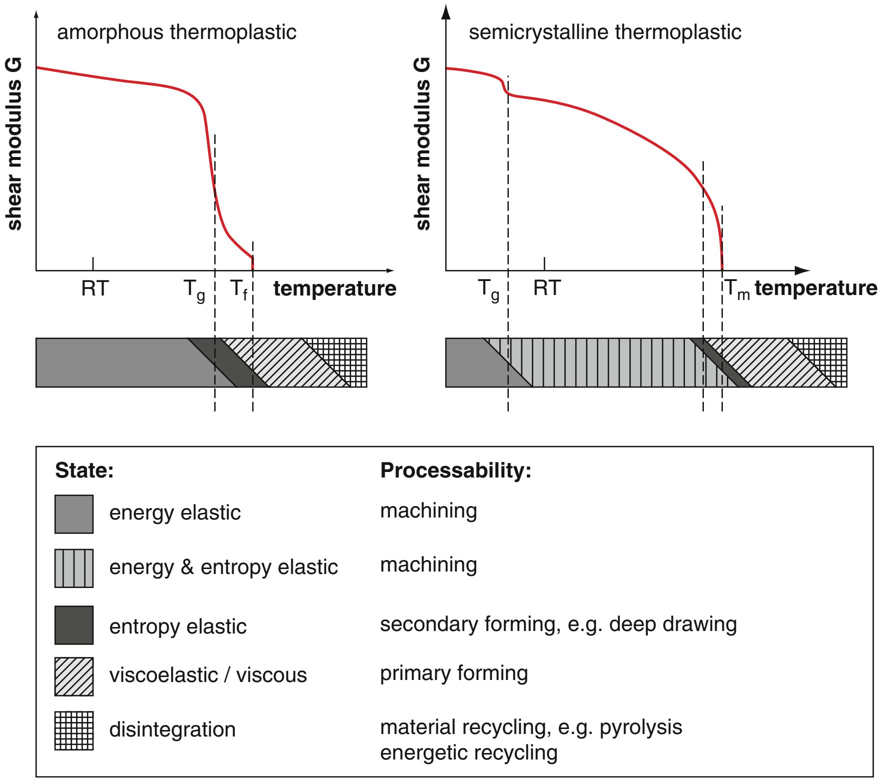


Fig. 10 Temperature-dependent state and processability of thermoplastics (derived from [3])

The two most important primary forming processes, injection molding and extrusion, are described below in somewhat greater detail.

4.1 Injection Molding

The injection molding process is used to produce complex moldings (structural component masses from the mg range up to 100 kg) in top quality and in large numbers.

Advantageous features of injection molding include

- Short-path process from raw material to final product
- Little or no reworking
- Process can be integrated and fully automated (discontinuous)

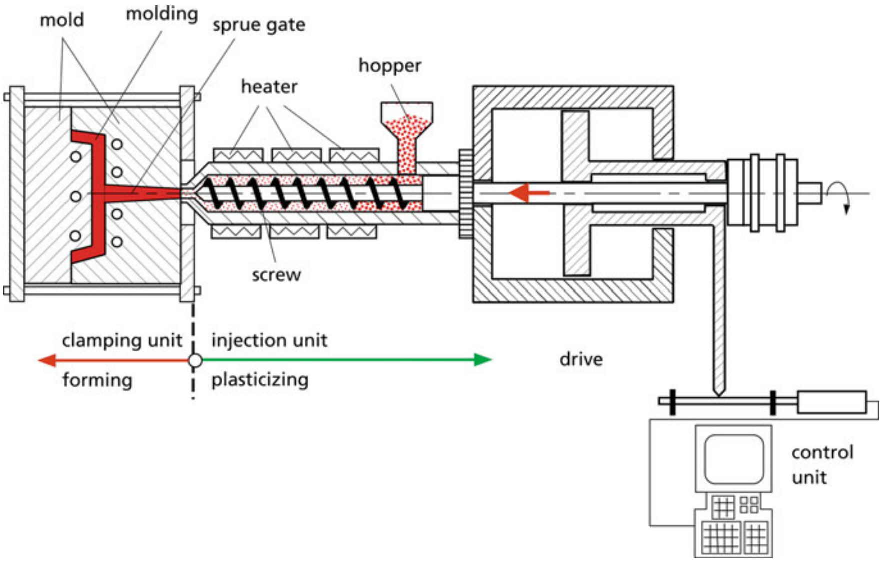


Fig. 11 Schematic drawing of an injection molding machine

- Highly reproducible production
- Low energy consumption for forming due to low processing temperatures (compared to metals).

In view of the large number of parameters influencing injection molding production, a considerable amount of know-how must be bundled and applied to ensure top quality production.

Technically speaking, “flow casting” would be a more accurate term than injection molding, since the mold is filled across a melt front and not, as in metallic diecasting (better: injection molding), by a jet of liquid.

Figure 11 illustrates the separation of two processes in injection molding machine function: plasticizing and forming. Figure 12, based on this schematic separation, demonstrates the injection molding process.

4.1.1 The Injection Molding Process (Fig. 12)

The plastic granulate or powder is plasticized in the plasticizing aggregate by the rotation of the screw and heated by an external source.

Once the molding tool has closed, the screw feeds the plastic melt axially (piston effect of the screw) into the mold (*step 1 injection*).

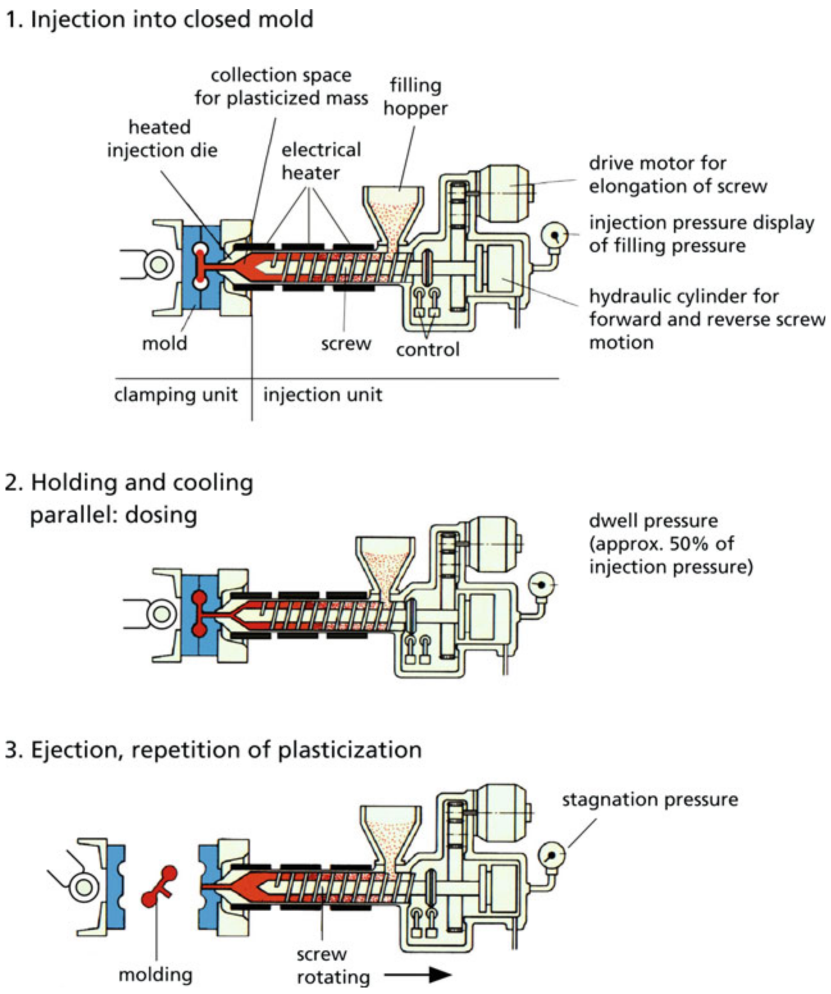


Fig. 12 Schematic illustration of the injection molding process (Demag)

To compensate for material shrinkage, additional melt is pressed through the sprue gate. Thermoplastics then cool in the "cold" (50–80 °C) molding tool, elastomers and duroplastics vulcanize/crosslink in a heated molding tool (150–200 °C) (*step 2 dwelling and cooling*). During the cooling and crosslinking time the screw feeds in new material, the plasticizing process begins anew while the mold opens and ejecting rods push out the solidified/crosslinked molding (*step 3 ejection*).

Taken together, these overlapping partial steps add up to an injection cycle. Reduction of the cycle time is always a desirable goal to increase yields per unit of time.

However, high-quality product specifications often stipulate process parameters that run counter to faster production. For instance, a high mass temperature means fast, efficient mold filling, but increases the cooling time. In such cases, the mold is cooled well and its wall thickness is reduced. The resulting high cooling rates across the wall cross-section may, however, lead to internal stresses with a later tendency for stress cracking. Depending on the plastic used, a high mass temperature can also result in molecular disintegration, for example with reduced impact strength in the manufactured structural component. Similar chains of causality can be observed involving the many other process parameters listed in this chapter in Sect. "Processing of thermoplastics."

Figure 13 shows the curves for the parameters cavity pressure, mass temperature, and viscosity against cycle time. Injection begins at 10 s. Up to that point, the mass temperature heats up to melt or flow temperatures and the viscosity is reduced to the point of flowability.

Semicrystalline thermoplastics require longer applications of dwell pressure to eliminate the crystallization heat.

The dwell pressure compensates the volumetric shrinkage resulting from cooling by forcing in additional melt and is thus essential in terms of dimensional accuracy.

The farther away from the extrusion die, the less effect the pressure from the power-driven pump exerts. This example demonstrates that the molding compound solidifies under a wide variety of different local pressure conditions. Another factor causing a degree of inhomogeneity is the temperature of the mass and of the mold. The molding compound as it leaves the extrusion die is generally characterized by a temperature profile that varies according to time and localization. When processing thermoplastics, it is important to keep track of the pressure and temperature differences to ensure at all times a correct grasp of such quality parameters as homogeneity, temperature constancy, reproducibility, dimensional constancy, etc.

Figure 14 shows the curve of specific volume in relation to mass temperature plotted against the parameter of pressure in the melt of an amorphous thermoplastic assuming free shrinkage of the dimension under observation. These curves are of decisive importance for plastics processors and the mechanical engineers designing the tools, since they provide information on the overdimensions required for tool construction to obtain accurate dimensions in the molding.

4.1.2 Process Variants in Injection Molding

Plastic processing in general, and injection molding in particular, is characterized by a wide variety of process combinations and integration of secondary processes (see summary of process variants at the beginning of Sect. "Processing of thermoplastics") [32].

A number of injection molding variants are listed and briefly described below, based above all on [6].

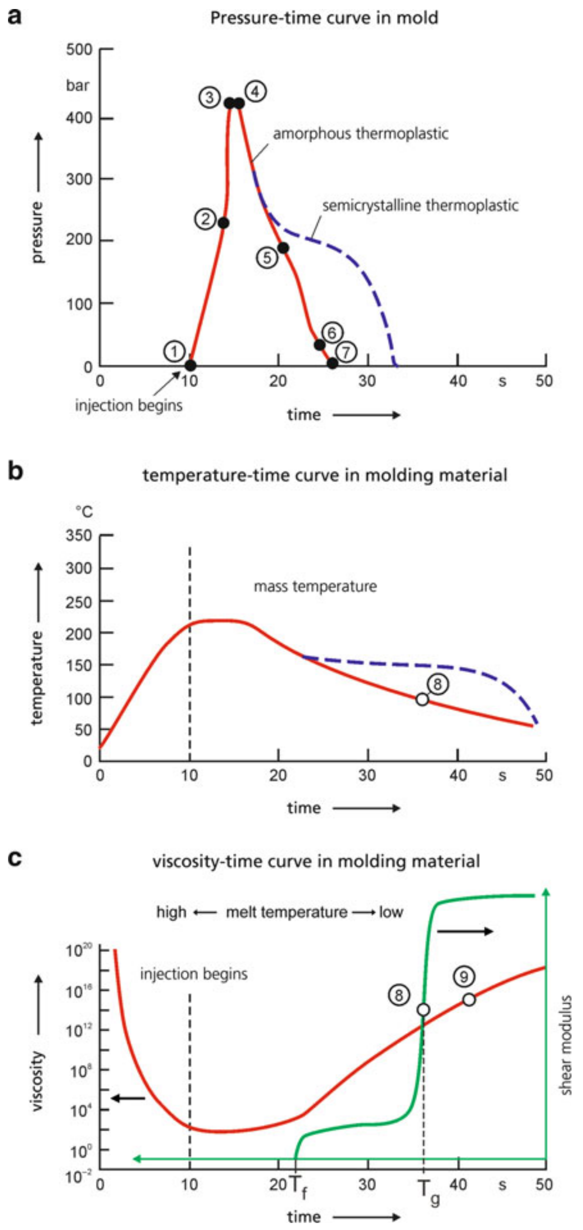


Fig. 13 Pressure, temperature and viscosity curve for an amorphous thermoplastic in an injection mold, near the sprue, (**a**) derived from [15] (1) to (2) Injection process, (2) Mold volume is filled, (2) to (3) Buildup of injection pressure, (4) Switchover to lower dwell pressure, (4) to (5) Pressure drop-off, (5) Dwell pressure level is reached, (6) Sprue solidifies (sealing point), (7) Atmospheric pressure reached, but the inherent rigidity of the molding is still low, since glass transition temperature has not yet been passed. (8) Glass transition temperature T_g with main softening range, (9) Rigidity is now great enough to facilitate ejection. Molding temperature below T_g

4.1.3 Multiple-Component Injection Molding

The terminology in the field of multiple-component injection molding is multifarious and confusing. Figure 15 helps clarify the designations. Michaeli and Lettowsky [32] and Jaroschek [31] describe new developments in this field.

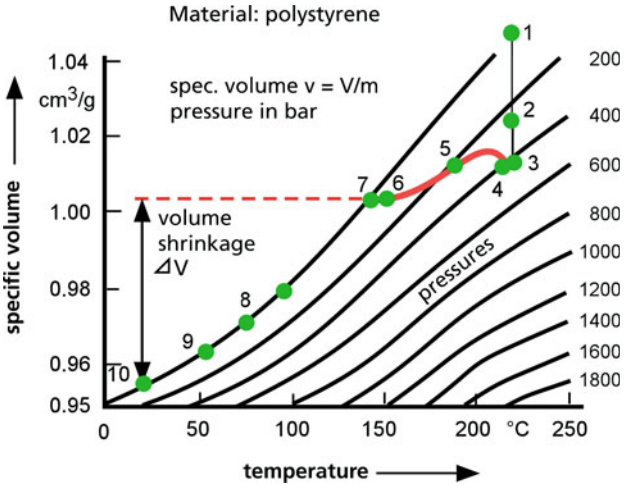


Fig. 14 *p*, *v*, *T* diagram (diagram of state) (pressure, volume, temperature diagram) (based on [15]) for an amorphous thermoplastic melt in the injection mold (taken from Fig. 15; items 1–7 are identical). *p*, *v*, *T* diagram information is a useful indicator for molding quality, in particular regarding shrinkage. (8) to (9) Rigidity/strength reached (isobar gradient change at T_g), (9) Part is ejected, (10) Ambient state reached

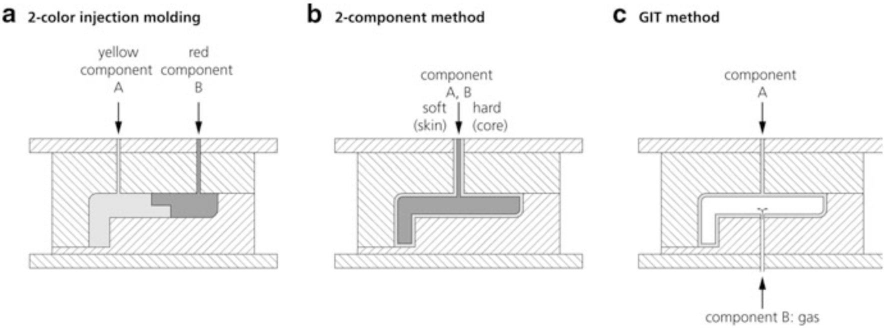


Fig. 15 Classification of multiple-component injection molding methods (based on [6])

Some of the normally used terms are matched up to the corresponding pictures of Fig. 15 a, b and c above.

a. Two-color injection molding (IM)
   Multicolor IM
   Two-color/multicolor molding
   Joint molding
   Add-on molding

b. Sandwich injection molding
   Two-component IM
   2C-IM
   Coinjection molding
   Insertion IM
   Sequential molding
c. Gas injection technique (GIT)
   Internal gas pressure (IGP)
   Gas-assisted injection molding (GAIM)

Variant c is very similar to b, the difference being that a gas (nitrogen) is used as the secondary component instead of a second melt.

In *two-color or multicolor IM* (a) the main objective is optical effects, for instance in car tail lights or dashboard elements.

Sandwich or 2C injection molding (b) makes it possible to combine hard components with soft ones, for example molded-on sealing lips for body parts or impact-absorbing, rigid-core layers for door linings.

Another variant is to surround a core of recycled material with an outer sheath of new material.

4.1.4 Characteristics of Two-Component Injection Moldings (2C IM)

Advantages:

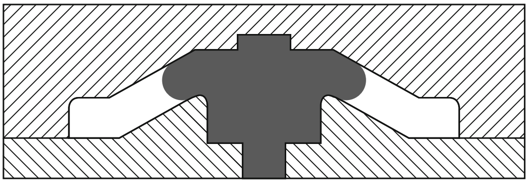
- Economical production (one processing step) of composite structural components with for example a hard core and soft surface (sealing function, haptic aspects, impact)
- Cores can be made of recycled material
- Moldings with high surface quality

Questionable and disadvantageous aspects:

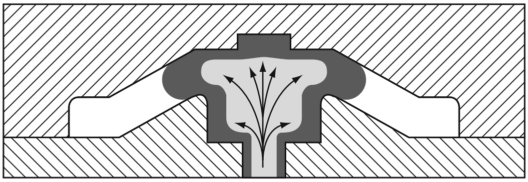
- Principles of the mold filling procedure
- Breakouts, reliefs, stiffening ribs
- Sprue not pure type, therefore not recyclable
- Melt temperature and shrinkage differences between plastics used
- Mutual tolerance of plastic types
- Investment required is 1.5 times that for 1C IM
- Material recycling (composite)

With *GIT injection molding* (c) hollow parts with a defined smooth outer surface can be produced. Areas of application include suitcase handles, gripping handles in car interiors, garden tables, hollow-seamed ribbed feet (avoidance of sink marks),

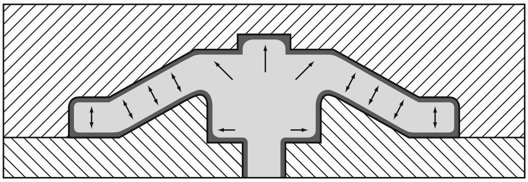
Fig. 16 Mold filling process in GIT molding



Mass filling phase
Injection of predefined melt volume



Gas filling phase
Gas introduced through the injection nozzle displaces the plastic core and fills the cavity (avoid gas breakthroughs)



Gas dwell pressure phase
Internal gas pressure (approx. 200 bar) impresses cavity precisely upon undefined interior hollow space contour

sanitary fixtures, handles for children's seats, small containers, etc. Figure 16 is a schematic sketch of the mold filling procedure, which is basically the same as with 2-component injection moldings. A gas (nitrogen) under ∼100–200 bar is used instead of a plastic melt as a second component.

The "plastic core" (melt at the middle of the cavity) solidifies more slowly than the outer layers and can therefore be moved by means of the injected gas (marked yellow in Fig. 16). The GIT process is summarized by Eyerer et al. in "Gas Injection Technique" [18].

In *two-component IM* (b), structural components with movable joints can be produced by selecting suitable melt temperatures and shrinkage parameters and employing inmold assembly techniques. Examples include hinges, toy figurines with movable limbs, and automotive ventilation valves [31].

4.1.5 Injection Compression Molding

Injection compression molding (ICM) is, similarly to the gas injection technique and thermoplastic foam injection (TFI), particularly well-suited to making thick-walled moldings with little warping and few sink marks. However, thin-walled parts with long flow paths can also be produced efficiently by means of ICM.

In ICM, injection is followed by compression. A precisely predosed plastic melt is injected into the mold, through the compression gap opening, during the injection phase.

The melt cake is distributed in the mold cavity by closure of vertical flash face only half of the mold (compression phase), whereupon the closed cavity is filled with the sprue gate closed as well.

The cavity pressures in ICM are lower (by about half) than in injection molding.

The main applications of ICM are in the areas of duroplastic and elastomer processing, although both thick-walled and thin-walled moldings requiring a high degree of dimensional accuracy, for example optical lenses and membranes for microphones made from thermoplastics, are manufactured using this method.

4.1.6 In-Mold Lamination Technique

The combination of decorative films (also textiles), placed in an injection mold with back-injection of the molding is known as inmold lamination. The decorative material is fixed along the mold separation line. In back injection, the melt temperature, injection pressure, mold filling, and melt viscosity must be selected so as to fill the cavity, press the film without wrinkling it against the mold wall and not press the melt through it. A delamination-free film–plastic bond is what is needed. Applications for inmold laminated moldings include mainly automotive items: door moldings, A, B, C pillar moldings, trunk covers, ceiling moldings, hat racks, dashboards, front interior moldings, etc.

In the interest of more gentle processing (lower pressures) *inmold lamination with ICM techniques* are being used increasingly in applications involving longer flow paths.

4.1.7 Press Molding

Hot press molding is used mainly with duroplastic molding compounds as well as with elastomers, whereby the term used is transfer molding (TM) (see Sects. “Processing of elastomers” and “Processing of duroplastics”). More recently, hot press molding has also been used in processing of long-fibered thermoplastic composites (see Sect. 4.4.4).

4.1.8 TFI

TFI is one of the oldest special injection molding processes. This method is used to produce large, thick-walled, rigid parts with a thick outer layer over a foamed core.

Examples of applications include housings, containers, pallets, and sporting equipment, usually made of high-impact polystyrene or polyethylene. In “low-pressure” TFI, molding mass filled with blowing gas is injected in an open jet at the thickest part of the mold, filling it 60–80%. The mold must withstand only the expansion pressure of the mass, 10–20 bar, and can have a light structure accordingly. The cooling times of TFI parts are much longer than those for normal compact injection-molded parts. For this reason, multi-station machines with alternating clamping units are in frequent use [17].

4.2 Extrusion (Flow Process; Continuous Process) With Contributions from Dietmar Völkle and Jan Diemert

An extruder, Fig. 17, has essentially the same structural components as the plastification unit in a screw-type injection molding machine, Fig. 11. The screw in this case is not an axial plunger: in the extruder it only rotates. The significance of extrusion per se is the continuity of the process. The method is used to produce plates, tubing, profiles, films, etc.

The extrusion process can be divided into phases as follows:

- Feeding, compacting
- Melting, mixing and homogenizing
- Forming in the extrusion die, followed by calibration/cooling, take-off and saw-off.

The processing zones in the extruder are the solid zone – feed section, transformation or plastification zone, the pumping or metering section (screw) and the mold. Feeding in the solid zone is the main determinant of machine output.

The melt energy is partly introduced through the cylinder wall and partly through screw friction. Just as in screw injection aggregates, polytropic function is differentiated from adiabatic.

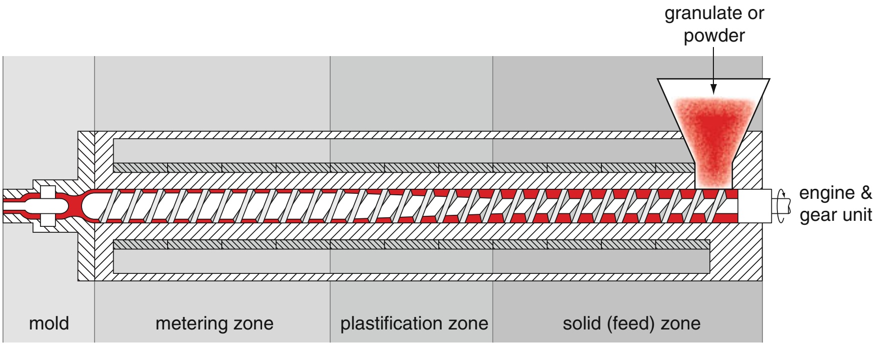


Fig. 17 Sectional drawing of single-screw extruder with functional zones

The *extruder* is the main element in an extrusion aggregate.

The following extruder design types are in use (screw-type machines):

- Single-screw (plastification and melt extruder)
- Twin-screw (co-rotating, counter-rotating)
- Special types (ram extruder, planetary roller extruder, cascade extruder, Weissenberg extruder).

An *extrusion facility* includes material supply, extruder, die, calibration, water cooling, cooling line, caterpillar take-off and saw.

In polymer engineering, extruders are used primarily for feeding, mixing, coloring, and degassing of polymer melts. The action of rotating screws is utilized in most cases, whereby structurally simple machines with only a single screw are in the majority. The mold flanged to the extruder forms the polymer melt into semifinished products, moldings or coatings. The residence time of the polymer in the extruder must be technically adjustable for use of the extruder extending beyond this, in particular for reactive extrusion. Polymer modification thus requires a special machine technology, whereby the following performance parameters are expected from the extruder:

- Reliable feeding of materials of widely varying viscosity
- The possibility of flexible dosing of the components
- A rapid mixture of the components (homogenization) and
- Efficient degassing of volatile reaction productions (otherwise known as devolatilization).

4.2.1 Machine Technology [19]

Extruders are classified according to structural design. A single-screw extruder is characterized by a simple design and is almost exclusively used as a plastification extruder. This restricted range of application is due directly to the reduced mixing and self-cleaning functions due to the lack of forced feeding of polymer melt in the extruder. Advances in extruder technology have brought multiple-screw extruders, in particular twin-screw extruders with combing screws, to the fore. These developments were necessary because of the many tasks single-screw extruders could no longer master.

Twin-screw extruders with co-rotating, combing screws do not have closed feed chambers. The melt flows around both screws due to drag flow in an eight-part motion. The melt is shifted and intermixed along the flanks of both screws. Melt adhering to the screws is displaced here. At the same time, the displacement at the screw flanks also generates low-viscosity medium feed.

The flexible use of twin-screw extruders is facilitated by the building-block design. Cylindrical, feeder, kneading and mixing elements can be combined as needed. On the whole, extruder technology can be adapted by these means to the requirements of polymer modification.

The way an extruder cylinder is constructed will depend primarily on the peripheral equipment to be integrated. The individual cylinder elements feature in particular special openings, for example for addition of a lateral feed, an injection die, or a vacuum muff. However, the cylinder opening deviates in only a few special cases from the basic 8-shaped cross-section. The screw configuration depends on the required melt residence time, which on the other hand is mainly determined by the feed performance of the screw elements. A further complicating factor is the dependence of the complex flow processes on the pressure buildup behavior in the individual screw elements.

Positive feed elements with maximum drag flow performance levels that exceed the sum of leakage flow and actual throughput can build up pressure. If the polymer throughput is increased, but the feed effect of a downstream element is less due to a lower gradient, positive feed elements can also be pressure consumers. These must then be overflowed by elements with a greater drag flow performance just like return elements.

In general, plastic modification makes it necessary to feed liquids into the extruder in addition to the solids. The relevant material data for selection of the suitable metering pump are density, viscosity, compressibility, and boiling point. It can be just as decisive whether the liquids are flammable or aggressive and whether they contain solid particles. For these reasons, the pump types used in process engineering are all used in plastic modification engineering as well – piston, membrane, geared and screw pumps. As a rule, the liquids are moved by the pumps through the tubes or capillaries, then through a nozzle into the flank area of the twin-screw extruder, whereby the nozzle design depends on the liquid and pressure status in the extruder.

After impregnation and modification, polymer melts usually contain low molecular or other volatile components. Besides recovering solvents, the degassing of such polymer melts also removes monomers and other volatile compounds. When designing the degassing zones, the structure of the degassing openings is an important factor in addition to the screw configuration. Depending on polymer behavior parameters, only some parts of the screw channel are opened to the top.

4.2.2 Extrusion: Example of Polyvinyl Chloride – Material Technology and Processing [20]

Polyvinyl chloride (PVC) is one of the most important plastics on the world market with an installed global production capacity of 32 million t/a. This material is highly variable. Applications include everything from window profiles and pipes to floor coverings and cable insulation, toys, and medical products. No other material can be tailored to such a great extent by use of additives, fillers, and modifiers for specific applications. The result is that PVC is not given a tailor-made formulation by the raw materials supplier or compounder like nearly all other thermoplastics, but that the finished formulation is batched up by the actual material processor. This close proximity of formulation and product processing has many advantages, but also results in a long list of different PVC mixtures, additives, and fillers.

Properties of Different PVC Polymers

Depending on the polymerization method used, these PVC types are differentiated: suspension PVC (S-PVC), mass PVC (M-PVC), and emulsion PVC (E-PVC). S-PVC is the material used in most modern applications by far.

As a residue from the production process, S-PVC contains a small amount, from 0.05 % to 0.2 %, of suspension additives [21], whereas the E-PVC produced by means of an emulsion method contains ~1–2 % emulsifier residues (in most cases metallic soaps). Mass-polymerized M-PVC contains, in contrast to the above-mentioned PVC types, no emulsifiers or suspension additives and is therefore well-suited to use in transparent PVC mixtures. Besides these pure PVC polymers, the chemical structure of which is shown in Fig. 18, types with chemically enhanced impact resistance are also used in applications requiring greater impact strength such as window frame profiles. Elastic regions are formed in the much harder PVC matrix in reaction to the addition of polybutylacrylate (PBA) or afterchlorinated polyethylenes. Any cracking potential in these areas is then compensated.

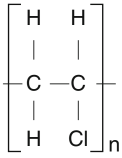
One of the most important criteria for classification of PVC materials is the so-called K value (DIN 53726), which is determined by measuring the viscosity of a PVC solution. This parameter is directly related to the degree of polymerization and thus with the molar mass of the PVC. It provides important information on processability and additive requirements of a material and may also be used in detection of damage to the PVC material or incorrect processing.

Suspension PVC (S-PVC), used in most profile and pipe extrusion processes today, shows a characteristic PVC grain morphology due to the nature of the production process [21].

The substructure of the S-PVC grain, consisting of agglomerates, domains, and microdomains is of considerable importance in terms of the later compounding process and the properties of the PVC mixture, since the resulting porosity allows low-melting additives to penetrate into the grain.

Additives for PVC Mixtures

The broad range of uses to which PVC materials are put today is due to the large number of different additives and fillers used to engineer the property profile of the basic PVC within a correspondingly broad range.



$$\left[-\overset{\displaystyle H}{\underset{\displaystyle H}{C}} - \overset{\displaystyle H}{\underset{\displaystyle Cl}{C}} - \right]_n$$

Fig. 18 Chemical structure of polyvinyl chloride (PVC)

Stabilizers and Costabilizers

Since in unstabilized PVC the hydrogen chloride splits off from the PVC macromolecule beginning at a temperature of ~100°C [22], and many of the potential degradation reactions are autocatalytic, thermoplastic processing of PVC is not possible without the addition of stabilizers.

The traditional stabilizer for hard PVC, harking back to the beginnings of PVC processing, is the cadmium-based stabilizer that was subsequently replaced by lead-based stabilizers for the most part in the 1980s. The demand for PVC formulae free of heavy metals has today led to an increasing use of calcium–zinc stabilizers free of heavy metals [23]. The many different demands made on modern PVC mixtures can hardly be met by one stabilizer alone, so that current practice frequently combined different stabilizer systems. Stabilizers are added to mixtures at ratios of around 14% by mass.

The references [23–25] and Sect. “Functional additives” in Chap. “Properties of Plastics in Structural Components,” for example, provide further information on the different stabilizer systems.

Lubricants

Internal and external lubricants are differentiated. *Internal lubricants* are compatible with the polymer matrix and serve mainly to reduce the friction inside the material and thus the shear heating. To achieve the necessary compatibility with the polar basic polymer PVC, internal lubricants are in most cases polar substances. *External lubricants*, on the other hand, service mainly to reduce the friction between the polymer and the metallic surface at the boundary of the flow channel. These substances are less compatible with the basic polymer and therefore unfold their effects mainly at the boundary to the metal. This external effect is achieved by means of a specifically adjusted incompatibility with the polar basic polymer. Most external lubricants are therefore chemically nonpolar. Standard lubricants are marketed in fine gradations between purely external and purely internal action, hence also with wide variations in polarity.

The substances normally used as lubricants are higher alcohols, higher fatty acids, hydrogenated fats, and esters. They are added to processable mixtures in amounts of 0.2–2 %.

[26] and Sect. “Functional additives” in Chap. “Properties of Plastics in Structural Components,” for example, offer further information on the different lubricant systems.

Acid Scavengers

Acid scavengers bind the acids (mainly HCl) constantly set free in PVC mixtures by unavoidable degradation reactions. Metallic soaps are used for this purpose.

The substances used in most cases for this purpose are metallic soaps, which also have a mild stabilizing effect.

Fillers for PVC Mixtures

Fillers account for a significant proportion of the material in many PVC mixtures – in some applications as much as 60 % by mass. Fillers are added to PVC mixtures for both technical and economic reasons. They influence such properties as density, rigidity, impact strength, surface hardness, shrinkage, as well as thermal properties such as thermal conductivity and thermal capacity of a PVC mixture [27]. The most interesting fillers in PVC processing, both technically and economically, are the calcium carbonate fillers (chalks), whereby there are differences between natural mined chalks of varying grain size and synthetic, chemically produced chalks, see also Sect. "Organic and inorganic fillers" in Chap. "Properties of Plastics in Structural Components."

Synthetic chalks are produced, for example, as waste products in soda production. They are characterized above all by finer grain size and a larger surface than natural chalks and therefore do not disperse as well in the melt. They are therefore often added in smaller amounts than natural chalks.

The grain structure of natural mined chalks can be adjusted for the various applications in the compounding and finishing processes.

Many fillers are covered with a coating to improve their processing qualities. This measure reduces the attractant forces between the particles and improves their dispersibility in the PVC. The coating materials used in most cases for fillers based on carbonates or oxides are fatty acids and fatty acid esters, and silanes, titanates and chromium complexes for fillers based on silicates and hydroxides. The amounts of coating substances added in relation to the amount of filler used may be as high as 3 % by mass.

As is the case with all fine powders, inorganic fillers may absorb a certain amount of water due to their chemical and morphological structure. Moisture may adhere to the very large grain surface or penetrate as crystal water into the crystalline structure. The use of coatings appreciably reduces moisture regain, in particular absorption into the inside of the grain, see also Sect. "Organic and inorganic fillers" in Chap. "Properties of Plastics in Structural Components."

Compounding of PVC Mixtures

The compounding of processable PVC mixtures is done, as related above, mainly on the processor's premises, where the basic PVC material is mixed with the additives or additive mixtures, plasticizers, fillers and other additions using combinations of heating and cooling mixers [28], see also Sect. "Additives for plastics" in Chap. "Properties of Plastics in Structural Components." In a first step, the mix components are heated in the heating mixer to ∼90–120 °C, whereby mainly mechanical energy is applied. The low-melting components such as lubricants melt in the process and diffuse into the PVC grain [21]. The components that are not fusible at these temperatures, such as fillers and some stabilizers, attach to the surface of the grain. To prevent agglomeration of the PVC grains, which are sticky in this state, the finished mixture is cooled in a cooling mixer while stirring is continued. The mixtures produced in this process are known as dryblends.

Extrusion of PVC Mixtures

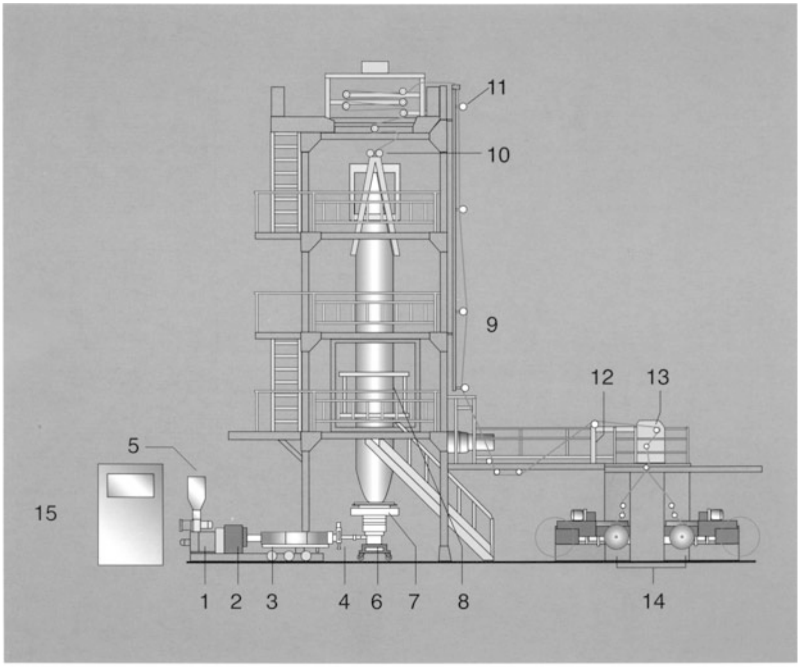
By far most of the PVC produced is then further processed by extrusion to make products such as pipes, plates, and profiles for the construction industry. Processing of PVC dryblends to make plasticizer-free hard PVC is done almost exclusively on counter-rotating twin-screw extruders, whereby the process engineering is geared to the specific material requirements. The chamber feed resulting from the screw geometry of the counter-rotating twin-screw extruder facilitates efficient plastification at precisely controlled temperatures – an important aspect for PVC [29].

Customer demands for greater throughput from machines of the same size and capable of handling more and more different formulae have necessitated the development of a new aggregate concept in recent years accommodating longer preheat zones in the screw [30]. The increasing filler volumes – due mainly to economic considerations, and new lean PVC formulae with additives reduced to a minimum are, however, narrowing the processing window and in some cases making formula-specific screw designs necessary, which in turn means a lot of retooling and high investment sums due to the greater variety of products to be produced in smaller batches.

In the screw preheat zone in particular, and at the onset of plastification, microwave technology offers promising solutions to the process engineering problems in extruder design mentioned above. Energy transfer in this technology does not involve heat conduction and makes for an efficient transfer of energy into the compacted bulk powder materials with poor heat conductance properties present in the extrude in this phase of the plastification process (For details, see Diemert [20]).

4.2.3 Blown Film Systems

Blown film systems (Fig. 19) are used to produce very wide tubular films. These systems comprise extruders fitted with a blown film die, normally a spiral mandrel (melt distributor). The tubular film is extruded vertically, passing through a cooling ring in which it is air-cooled. The tubular film is blown up to the desired circumference by introducing air into the interior. At the upper end of the tower, the tubular film is then folded in the flattener, whereby the air is held back by nip rolls. Then the films are wound onto cores. A so-called calibration basket may be placed between the cooling ring and the flattener. This device defines the blown film circumference and stabilizes the tubular film in this state.



1. AC main drive
2. Temperature controlled grooved feed throat
3. Wear-resistant screw and barrel
4. Screen changer
5. Gravimetric metering and throughput control
6. Automatic die
7. Internal bubble cooling (IBC)
8. Film stabilizing cage with non-contact ultrasonic bubble sensor
9. Film thickness gauge
10. Oscillating haul-off and bubble collapsing unit
11. Tube width measuring and controll system
12. Web edge and center control
13. Treater for two sided treatment
14. Center/surface winder with digital drive control system
15. SUPEX Operation automatic control system

Fig. 19 Blown film aggregate [33]

4.2.4 Coextrusion

To produce multilayer and multicolor extrudates, for example for cable sheathing, packaging films with barrier layers and/or recycled layers, two to seven extruders can be fitted with multiple-layer blown film fittings with the same number of nesting spiral mandrels to distribute the melt flows (Fig. 20).

Production of permeation-proof plastic fuel tanks can be realized using coextrusion with tubular die systems, followed up by hollow article extrusion blow molds. Using slit dies, multiple-layer, flat films or plates can be produced, which can then be deep-drawn. When the melt is united before the die, oxidizing gas can be blown into the airstream as an adhesion promoter, or adhesion promoter layers can be extruded into the material by means of coextrusion. Using a rotating mass distributor, sheathing with spiral markings can be made for switch wires, tubes and marbled profiles.

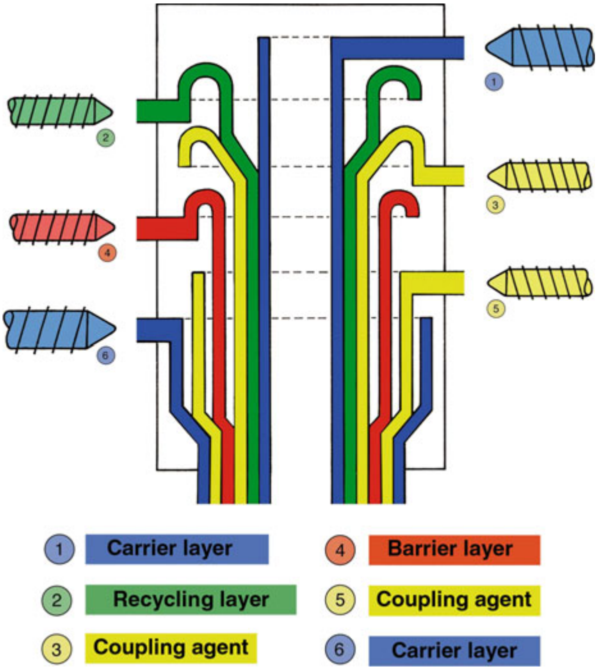


Fig. 20 Six-layer co-ex structure [34]

4.2.5 Extrusion Blow Molding

The product (bottles, canisters, drums, ventilation conduits, surfboards, suitcase shells, roof luggage racks, heating oil tanks, automobile fuel tanks, etc.) of extrusion blow molding is produced in two parallel processes (Fig. 21):

- Continuous preform extrusion (primary forming) and
- Transfer and molding of the preform in cycles by blowing air into the mold (secondary forming).

In stretch blow molding, a lengthwise stretching mandrel stretches the macromolecules additionally in the lengthwise direction. The result is a more intensive lengthwise orientation with a corresponding increase in strength in the direction of stretching (in practice, only hollow articles with rotational symmetry and an oval cross-section can be produced by this method).

The steps in the extrusion blow molding process are as follows, Fig. 21:

A tube is extruded into the opened mold, then a blowing mandrel is introduced into the tube.

The mold is closed, the tube is nipped on both sides and leaktight. The inside of the bottle filling opening is formed around the blowing mandrel with the threads on the outside for the cap with which the bottle will be used. The tube section has been pressed against the water-cooled wall of the mold, and formed, by compressed air.

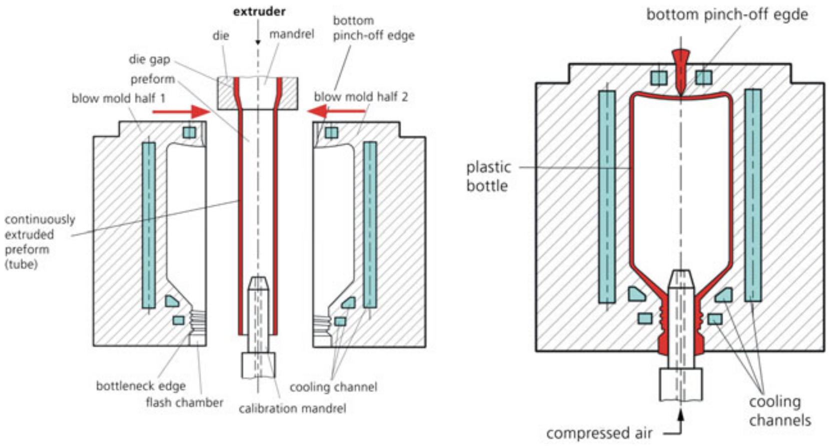


Fig. 21 Extrusion blow molding (BASF, Ludwigshafen)

The protruding part of the tube, the flash, must subsequently be removed along with the flash next to the filling opening. The bottle is ejected when it has solidified.

Preforms with differing wall thickness distribution are required to produce containers with different peripheral stretching factors while maintaining constant end product thickness. This can be realized by means of wall thickness programming in a movable extrusion die.

4.3 Foaming

The present chapter treats the general technology of foams as well as foaming of thermoplastic foams and, here in particular, production and processing of particle foams.

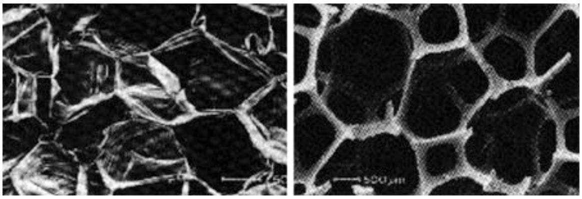
4.3.1 Definition, Principles, Classification, and Production Processes

According to DIN 7726, a foam is "a material with cells (open, closed or both) distributed throughout its entire mass with an apparent density lower than the density of the skeletal substance." Table 8 shows the main characteristics and classifications of this material:

4.3.2 Foaming of Thermoplastics

The most important thermoplastic foams are based on thermoplastic polystyrene and on the polyolefins PE, PP and PVC. The foaming process generally involves expansion resulting from use of chemical or physical blowing agents (Table 6).

Table 6 Classification of polymeric foams and foaming processes [35–40]

Characteristic	Type
Hardness	Hard, semihard and soft elastic foams
Cell structure	Closed-cell, open-cell and mixed-cell
	 SEM images: *left*: closed-cell polyethylene foam, *right*: open-cell polyurethane foam
Cell form	Spherical, honeycomb, polyhedral
Cell diameter	Microcellular <0.3 mm, fine-cell 0.3–2 mm, coarse-cell >2 mm
Density	Light foams <100 kg/m^3, heavy foams >100 kg/m^3
Density distribution	Foams with uniform density distribution Structural foams with a compact edge zone
Polymer phase	Thermoplastics (PE, PS, PP, PVC, EVA, PEI, etc.) duroplastics (PUR, EP, UF, UP) Elastomers (EPDM, NR, NBR, SBR, SI)
Chemical structure	Crosslinked, uncrosslinked
Foaming/production process	– *Frothing process*: Beating or blowing of air/gas into a plastic, e.g., for *elastomeric foams* such as latex foams – *Mixing process*: Combination of at least two liquid, reactive components, and usually one blowing agent, in a mold, where parallel gas-releasing, crosslinking chemical reactions taken place. (Special case of expansion process), used mainly to produce *duromeric foams* such as polyurethane – *Expansion process*: Expansion processes are by far the most frequently used methods of producing *thermoplastic foams*, *in particular polyolefin foams*. These processes are based on expansion of a gaseous phase that disperses in the polymer melt. Common expansion processes include extrusion foaming and particle foaming (extruded/autoclaving)
Foaming processes – blowing agents	– Chemically (exothermic or endothermic) and – Physically expanded foams

4.3.3 Steps in the Expansion Process

No matter what type of blowing agent is used, the foaming of polyolefins and polystyrenes using the expansion method comprises three fundamental process steps:

- Nucleation (bubble formation)
- Bubble growth
- Stabilization

Nucleation takes place at points within the polymer melt with local blowing agent oversaturation. This state of oversaturation can be achieved by means of decompression or heating of a balanced system with a *physical blowing agent (PBA)* or by heating of a polymer containing a decomposable *chemical blowing agent (CBA)*. Once a bubble has reached a critical size, further bubble growth is due to the blowing agent diffusing into the bubble. The growth process continues until the bubble *stabilizes* or its walls tear or burst.

The thin, highly stretched cell walls are still very unstable and must be stabilized to prevent the cellular foam structure from being destroyed.

Two different stabilizing methods are used for polyolefins:

- Cooling to increase viscosity/strengthen material
- Chemical crosslinking

When using PBA, and in particular volatile organic blowing agents (VOBA) that are in liquid form under normal ambient conditions, the melt viscosity is increased when the melt is cooled due to evaporation enthalpy and a small amount of heat energy is lost to the surrounding atmosphere due to the displacement work of expansion. On the other hand, if foaming is initiated by heating instead of by pressure reduction, the bubbles must be stabilized by crosslinking, in particular by the use of chemical blowing agents, which usually decompose in exothermic reactions after introduction of the activation energy. Crosslinking stabilizes the bubbles by raising the melt viscosity by a considerable degree compared to the uncrosslinked melt.

As seen in Fig. 22, crosslinking widens the temperature window within which foaming can succeed.

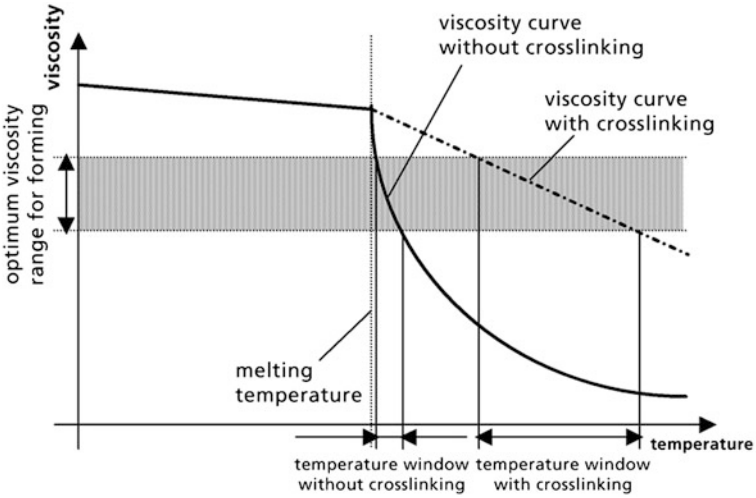


Fig. 22 Effects of crosslinking on the suitable foaming temperature interval

On the other hand, Crosslinking also, at least partially, transforms the thermoplastic melt into a duroplastic, which is often undesirable from the point of view of further processing and may limit recycling options.

4.3.4 Direct Extrusion Foaming of Thermoplastics

Extrusion foaming is in principle the simplest and most economical foaming method for thermoplastics. A conventional extruder plasticizes the basic polymeric material, mixes in the blowing agent and disperses it homogeneously in the melt. This is followed by cooling to the lowest possible temperature, the foaming temperature, and extrusion through the mold opening to form the strand. The mold must be constructed so that the stagnation pressure is reduced in the extrusion direction to the point where bubbles are still nucleated, but cell growth, and thus the actual foaming, do not begin until the material has left the mold. Following rapid cell growth, the foamed corpus is then cooled and stabilized.

Extrusion process steps:

- Feed-in and plastification of the basic polymer,
- Dispersion and dissolution of the blowing agent in the polymer melt,
- Cooling of the mixture to a homogeneous temperature,
- Forming of the melt through an extrusion die,
- Expansion of the melt into a stable, cellular structure,
- Cooling and stabilizing of the foam.

Products produced by extrusion include profiles, PE foams, extruded foam plates (XPS) and semifinished products that are finished in assembly procedures.

4.3.5 Production of Foam Particles (Beads) and Moldings

The arguments in favor of production of thermoplastic moldings beginning with the detour to foam particle production and fusion of these particles lie in the material and processing characteristics of these polymers. Stabilization of the cells formed in thermoplastic materials is only possible by cooling the melt. In voluminous moldings, the heat cannot escape from the middle of the structural component fast enough, resulting in cell collapse, i.e. smaller cells collapse to form larger cells due to surface strain on the plastic cell walls. Uniform cell distribution, similar to that in thin-walled foam films, semifinished products and profiles can only be ensured by production of small foam particles (so-called beads). The beads can then be fused or sintered to make a molding in the following process step, the molding process, by exposing them to hot steam in a porous, forming mold. Essentially, the three main known thermoplastic polymers PE, PS, and PP are used in production of EPS (expanded polystyrene), EPE (expanded polyethylene), and EPP (expanded polypropylene).

4.3.6 Extrusion of Foam Particles (EPS, EPE, EPP)

The main difference between this process and direct foaming is the use of an extrusion die in the form of a special perforated plate with the perforation cross-sections in the direction of extrusion engineered to facilitate nucleation in the channels, but not the actual expansion. The melt strands are not foamed until the abrupt pressure drop occurs when they exit from the perforated plate, and the strands are then chopped by rotating cutters into nearly spherical particles, and cooled in a water bath. Both the temperature drop and the diffusing out of the blowing agent, also serving as a plasticizer, contribute to the increase in expansion viscosity required for stabilization. Agglomerated particles are then separated out and the beads are dried and aged. During the aging process, the cellular skeleton continues to stabilize, the blowing agent diffuses out and is replaced by air. As a rule, polyolefins are used, here essentially polypropylene. Figure 23 shows a schematic drawing of a foaming installation.

Despite its continuity and low-level technical expenditure, the process is fraught with numerous difficulties. Exact temperature control has proven to be a particularly critical factor. Usable particles can no longer be produced just a few degrees outside the optimum foaming temperature range.

4.3.7 Production of EPP/EPE Foaming Particles in the Autoclaving Process

To date, the autoclaving process has been the one most frequently used to produce foam particles, in particular EPP (expanded polypropylene). In the autoclaving process, a suspension of compact polypropylene microgranulate and a liquid is placed under a pressurized atmosphere with inert gas and blowing agent while

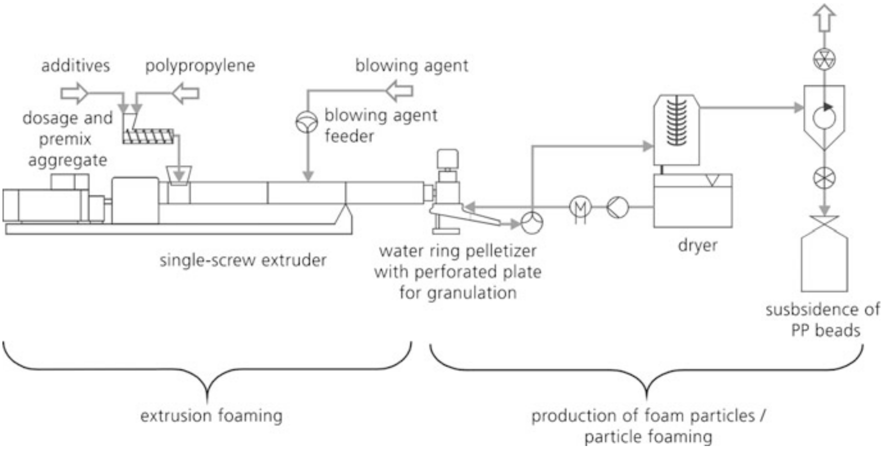


Fig. 23 Schematic technical diagram: extrusion of foam particles (altered according to Berstorff)

being stirred and heated constantly. The blowing agent concentrates in the polypropylene particles due to diffusion. As soon as the desired blowing agent content level is reached, i.e. after a sufficient residence time, the contents of the container are transferred to a room with a lower atmospheric pressure, whereby the impregnated blowing agent expands and the granulate foams. The enthalpy required to evaporate the blowing agent and at least part of the liquid draws heat out of the polymers parallel to this expansion. This cooling effect facilitates solidification of the cellular structure and stabilization of the foam particles formed.

4.3.8 Expansion of Polystyrene

Production of expanded polystyrene (EPS) particles begins with production of microgranulate. Suspension polymerization of styrene takes place in the presence of pentane, whereby the blowing gas goes into solution in the reaction product and remains in that state for months. The foaming of the EPS microgranulate takes place in the expander, a stirring container through which steam is passed. The pentane (boiling temperature 35 °C) evaporates, expanding (blowing) the granulate into foam beads.

In the process, ~50 % of the blowing agent remains in the foam particle. The fresh beads can then be further processed 1 day to 1 week after prefoaming (expanding).

4.3.9 Structural Component Molding from Particle Foams

Water steam is used as the energy carrier in the molding process. The steam heats up and melts the foam particles inside the forming mold. Mold walls permeable to steam and air are necessary to expose the beads inside the cavity to the steam at all. The mold is located inside a steam chamber, split into two halves like the mold to facilitate ejection by an opening stroke.

EPS and EPP/EPE processing employ very similar processes for molding production. The process and mechanical engineering principles used were developed for EPS and later adapted to the new particle foams EPE and EPP. Nonetheless, there is one essential difference between processing of EPS and the polyolefin particle foams: EPS still contains blowing agent during the molding process, EPE/EPP do not. A consequence of this is that the particles still have an expansion potential due to the evaporating blowing agent. The foam particles expand into the flank areas of the bead bulk due to the internal pressure, resulting in the large contact surfaces required for efficient fusing. EPP/EPE, in contrast to EPS, is fed into the mold against pneumatic overpressure, compressing the foam particles. The particles then expand after the stagnation pressures drop off – an important factor in increasing the contact surface area between the individual beads.

Figure 24 shows the further process steps. Following the molding process, the molding can be dried by tempering. The condensate evaporates and diffuses

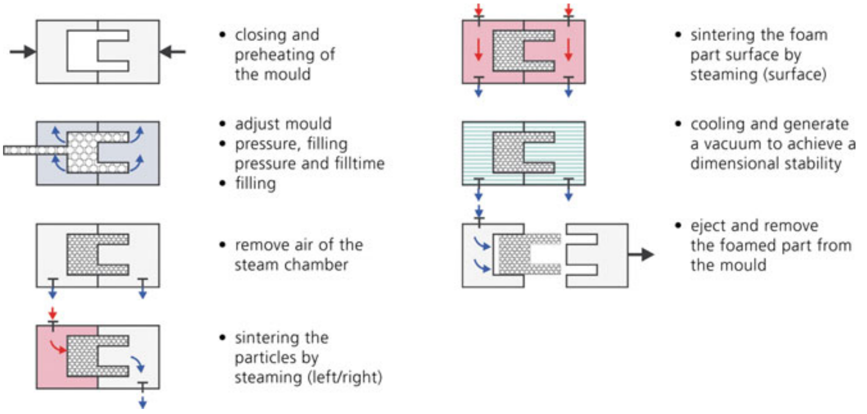


Fig. 24 Schematic diagram of EPP molding production cycle using the pressurized filling method

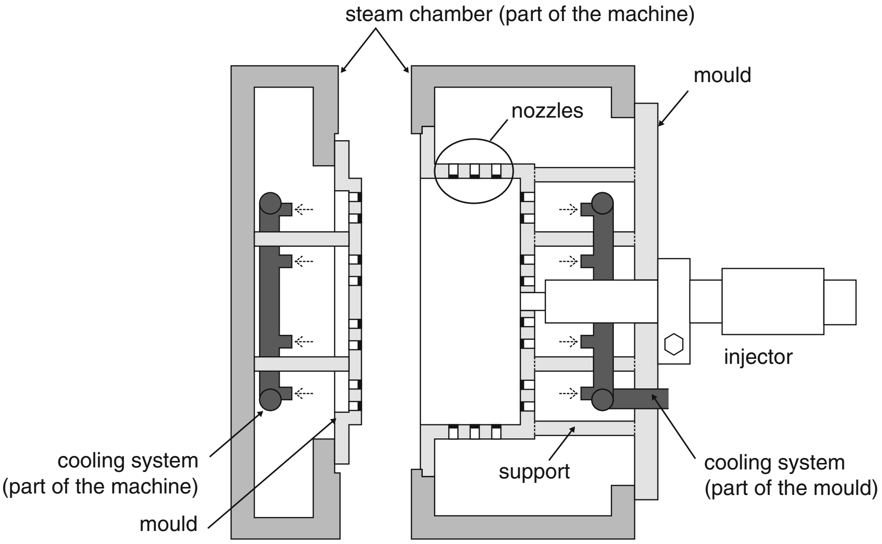


Fig. 25 Schematic drawing of an EPP mold inside the steam chamber

outwards, whereas at the same time air diffuses inwards. Warpage and sunken surfaces recover. The tempering time takes from a few hours to an entire day, normally 6–8 h at 80 °C.

Particle foam molds are characterized by integral channels in the mold walls that facilitate the escape of the air in the mold cavity during the filling process as well as exposure of the molding material to steam passed through these channels, Fig. 25.

4.3.10 Particle Foam: Examples of Applications and Properties

EPP is currently used in transport packaging applications and, increasingly, in the automotive sector. Examples of articles made from this material include side-on collision protection elements, sun visors, column and door moldings and bumper core elements (Figs. 26–30). EPS is used mainly for packaging and heat insulation in the construction industry (Table 7).

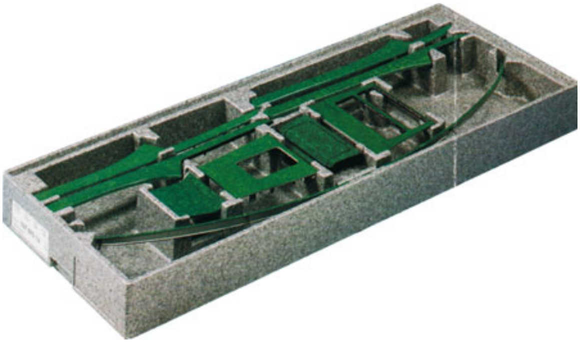


Fig. 26 EPP loadbearing element (Febra)

Fig. 27 EPP loadbearing element (Fagerdala)

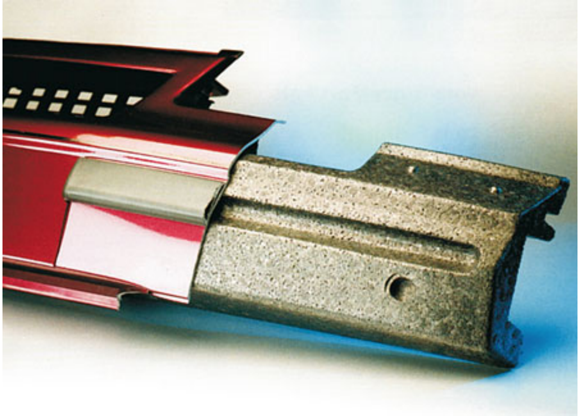


Fig. 28 EPP bumper core (Fagerdala)

Fig. 29 EPP seat cores (Febra)

4.4 Processing Techniques for Thermoplastic Fiber Composites [41]

4.4.1 GMT

GMT are used in major series production of large-surfaced, functionally integrated structural components. Cutouts from prepreg plates represent the starting material

Fig. 30 EPP sun visors (Febra)

Table 7 Properties of particle foams, compared to polyurethane

Property	Unit	EPP	EPE	EPS	PUR
Density	kg/m^3	30–45	35	25	90
Compressive stress at 50 % compression	kPa	150–350	90	250	20
Tensile strength at break	kPa	250–500	260	360	270
Elongation at break	%	25–15	33	<5	>30
Static hysteresis (ratio of plastic energy to total energy at 50 % compression)	%	75–85	52	82	70
Residual deformation after ½ h	%	1.5–3.0	1	16	2.0–3.0
Compression set after 24 h at 50 % compression	%	28–33	15	45	20
Water uptake (23 °C, 24 h)	% by vol.	1.5–1.1	1.2	1.7	7.0–8.0
Heat conductivity	W/(m K)	0.035–0.040	0.040	0.032	0.045

for the compression molding (CM) process. Mat GMT and short fiber GMT are differentiated.

Mat GMT is produced by means of needle-punching of glass fiber rovings. The design of the needle bed has a major influence on both the quality of the needle-punching and the subsequent flow properties (Fig. 31).

Impregnation with PP is done on a double belt press that consolidates the fibers with PP under the influence of pressure and temperature. After the composites cool, the GMT semifinished product can be cut for specific applications.

Short fiber GMT is produced using the Radlite® process, in which glass fibers with a length of 10–30 mm are mixed with PP powder and aqueous foam, then placed on belts and dried.

The cut semifinished product is heated in a forced-air oven to a processing temperature of ~230 °C, and placed in a compression mold by means of a transfer device. The semifinished product is formed into a structural component by means of extrusion at cavity pressures of up to 25 MPa. Depending on mold quality, the structural component must then be deflashed and cut with a punch to final contour.

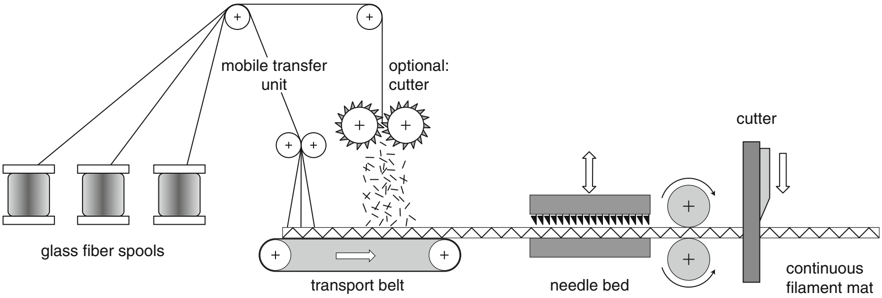


Fig. 31 Production of GMT semifinished products [42]

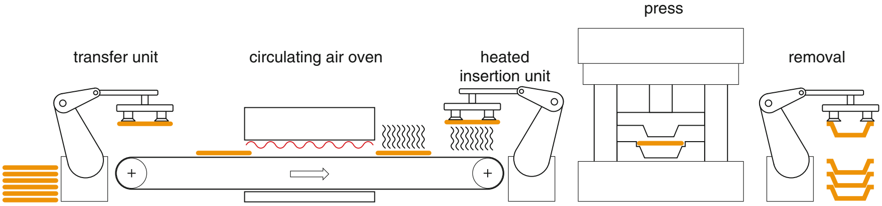


Fig. 32 GMT processing (according to [43])

The punching wastes from semifinished production can be added to the PP melt flow through a single-screw plasticizer.

Figure 32 illustrates the processing of GMT semifinished products into finished products.

Sommer et al. [60] present a successful new application combining the GMT/foaming processes (PP/PMI polymethacrylimide).

4.4.2 Sheet Thermoplastic Composites

A new method of production of long fiber-reinforced thermoplastic semifinished products is the “sheet thermoplastic composite” (STC) technology (Fig. 33). In this method, continuous fibers are worked into the polymer melt using a twin-screw extruder, whereupon a plate-like semifinished product is extruded using a special discharging device. The fiber rovings are completely wetted by the polymer melt before being pulled into the twin-screw extruder. The functional principle of long fiber wetting used in this process is shown in Fig. 37.

The wetting unit consists of two counter-rotating rollers, one of which is loaded with melt by means of an internal bypass. The melt builds up readily in the nip, improving fiber wetting. The glass fiber rovings are fed into the nip parallel and from above. They are gently and completely wetted with melt before they enter the co-rotating twin-screw extruder. A separate drive on the wetting unit rollers ensures

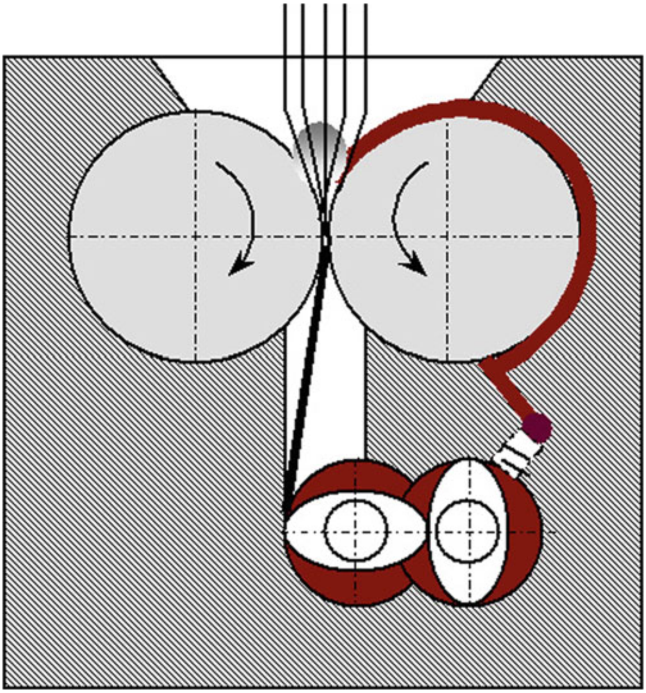


Fig. 33 Long fiber wetting in the STC process

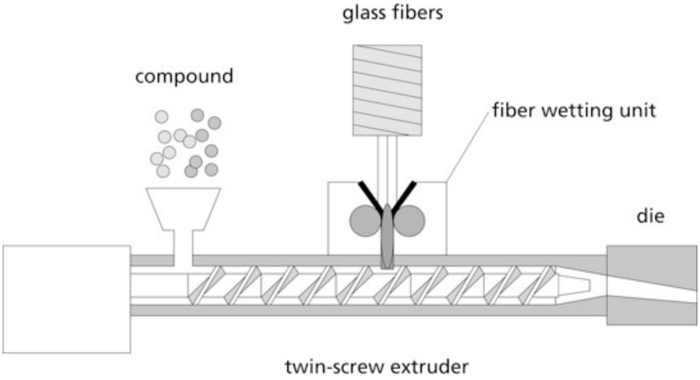


Fig. 34 Process installation STC

a continuous feed of wetted rovings to the extruder. Figure 34 illustrates the process installation.

The STC parameters for rigidity and strength are somewhat lower than in GMT, with impact strength at ~60 % of the GMT level. The advantages of the method include above all the avoidance of costs for semifinished production and the possibility of start/stop runs.

Two variants of the STC process are used in production practice.

In one system, a twin-screw extruder with a screw diameter of 60 mm and a process length of 42 D is in use. The polymer and additives are fed into the extruder. The plasticizing and compounding zone is used for melting and, optionally, degassing of the material. A bypass is used to direct a partial melt current onto the rollers of the impregnation unit. The glass fibers are conveyed into the impregnation unit and wetted with thermoplastic melt. The material, vacuum-degassed, exits in sheet form through a slit die. This specially optimized discharge die achieves a minimum of fiber orientation.

The second system is then already being loaded with a melt prepared, dispersed, and degassed in a twin-screw extruder.

4.4.3 Long-Fiber Granulates

Long-Fiber Granulates (LFT-G) are an alternative to GMT or STC.

LFT-G are supplied in the form of fiber bundles preimpregnated with plastic melt to provide for processing with a minimum of fiber damage in a single-shaft extruder. The molding compound thus produced is formed in the extrusion process into a structural component.

LFT-G are produced by means of pultrusion. In a variant of the pultrusion process, endless fibers are drawn through a thermoplastic melt then partially or completely impregnated, depending on the production process, by means of a mold, Fig. 35. In another variant, mixtures of glass filaments and polymer filaments are used for pultrusion, so-called hybrid fibers.

The processing of LFT requires high-precision compliance with the process parameters to minimize fiber damage and thus preserve the long fiber properties of the LFT, Fig. 36.

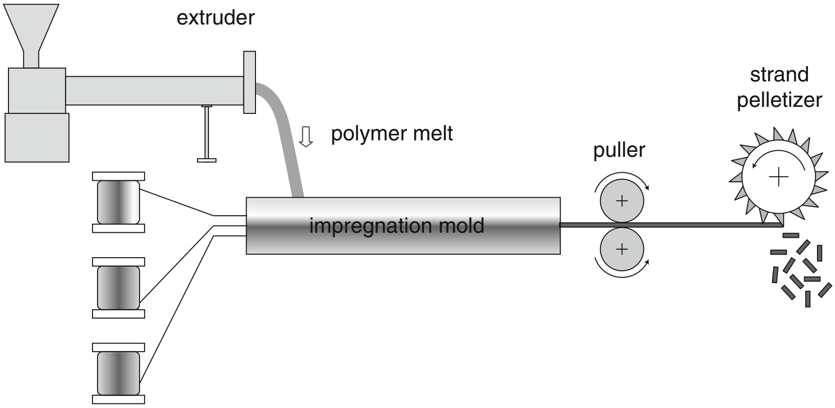


Fig. 35 Production of LFT-G semifinished products ([42])

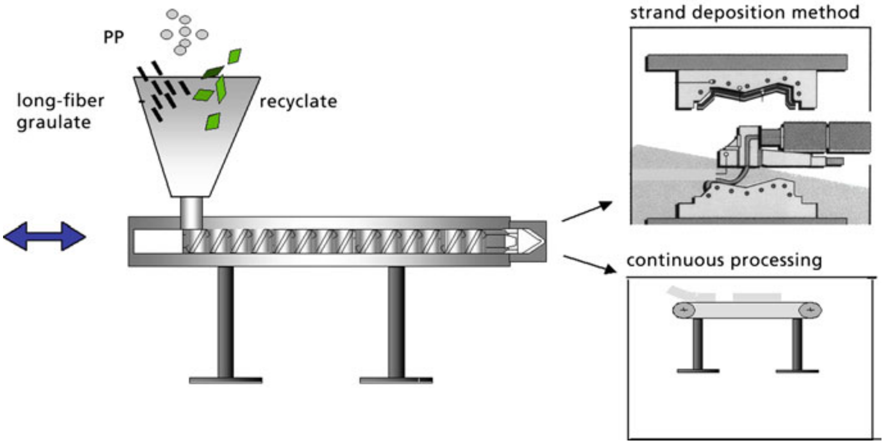


Fig. 36 LFT-G processing

The LFT “rods” or granulates, cut to 12 or 25 mm lengths, are plasticized for processing and production of structural components in a single-screw extruder, placed in a compression mold in the form of a melt cake and formed into a structural component. One of the main advantages over GMT is that the processing machine can be fed with bulk material in a vibrating hopper instead of requiring application-specific material cutouts. In this way, comminuted cutouts or used structural components can be directly recirculated into the production process.

Among processing methods of LFT-G, discontinuous processing in the so-called strand deposition method is differentiated from continuous processing.

In the *strand deposition method*, the LFT-G is melted in a single-screw plasticizer and allowed to pile up against a closed cutter unit. As in injection molding, the screw wanders backwards during the plasticizing process. Once the planned mass yield has been plasticized, the cutting unit opens, the screw locks and forces the plasticized material through the die by means of a transversal motion. Closure of the cutting unit cuts off the strand. The strand is then either deposited directly in the compression mold by means of a motion carried out by the entire unit, or placed in the mold by a handling robot equipped with needle grabbers.

In *continuous processing*, a fixed transversal screw, comparable to extrusion, continuously forces out a plasticized strand onto a heated discharge belt.

A further development of the LFT-G processing method is based on so-called “downmixing” of highly loaded LFT-G with glass fiber percentiles as high as 75 % by mass. By adding polymer granulate, these long fibers are “mixed down” to the glass fiber content level of the structural component during processing. For instance, it is possible to adapt the material to the product properties in a specific way by adding a PP with modified enhanced impact strength, whereby throughput and mixture quality do impose limits. “Downmixing” does offer a significant potential for cost savings compared to processing of conventional LFT-G.

4.4.4 Direct Long Fiber-Reinforced Thermoplastic Process (Overview)

In direct processing of long fiber-reinforced plastics, the material and the structural component are created, so-to-speak, during the production process itself. For this reason, processing has a significant influence on the properties of the resulting structural components.

The disadvantage of the methods employing plate or rod-shaped semifinished materials is to be seen in the processing requirement to heat up and cool the materials twice in the process. To ensure stability for both processing steps and later use, large amounts of expensive additives must be used to prevent thermal and thermal-oxidative decomposition of the matrix polymers.

Flexibility in terms of variations in material combinations in structural components is also severely limited by use of semifinished products. Large volumes of the same material combination are produced to ensure economical production of the semifinished products. There is thus no application-specific modification or stabilization of the material and the glass fiber content cannot be adapted specifically to the mechanical requirements of the structural components. These are the reasons why semifinished products are available in a limited number of material variants only.

Increased cost pressure has resulted in development of the so-called direct methods, which are generally characterized by the uniting of at least two process steps into one.

The methods presented here combine semifinished production and further processing of the semifinished products into structural components for direct processing, see Fig. 37.

A fiber composite is made out of the raw materials, for example glass fibers and PP, in a single step, followed by production of a structural component.

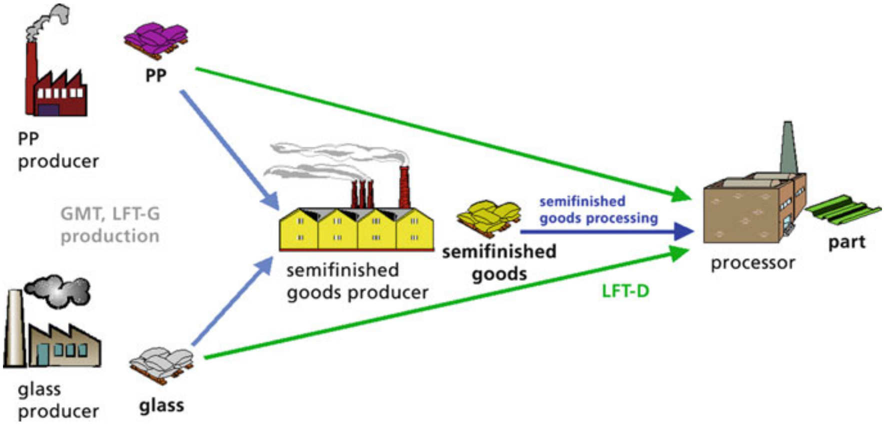


Fig. 37 Summary of the semifinished production and processing step in direct methods

Here is a summary of the advantages of these methods over semifinished product processing:

- Avoidance of the expensive semifinished production step,
- Reduction of the thermal and thermal-oxidative degradation of the polymer matrix,
- Greater flexibility in material selection, material adaptation and foreman logistics,
- More intensive competition and less dependence on specific raw material manufacturers.

This method can be used, for example, to realize different glass fiber content levels, vary the viscosity of the matrix polymers within given ranges and apply specific additives for modification (impact strength), stabilization, fiber–matrix coupling, and coloration of the material. Since production and processing of the material are completed in a single direct step, it is no longer necessary to warehouse a variety of material processed in a previous step, leading to a simplification of material logistics as well.

4.4.5 LFT-D Process

The original variant of a direct method for LFT-D has been in use for large-scale production since July 1997 [44, 46, 83].

This is known as single-machine technology, since material melting and processing into a composite are realized in one and the same twin-screw extruder. The polymer compound is melted and the fibers are drawn into the twin-screw extruder through an impregnation tool, Fig. 38. The fibers are chopped into long fibers, the molding compound is homogenized, and then discharged from a die as a plastification strand. This strand is pulled out onto a discharge belt and cut to structural component mass lengths by means of a cutter unit. A handling robot fitted with needle grabbers places the plastification strand cuts in the compression mold, in which the structural component is formed by extrusion. The final contour of the molding is produced by

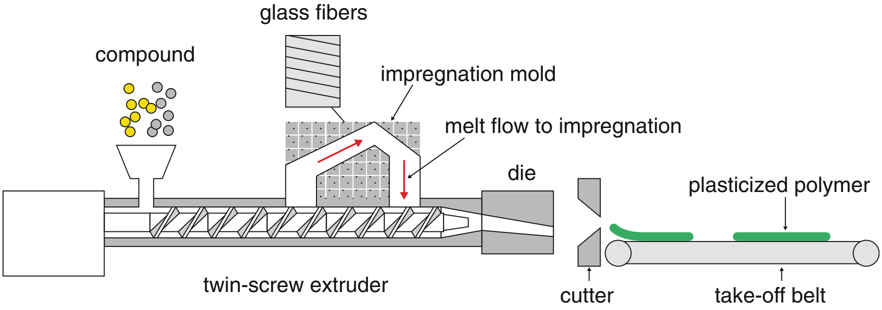


Fig. 38 LFT-D system scheme [61]

stamping, water jet cutting, or a combination of these methods. The resulting edge cuttings can be recycled back into the process. The recycled material percentage approved by the manufacturer for production of the first series part, the front-end mount for the Passat B5, was 30 %. Acceptance of recycled material additives means greater cost savings compared to the competitive GMT process.

The disadvantage of the single-machine technology for the LFT-D process is the necessity of using polymer compounds requiring stabilization for two-process steps and the utilization phase. The processing machine is also set to low rpms to ensure the process will result in the longest possible fibers. The result is lower throughput. Raising the throughput volume either shortens the fiber lengths or reduces the homogenization qualities.

4.4.6 CPI Process

There are other direct processes in addition to the LFT-D process. The CPI process named after Composite Products Inc. is based on a 1989 patent [62].

Figure 39 depicts the CPI process schematically. The matrix polymer is transported to the “A” extruder from the storage bunker by a gravimetric system. Material compounding of the matrix polymers and additives takes place in this extruder in a shearing and mixing process. Predrying precedes the process with moisture-sensitive matrices such as polyamides (PA) or polyethylene terephthalates.

The prepared melt is then transferred to the so-called “B” extruder, in which chopped glass fibers are fed and added gravimetrically. These so-called chopped strands have a defined initial length, for example 6 mm. In the feed section of this

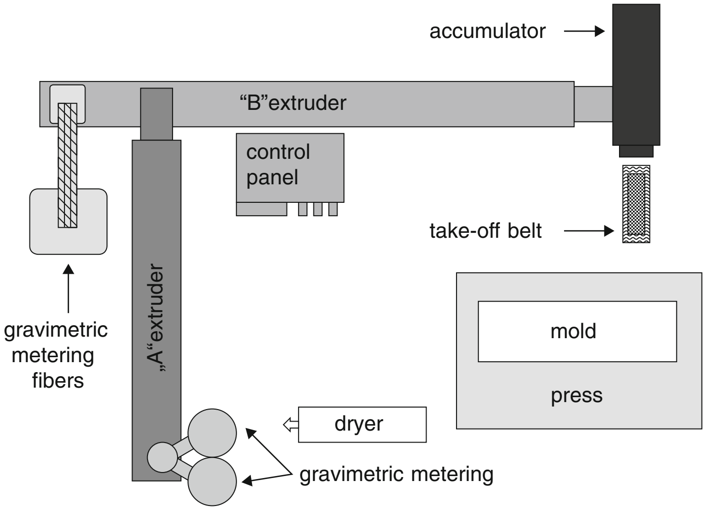


Fig. 39 Schematic presentation of the CPI process [45]

extruder, the fibers are preheated and the fiber bundles are opened, improving fiber impregnation with the matrix (Fig. 39).

The fiber composite melt is mixed with reduced shearing in extruder “B”, ensuring that the fiber lengths will be preserved.

Interim storage of the fiber composite material is realized in a heat accumulator, from which it is discharged in cycles by a ram, chopped into molding compound units by a cutter at the end of the accumulator, and transported on a discharge belt. The plasticized material produced in this way is transferred into a compression mold, then formed into a structural component in an extrusion process. The finishing steps are the same as in other CM methods used for long fiber-reinforced thermoplastics.

With separation of matrix compounding and fiber integration in two separate aggregates, the technology of the CPI process corresponds to the LFT-D-ILC process described in [41]. However, because of the limited length of the chopped fibers used, the resulting fiber lengths are much shorter than with the LFT-D-ILC process. This leads to reduced material parameters, in particular impact strength.

Feeding of the chopped fibers does not present any serious problems up to a length of ~6 mm, but with longer fibers the bridging effect sets in and renders controlled feeding difficult. Also, uniform wetting of the fibers is no longer ensured at higher fiber content levels. Because of the limited material homogenization capacity of a single-screw extruder, impregnation and homogeneity with this method are of low quality. The shear required to mix and homogenize the chopped fibers with the polymeric melt is much greater than in the LFT-D-ILC process. Poorly impregnated fiber bundles, so-called white spots, are observed on the surface of the structural component. Processing in the single-screw extruder also results in a lower throughput level than with the LFT-D-ILC process.

4.4.7 Inline Compounding in the Injection Molding Process

Direct processes based on the principle of injection molding are an important alternative to the methods described in which the fiber composite is formed by CM. They offer the advantages of a closed injection molding process that produces structural components with complex geometries that require no subsequent finishing steps. Fiber length, however, is limited by the process and the cycle time is much longer than in compression processes, depending on the geometry of the structural component.

The known processes are combinations of a compounding and an injection process respectively. A co-rotating twin-screw extruder is mounted on an injection molding machine as the compounding unit. Two different currently available systems are suitable for series production: Figure 40 shows the Krauss-Maffei variant featuring continuous compounding, a reliable basis for formula consistency. The cyclical injection molding process is compensated by buffering of the long fiber-reinforced plasticized material in a plunger injection molding aggregate.

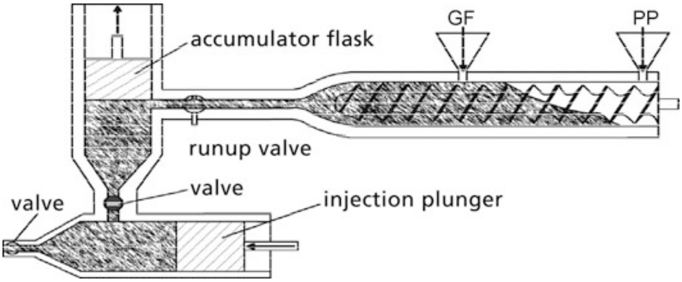


Fig. 40 Schematic diagram illustrating the continuous injection molding process [47]

Because the two-process steps are decoupled, the compounding process is carried out under uniform process engineering conditions, free of influences from the injection molding machine cycle. In the second variant, applied by the manufacturer Coperion, compounding and discontinuous injection are integrated in an intermittent, discontinuous process. The matrix material and gravimetrically fed additives, are plasticized in a twin-screw extruder. Endless glass fibers are drawn into the compounded melt, cut off by a tightly interlocking, co-rotating twin screw and integrated in the matrix polymer. The melted fiber-reinforced polymer is then transferred into a plunger injection unit. Once the entire injection volume has been compounded, the extruder terminates the plastification process and the plunger feeding unit injects the melt into the mold. Following the dwell pressure phase normal for the injection molding process, the next plastification cycle begins. The running speed of the twin-screw extruders is coupled to the gravimetric feeding system by a control unit.

5 Processing of Thermoplastic Elastomers

The processing of uncrosslinked plastics (thermoplastics, thermoplastic elastomers (TPE)) and crosslinked plastics (elastomers, duroplastics) differs in two main aspects:

1. Rubber or resin mixtures of filled (compounded) uncrosslinked polymers (prepolymers) are processed within a temperature range of 70–120 °C (max. 150 °C) to avoid premature crosslinking [7].
2. Rubbers and resins normally vulcanize/crosslink in heated molds at 150–220 °C. The cycle times are normally much longer than for uncrosslinked plastics [7, 63].

Table 10 compares several of the essential processing parameters of thermoplastics and elastomers. For instance, the viscosity differences lead to more robust,

Table 8 Basic processing parameters for thermoplastics and elastomers

Processing parameter	Thermoplastics (uncrosslinked)	Elastomers (crosslinked)
Processing temperature (°C)	200–390	70–150
Melting temperature (°C)	130–330	50–120 (uncrosslinked)
Viscosity (at 330/s respectively) (Pas)	200–800	800–2,500
Mold temperature (°C)	50–120 (form results from phys. cooling)	150–220 (form results from chem. crosslinking)
Injection pressures (bar)	300–2,000	200–400
Cavity pressure (bar)	200–1,500	10–40 (to 500)
Cycle time (s)	3–60 (300)	30 s to 30 min (h)

heavier machinery in elastomer processing. The process segments are for the most part liquid-tempered to dissipate the high levels of frictional heat produced. For this reason, the lighter machines, with lower drive output levels and often equipped with air cooling, are the better choice for thermoplastic processing in terms of investment and energy expenditures. Machine yield per hour is lower in thermoplastics processing.

Other differences, apparent in Table 8, above all cycle time, explain the energetic development of TPE over the past 20 years.

TPE are rubber-elastic at temperatures from −20 °C to +120 °C (assuming no major deformations), but show thermoplastic behavior in the melting range (160–180 °C).

TPE can thus be processed like thermoplastics, but show typical elastomer properties under moderate conditions, see Sect. “Structure of plastics” in Chap. “Properties of Plastics in Structural Components.”

The *processing of TPE* is realized with the same methods as thermoplastics. The discussion in Section “Processing of thermoplastics” therefore applies in principle to TPE as well.

The crosslinking elastomers in the TPE show two peculiarities:

1. The disperse crosslinked elastomer phase shows behavior similar to that of a polymeric filler. Viscosity is highly dependent on shear rate [7], but hardly dependent on temperature [7]. The flow exponent is between 3 and 5.
2. The die swell (see [7]): injection swelling) is, as would be expected, less than that of the matrix material as the concentration by volume of the crosslinked disperse elastomer phase increases. This may be advantageous in the extrusion process.

6 Processing of Elastomers

Many different substances are used in rubber processing. Fillers, plasticizers and processing agents are mixed into the rubber. Depending on the specification requirements applying to the finished rubber material, a number of different chemical agents are used in modern industrial operations (Fig. 41).

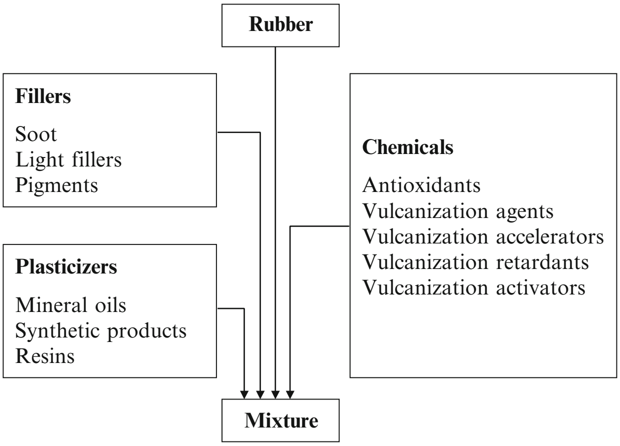


Fig. 41 Structure of a rubber mixture [64]

The components of a rubber mixture (Fig. 41) are supplied in a variety of different forms [65, 66]:

- As solids in the form of bales, crump, granules, chips or powder
- In paste or liquid form.

Elastomer processing covers the three (essential) process steps

- Weighing and mixing
- Forming (preform processing) and
- Crosslinking (vulcanization).

6.1 Weighing and Mixing

Mixtures are made up batchwise; all loading materials (Fig. 41) are weighed and laid out ready before mixing, or are automatically metered during the mixing procedure.

Table 9 shows an example of a formula for a truck tread mixture.

6.1.1 Mixing Procedure

- PremixingOnly for extremely high degrees of filling and/or polymers that do not tolerate blending well
- MastificationFrequently used in mixtures containing natural rubber (NR) after basic mixing

Table 9 An example of a tire formula (according to Goodyear Research Center) in percent by mass

10 % Steel cord	Example of a passenger car tire formula
3 % Textiles and bead wire	60 % SBR
42 % Elastomer (rubber)	20 % NBR
27 % Carbon black	12 % BR
8 % Oil	3 % IIR
10 % Chemicals (such as antioxidants, light stabilizer wax, stearic acid, zinc oxide, sulfur, accelerator)	5 % other

- Basic mixingInteractions with the polymers are initiated by integration of the main components. This applies in particular to strength-enhancing additives. Basic mixing is a dispersive mixing process.
- AftermixingIn highly filled, very hard/viscous mixtures (especially for tires) one or more additional procedures after basic mixing (aftermixing) are used to lower viscosity and elasticity for further processing.
- Final mixingLaminar mixing of the deformable and flowable crosslinking chemicals into the highly viscous basic mixture. Distributive mixing must be superimposed on the laminar mixing.

Mixing methods used by rubber processing operations:

- Discontinuous, batchwise processes in closed mixers (kneaders) and on mills and
- Continuous processes in mixing extruders.

6.1.2 Closed Mixers (Kneaders)

In a tempered kneading chamber, the loading materials are pressed into the kneading paddle section with rams and mixed. High shearing forces, and therefore considerable drive output, are required to cut the fillers and mix them with the highly viscous rubber. The intensive kneading work generates heat that must be dissipated by means of mantle tempering.

The advantages of making up the mixture in a closed mixer (kneader):

- Short mixing cycles (2–6 min) due to intensive integration and working of the material and
- Little release of dust or steam into surroundings because chamber is closed.

6.1.3 Mill

Although mixtures can be made up on mills alone, the normal procedure is to do the work in two stages: First, the basic mixture is made up in the kneader with high energy input within a brief period, without crosslinking chemicals. A considerable rise in temperature is taken into account. Then mixing is completed on a mill: First the hot mixture is cooled on the relatively large-surface mill rollers, then the crosslinking chemicals are added.

To produce a homogeneous mixture, a so-called stock blender can be used to remove the mixture sheet from the roller continuously, push it together and lay it back on the roller gap with an oscillating motion.

It becomes increasingly difficult to handle mixture charges on mills when batch mass exceeds 60 kg, making other techniques necessary, for example stuffing extruders.

6.1.4 Mixing Extruders

The high investment sums required for large closed mixer lines for making up mixtures from compact rubber bales led to the use of pulverized and crumped polymers in mixing extruders.

Two systems are preferred in practice:

- MVX systems (M for mixing, V for venting and X for extruding) by Farrel
- Twin-screw extruders (e.g., Leistriz, Coperion W&P).

For details, see Röthemeyer and Sommer [7].

6.1.5 Production of Semifinished Products (Preforms)

The finished mixture must be reduced, cooled and put into interim storage, whereby extrusion can be used to give the material a specific form (preform).

6.2 Forming (Preform Processing) and Crosslinking (Vulcanization)

Before it is vulcanized, the rubber mixture must be given the desired form. The molds are usually heated to facilitate vulcanization in the same step.

Many different methods are used, for example:

- Compression molding
- The preform, made with excess volume, is placed in a mold with a hinged lid and pressed between two heating plates.
- Transfer molding
- The mixture is transferred from an upper chamber of the compression mold, by a ram, through a sprue gate system into the lower section of the mold (cavity).
- Injection molding

- The mixture is injected by means of a ram into a mold heated to vulcanization temperature. The mold must then be kept closed until the desired degree of vulcanization is reached. Extremely fast vulcanization systems are used to optimize machine efficiency.
- Continuous vulcanization
- An extruder produces a profile strand that is carried on a conveyor belt through a tempering channel. Microwave energy, a hot air channel, a steam channel or a molten salt bath can be used for rapid heatup. After the required residence time, the strand is usually cooled in a water bath and wound or cut into lengths.
- Dipping
- Here is a listing of other production methods besides the three processes described for production of elastomer moldings.

For details see Röthemeyer and Sommer [7].

- Processes for production of rubber solutions
- Calendering of stripping and rubberized textiles
- Processes for production of rubber semifinished products by means of spreading
- Processes for production of rubber composites and structural elements (yarns, cord, fibers, threads) and rubber–metal composites.

6.2.1 Compression Molding (CM)

In CM, preforms are made from unvulcanized rubber mixture by means of extrusion followed by stamping or cutting. These preforms are placed in the cavities of the mold, which are heated to vulcanization temperature, then formed to produce the desired molding geometry by applying heat and pressure. Vulcanization sets in more or less rapidly after forming, Fig. 42 [7].

The flow process continues once the mold is completely closed, since the specific volume of the mixture increases in response to the heat, resulting in pressure compensation. This process can be shown in the *pvT* diagram of a rubber mixture [7].

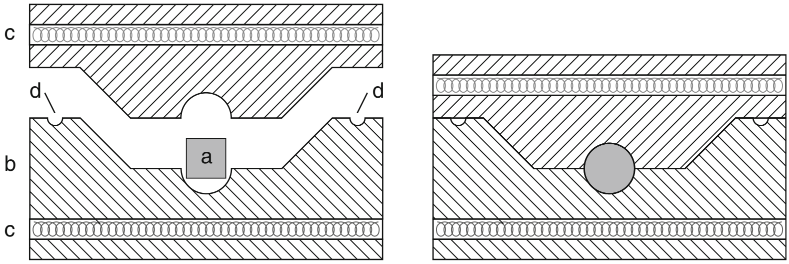


Fig. 42 The principles of compression molding (according to [7] (**a**) preform, (**b**) mold, (**c**) heating plates, (**d**) discharge groove

Injection Compression Molding (ICM)

An injection molding machine is used. The clamping unit is used as a press and preplasticizing is done in the injection unit. With this technique, much more precise feeding of the preplasticized mixture keeps the molding tolerances down.

In ICM, the predosed, preplasticized mass is injected into the opened mold. When the mold is closed, the flowing mass fills the mold cavity. Items with large surface areas such as flat packing, membranes, and flat product trays are suited to the ICM method.

6.2.2 Transfer Molding (TM)

Transfer compression molds have three sections, Fig. 43. The preform is placed between the heated upper and middle sections. When the mold is closed, the rubber mixture flows through the injection channels into the mold cavity in the lower section. After vulcanization, the press opens the mold and the mold cavities are emptied. The residual cake in the upper section and injection cylinders is discarded.

However, if the upper mold plate and upper part of the middle section are maintained at temperatures well below what would initiate crosslinking, the residual cake can be integrated in the following cycle (cold runner transfer mold).

6.2.3 Transfer Injection Molding

A further development of TM is to plasticize the rubber mixture in a screw-type extruder solidly attached to the press, heat it up and inject it into the transfer cylinder. Closing the clamping unit then fills the mold cavities as in normal TM, Fig. 44 [7].

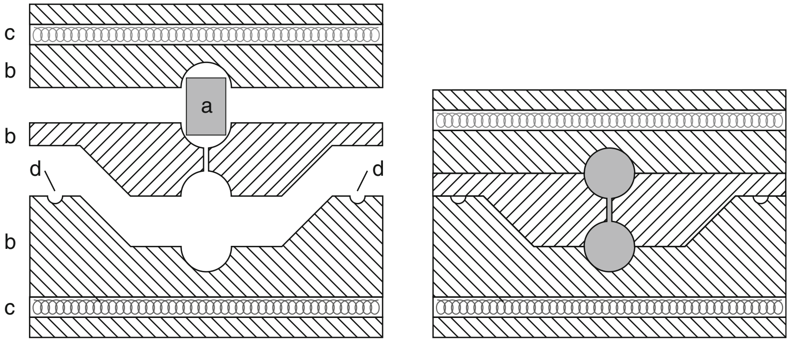


Fig. 43 Transfer molding (according to [7] (**a**) *preform,* (**b**) *mold,* (**c**) *heating plates,* (**d**) *discharge groove*

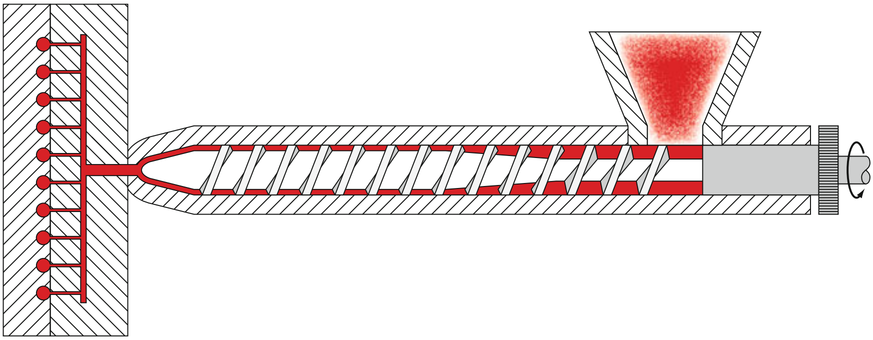


Fig. 44 Transfer injection molding method (according to [7])

Here as well, the projected article surface is always larger than the piston surface of the transfer cylinder, so that overpacking of the mold cavities due to pressure is not possible [7].

6.2.4 Injection Molding

Compared to both compression and transfer CM, injection molding requires shorter vulcanization and cycle times as well as better automation. On the other hand, mold costs are so high that only large-series production is economical.

Figure 45 [7] demonstrates the principle of injection molding for elastomers, which is in principle identical to injection molding of thermoplastics. The differences between the two processes are in the process parameters (injection time, dwell time, plastification time, cycle time, injection pressure, dwell pressure, static pressure, screw rpm, injection rate, cylinder temperature, die temperature, mold temperature, clamping force, expansion force, locking force, residual clamping force, injection path, dwell pressure path, residual strokeand feeding stroke). The amount of vulcanization time required, and the way the mold is heated for the crosslinking reaction are quite different.

The injection temperature is a major determinant of cycle time in injection molding of elastomers, especially for thick-walled parts.

The following rule of thumb applies:

$\Delta T = 4\text{–}5$ K/100 bar.

Thus, the temperature rise ΔT is higher by 4–5 K/100 bar of injection pressure. At 1,000 bar, the temperature increase would be ~45 K.

6.3 Opportunities and Risks in Elastomer Processing

Schobert et al. [67] describe, in Röthemeyer and Sommer [7], the example of Continental's Eco Tire, a particularly impressive example of the opportunities and risks involved in a *new tire formula*.

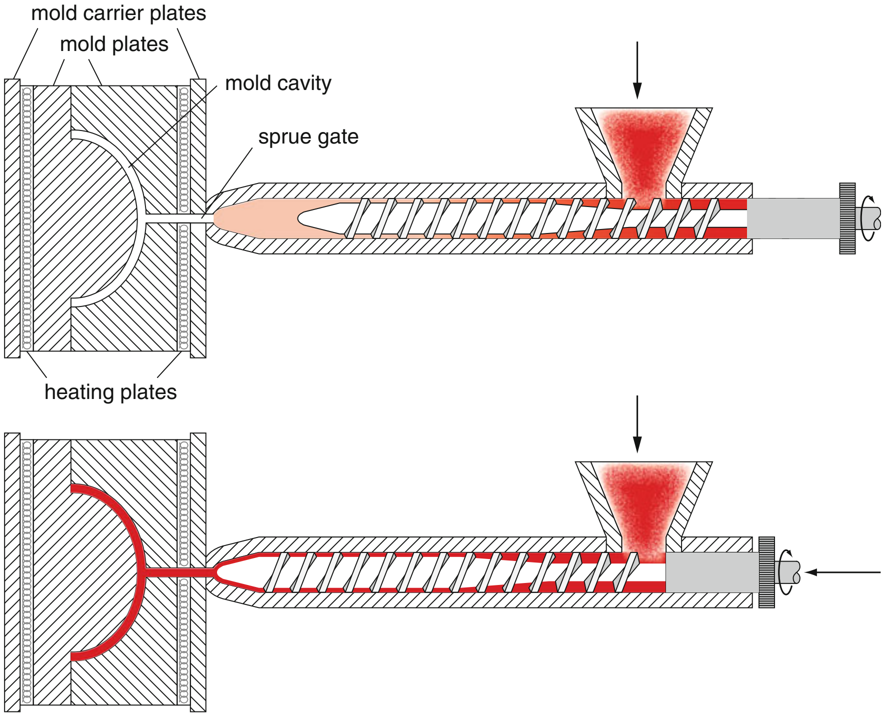


Fig. 45 Principle of reciprocating screw injection molding (according to [7])

To reduce the rolling resistance of automobile tires and improve their wet nonskid properties at the same time, the carbon black in the tire formula is replaced by active silicic acid with added organosilane.

A new risk arising in the mixing process is the ethanol released in the primary reaction, which temporarily exceeds current process limits. The resulting annual output of ethanol waste product is 540 t.

On the other side of the ledger stands an enormous opportunity to prevent emission of 4,750,000 t/a CO_2 [67], since the lower tire rolling resistance results in correspondingly lower fuel consumption levels. This balance does not yet include accidents, and later sequelae of accidents, avoided because of enhanced driving safety factors.

Today, the principles of holistic balancing are used to analyze and evaluate such examples correctly [68, 69], see also Sect. "Holistic balancing (lifecycle engineering)" in Chap. "Plastics and Structural Components – The Environment and Recycling."

Anyone who has ever visited an older production facility for tire vulcanization will be sure to remember the smell of the *vulcanization vapors*.

Schuster et al. [70] have defined two groups of emissions: Passive and active components of vulcanization vapors:

1. Volatile components of raw and loading materials: Monomers and dimmers, solvents, plasticizers, mineral oils, and antioxidants
2. Volatile reaction products of: Accelerators, activators, retarders, sulfur donators, and blowing agents.

All told, 0.05 % of the emitted vapors from the vulcanized material enter the environment every year as tons of waste gases through extraction equipment and, depending on the toxicity level, either retained or transformed by purifying units. Clearly one of the risks of tire production. However, the opportunities we consumers see in unrestricted mobility lets us ignore such risks for the most part.

In another example, Schobert et al. [67] address the *nitrosamine problem*. In view of the health relevance of the subject, their study is quoted verbatim for the most part (cited in a somewhat shortened form in Röthemeyer [7].

N-Nitrosamines, some of which are classified as carcinogenic, can form in a chemical reaction of certain amines and nitroso compounds. The formation of stable nitrosamines in rubber and other vulcanized materials requires the presence of:

- Secondary amines and
- Nitrosing agents (NO_x).

The reference [71] cites a number of comments on the formation reaction and possible sources.

As these things came to light, the rubber processing industry was the obvious first choice to remove the nitroso compounds from the raw material pallet since substitutes were available in order to eliminate one of the components in the material itself. On the other hand, the nitrous oxides, which are adsorbed to the active surfaces of the fillers or present in the air we breathe as combustion gases from vehicle engines, cannot be eliminated. These particular substances can be reduced by optimized combustion and catalysts, but not avoided completely. Substances that form nitrosable amines include, among others, di-*n*-alkyl dithiocarbamates, di-*n*-alkyl thiurame sulfides, *N*,*N*′-dialkyl benzothiazyl sulfenamides and benzothiazyl sulfene morpholide.

These are accelerators and crosslinking agents with which in particular heat-resistant vulcanizates can be produced based on natural and synthetic rubber, as well as filler activators based on amines.

These substances have now been quantitatively eliminated from tire production, but substitution has not yet been completely realized for technical products (rubber–metal compounds, hoses, drive elements, etc. – i.e. products used under the hood exposed to higher temperatures (in some cases due to efforts to reduce noise emissions by means of engine encapsulation). Other vulcanization accelerators decompose to produce secondary amines that are less toxic, but these materials have other major drawbacks that prevent their being considered, for instance a much higher molar mass requiring much higher dosing to achieve the same effect, at which concentrations they are no longer soluble in the matrix and therefore bloom. Another aspect is that the new products often cannot meet customer specifications.

Another approach under study is the search for so-called nitrosamine formation inhibitors. Vitamin E (dl-α-tocopherol) was under discussion some time ago [72], but we are not aware of any applications on a technically useful scale. There is a legal regulation providing for special protective measures when handling *N*-nitrosamines (Technical Regulation for Hazardous Substances TRGS 552 – *N*-Nitrosamines [73]) as well as substantial reference materials [74–78]. The TRGS lists areas in which state-of-the-art technology involves unavoidable formation or release of carcinogenic *N*-nitrosamines. The examples explicitly listed for the rubber industry are: weighing, mixing, semifinished processing, aftertreatment, storage, and vulcanization. The areas listed as "critical" are: calender, extrusion systems, salt baths, vulcanization in molds, inspection, storage of technical rubber articles and tires.

In storage areas, the nitrosamines often penetrate deep into the walls, where they persist for longer periods. Contaminated walls can be wallpapered or painted using special protective materials in order to "encapsulate" them as protection against the contaminants. The TRC values (TRC = technical reference concentration) is listed as 2.5 $\mu g/m^3$ [67].

Röthemeyer and Sommer [7] provide detailed information.

7 Processing of Duroplastics

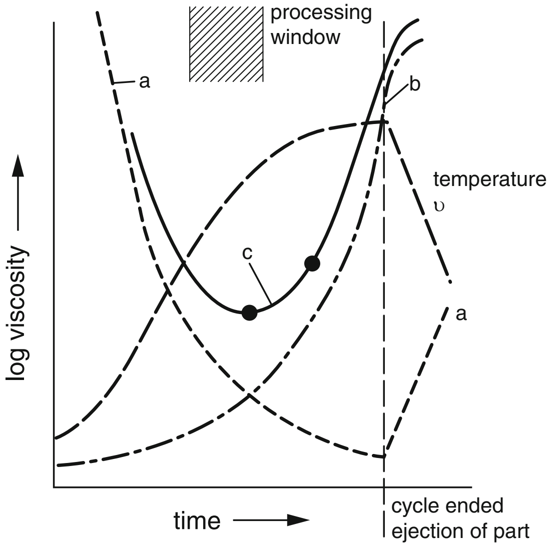
7.1 Processing Principle

Duroplastic molding compounds consist of a thermosetting resin (for example phenolic resin, urea–formaldehyde resin, melamine resin, polyester resin and epoxy resin), a reactant (curing agent), filling and reinforcing materials, and a number of other additives. As a rule, the resins are prepolymerized and therefore consist of macromolecules with a medium-level molar mass but with a degree of crosslinking that is still very low. The resins are primarily formable. The primary forming is done in molds, usually heated, by means of CM, TM, or injection molding. The molding compound polymerizes in the mold and crosslinks to form an unmeltable and insoluble duroplastic. Because of the high level of inherent rigidity of end-crosslinked duroplastics, demolding is usually done from the hot mold, usually at 150–180 °C, without cooling. There are also cold-curing, exothermically crosslinking duroplastics, for instance some epoxy resins.

Figure 46 shows that the processing time window is narrow, defined on the one hand by the drop in viscosity due to heatup and on the other by the viscosity increase due to crosslinking. Beginning at a certain degree of crosslinking the material is no longer deformable. The curing rate of a molding compound can be adjusted by changing the degree of precondensation. This can also be done chemically by selection of certain types or amounts of curing agents.

Figure 47 shows the influence of the degree of crosslinking on the materials properties for shear modulus and in principle for the A, B, and C states. The glass transition temperature rises at higher degrees of crosslinking. The deterioration of

Fig. 46 Viscosity curve of a molding compound introduced in cold state into a hot mold; (**a**) Influence of heatup on viscosity. (**b**) Influence of crosslinking. (**c**) Resulting viscosity curve, qualitatively plotted against time as a superimposition of the effects of **a** and **b**



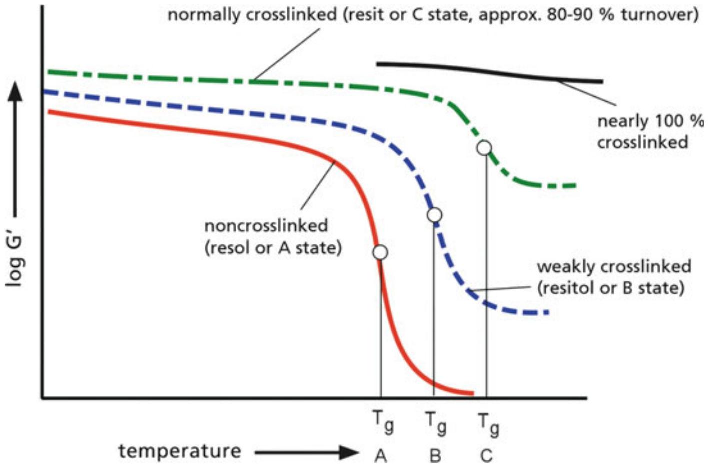


Fig. 47 Shear modulus (qualitative) for a duroplastic at different condensation stages

properties in the main softening range is clearly reduced with increasing crosslinking, as shown in Fig. 47.

The viscosity of the curable molding compounds (before curing is completed) is usually very low (at 70–120 °C) – around 1–50 Pa s. Thermoplastic melts are between 200 Pa s and 800 Pa s (see Table 10, Sect. "Processing of thermoplastic elastomers"). In contrast to injection molding of thermoplastics, duroplastics form flashes and skins the subsequent removal of which is expensive.

Mold gaps must be minimized by means of increased clamping force and vertical flash faces, whereby increased tool maintenance should be scheduled due

Table 10 Crosslinking reactions and their secondary products for processors

Resin types	Abbreviation	Resin building block	Duroplastic networking reaction	Reaction product split off in crosslinking	Residual monomer[a]
Phenoplastic	PF	Phenol and formaldehyde	Polycondensation	Water	Formaldehyde
Aminoplastic	UF	Urea and formaldehyde	Polycondensation	Water	Formaldehyde
	MF	Melamine formaldehyde	Polycondensation	Water	Formaldehyde
Unsaturated polyester	UP	Unsaturated diacid and diol	Polyaddition	None	Styrene
Expoxide	EP	Bisphenol and epichlorohydine	Polyaddition with diamine or diacid	None	Diamine
Diallyl phthalate	DAP	Monomeric diallyl phthalate	Polycondensation	Water	Diallyl phthalate

[a] Potential residual monomers following the crosslinking reaction, purportedly harmful to health

Cause: Formulation (stoichiometry) incorrect; crosslinking conditions false: temperature too low, time too short

to wear at high production counts and long running times. Also, the molds require more cleaning after demolding than is the case with thermoplastic processing (Table 11). The same usually applies to use of mold release agents.

After demolding, deflashing in revolving drums (with mixtures of nuts and apricot pits) or by blasting (with soft granulate) is usually necessary. Since the curing process necessitates a longer cycle time, especially for thin-walled parts, automated production is a major factor in terms of the competitiveness of a given operation [17].

Table 12 provides an overview of duroplastic processing based on existing standards.

Duroplastic are used almost exclusively as filled or reinforced materials. Without filling or reinforcing materials they are often brittle (phenolic resin, melamine resin), show excessive shrinkage (polyester resin), are too expensive (phenolic resin, epoxy resin), or are not strong enough. The filling and reinforcing additives are selected according to a very wide range of applications.

In general, fillers should make the material less expensive.

Reinforcing materials usually increase its strength, see also Sect. “Reinforcing materials” in Chap. “Properties of Plastics in Structural Components.”

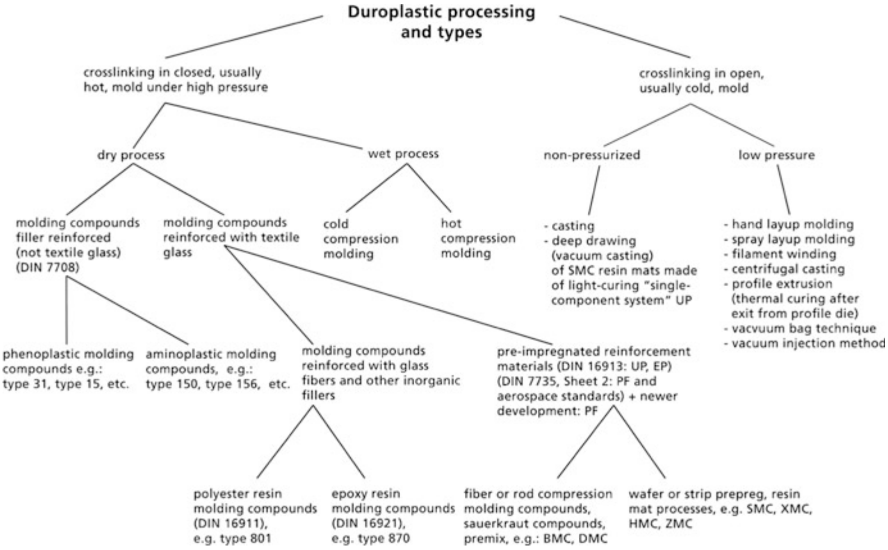
Examples of fillers:

- Quartz powder
- Chalk
- Calcium carbonate
- Wood meal
- Cellulose

Table 11 Potential resin/filler combinations for curable molding compounds

Components		Examples of molding compound types				
Constant	Variable					
Resin	Filler	Phenolic resin with	Wood flour = type 31	Cellulose = type 51	Textile fiber = type 71	Textile chips = type 74
Filler	Resin	Cellulose with	Urea resin = type 131		Melamine resin = type 152	Phenolic resin = type 51
Resin	Filler mixture	Phenolic resin with	Wood flour and textile fiber = type 83		Cellulose and textile fiber = type 84	Cellulose and wood flour = type 85
Resin mixture	Filler	Melamine and phenolic resin with		Wood flour = type 180		Cellulose = type 181
Resin mixture	Filler mixture	Melamine and phenolic resin with		Stone flour and wood flour = type 182		Stone flour and cellulose = type 183

Table 12 Categories of duroplastic processing



Examples of reinforcing materials:

- Glass fibers
- Carbon fibers
- Carbon black
- Aromatic polyamide fibers
- Fabric chips
- Natural fibers (cellulose, etc.)

7.2 Types of Duroplastics (Curable Molding Compounds)

The most important resin types used in production of curable molding compounds are phenolic, urea, melamine, unsaturated polyester, epoxide and diallyl phthalate resins. Curable molding compounds built up with these bonding agents are described in DIN 7708[4] (Phenoplasts and Aminoplasts), DIN 16911[5] and 169132[11] (Polyester Molding Compounds and Polyester Resin Mats), and DIN 16912[6] (Epoxy resin Molding Compounds). There is as yet no standard for diallyl phthalate masses, for the test method see ISO 1385 – 1.02.1977.

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[4] soon to become DIN EN ISO 14527.

[5] soon to become DIN EN ISO 14530.

[6] soon to become DIN EN ISO 15252.

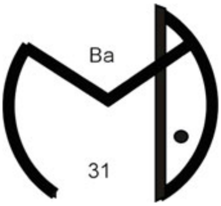

Fig. 48 Monitoring symbols for classified molding compound types. Type number Ba company initials (manufacturers). (Seal of quality of the private quality association AVK-TV)

The aim of standardization of certain curable molding compounds is to establish a system among the many different substances and facilitate ordering of defined materials by processing operations. The type tables define minimum specifications for typical properties determined, in accordance with relevant standards, on the basis of defined test objects.

If a molding compound meets the type property specifications, the manufacturer has the right, after certain formalities have been observed, to obtain and use for his molding compound the Seal of Quality of the private Quality Association AVK-TV (www.avk-tv.de/guetezeichen), Fig. 48.

7.2.1 Formaldehyde Problem in Wood and Wood Production

The bonding agents used in wood-based fiberboard are usually phenoplasts or aminoplasts. Formaldehyde emissions from wood fiberboard occur when formaldehyde (residual monomer) is still present after the crosslinking reaction, and in hydrolytic processes during use of the wood fiberboards.

"Formaldehyde-free" wood fiberboard is bonded with isocyanate MDI. When hydrolytic processes ensue, wood fiberboard with UF[7] is the worst, MF[8] is better and PF[9] is the best, since formaldehyde bonds most strongly with phenol (Novolak). The wood itself emits formaldehyde in small amounts, noticeably at higher temperatures [81].

7.3 Processing Methods

7.3.1 Compression Molding (CM)

Mechanical or hydraulic presses and two-part or multiple-part molds are used in this process. They can be made of GF-reinforced UP resins for cold CM. Medium-sized series are produced by means of cold CM, large series with hot CM. In

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[7] Urea resin (UF).

[8] Melamine resin (MF).

[9] Phenolic resin (PF).

thermoforming, either the wet method or preimpregnated reinforcement material (SMC) can be used.

For heatup and plastification of the molding compound, basic times of ≥1 min and 15–60 s/mm wall thickness are calculated for curing, depending on the molding compound type used.

This results in curing times of several minutes that increase with wall thickness. The curing times can, however, also be shortened considerably by preheating the molding compound:

Possible methods:

- High-frequency, microwave, infrared preheating, especially for tabletted molding compounds out-of-mold
- Heat conduction from the hot mold walls into the molding compound (takes a lot of time)
- In an oven at temperatures that do not lead to particle adhesion
- By means of friction (only possible in injection molding and ICM or in screw aggregates installed upstream from the CM automats)

In screw aggregates, the molding compound, as in injection molding, is plasticized with the rotating screw, after which the screw acts as a ram to eject the compound into the compression mold (feeding). In the latest technical developments, one or more twin-screw extruders are used, from which the plasticized material is transferred by means of robot handling technology into the compression mold.

The compression process (forming) occurs either at the same time as the melt is heated or during the densification phase when the mold is closed. As described above, injection from the screw cylinder is also possible. The compression molds are heated, as described in 7.2, in contrast to thermoplastic injection molding.

The pressures in the mold are around 50 bar for moist masses, for preheated masses around 150 bar, up to a maximum of 400 bar. Now the molding compound is crosslinked in the mold cavity by means of a chemical reaction (curing): Curing time is a major factor in cycle time.

Figure 49 shows the normally used mold types.

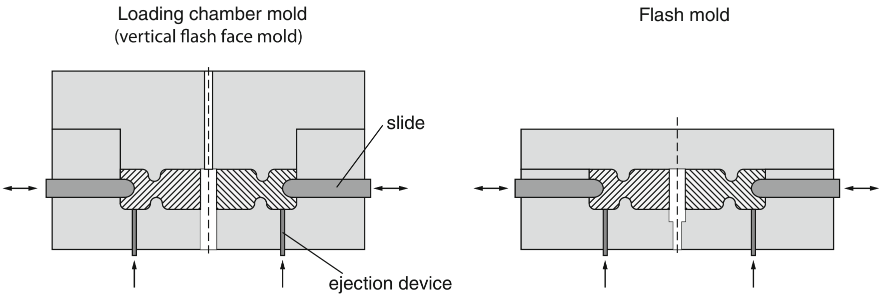


Fig. 49 Compression molds for processing of duroplastic molding compounds

Vertical flash face molds cost 10–15 % more than flash molds. On the other hand, deflashing requires less work with the vertical flash face molds. If the molding compound feed is not controlled precisely, voids or pores result from underdosing and internal stress from overdosing. Charge cavity molds are therefore used especially for large parts, since mass feed is simpler with them. On the other hand, flash molds are run with overflow for small parts and on CM automats in particular.

Then the moldings, as in injection molding, are demolded by ejection devices and the mold is cleaned by means of a blower device. Since volatile components are produced during curing of, for example, phenolic resins and aminoplast masses, ventilating the mold by raising the upper die briefly and sucking out the air is a useful procedure.

As described above, the thermoformings must be deburred and deflashed above drilled holes, for instance by means of water jet cutting.

Inmold powder lacquering or inmold painting can be used to produce surface coating on some compression molded parts. Powder lacquer, preferably UP resin, is injected electrostatically into the hot mold, which is opened by 100–200 μm and forms an integral layer with the molded part when the mold is reclosed.

7.3.2 Transfer Molding (TM)

Whereas in CM the mass filled into the mold is plasticized from the walls, plastification of the plastic in TM takes place in an additional cavity (Fig. 50). Similarly to injection molding, the plasticized mass is injected through a sprue gate into the mold cavity. Another method is to heat mass tablets before placing them in the cylinder, for instance using high-frequency waves [6].

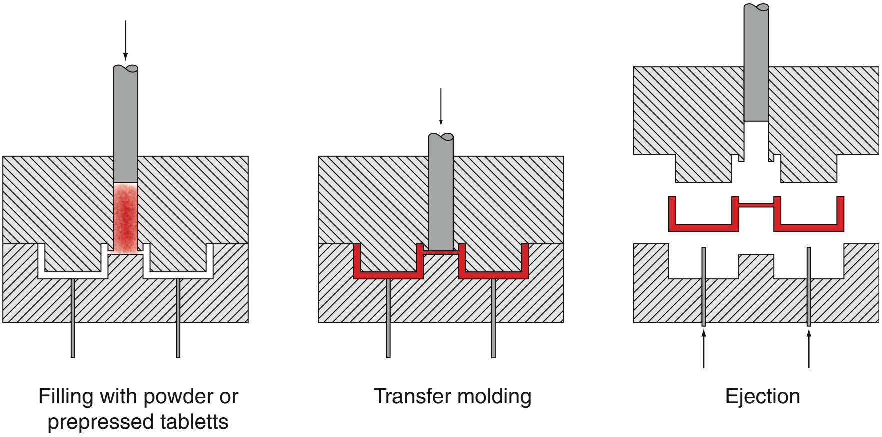


Fig. 50 Transfer molding

7.3.3 Injection Molding

The technology of injection molding of duroplastics is, in principle, the same as in thermoplastic processing, Fig. 51. To avoid premature initiation of crosslinking in the plastification cylinder, the temperatures must not exceed 80–120 °C. As in elastomer processing, the frictional heat must be dissipated, for which reason the aggregates are liquid-tempered for elastomer processing as well. The working mold temperatures are usually between 160 °C and 200 °C.

In principle, the screws used for processing of crosslinking compounds are shorter, and have a deeper-cut feed section, than thermoplastic screws.

The compression is low-level with duroplastic screws. There are practically no shut-off nozzles or nonreturn valves for blind corners and crosslinking deposits.

Because of the much lower viscosity of uncrosslinked molding compounds, parting lines and breakouts must have very smooth surfaces. If the controls and structural design features are insufficient, there will either be flashes or overflow and/or insufficient cavity filling.

7.3.4 Casting

The thermosetting resins are supplied in a highly viscous state dissolved in styrene. Under favorable conditions (cool, dark), the storage stability can be as long as 6 months. According to processing specifications, part of the resin is mixed with curing agent (peroxide) and the rest with accelerator. Then these premixtures are combined and mixed. After this, the charge remains workable for a limited length of time. Direct mixing of curing agent and accelerator will result in an explosion.

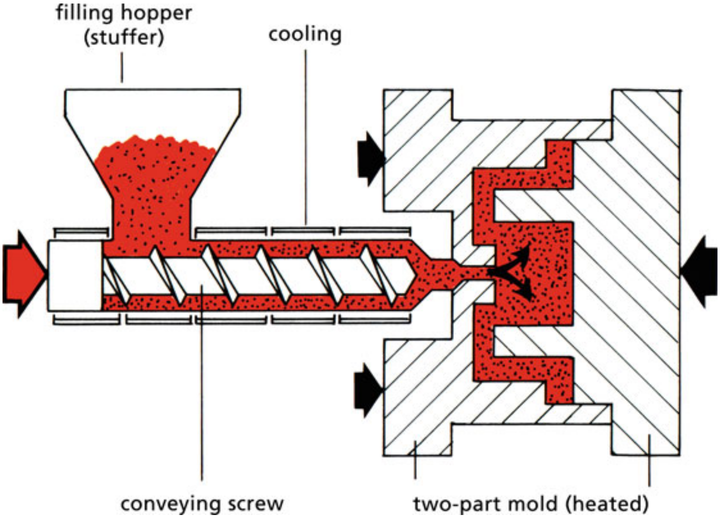


Fig. 51 Injection molding with screw feed (schematic)

Cold-curing resins crosslink at room temperature. Postcuring is done over a period of 4–5 h at 80 °C or for several weeks at room temperature. Hot-curing resins crosslink at temperatures between 80 °C and 120 °C rapidly and uniformly. They require no postcuring.

The unreinforced casting resins are used to make monophase moldings, also with embedded preparations.

7.3.5 Glass Fiber-Reinforced Thermosetting Resins: Hand Laminating

Numerous methods have been developed in the course of time for processing thermosetting resin mixtures. The best-known is hand laminating. It is used mostly for individual articles, small series, and articles with large surfaces. Little investment is required. This method is therefore best suited for applications at craftsman's shops.

The glass fiber reinforcement materials are impregnated by hand with the thermosetting resin using rollers or brushes. Highly resinous covering layers are applied by brush or spraygun to improve the appearance and protect the surface (Fig. 52).

7.3.6 Profile Extrusion, Pultrusion, Pulforming

The methods of producing GF-reinforced profiles made of UP and EP resins known under the collective term pultrusion result in molding material bending strengths up to 700 N/mm^2. Take-off speeds exceeding 1 m/min are achieved.

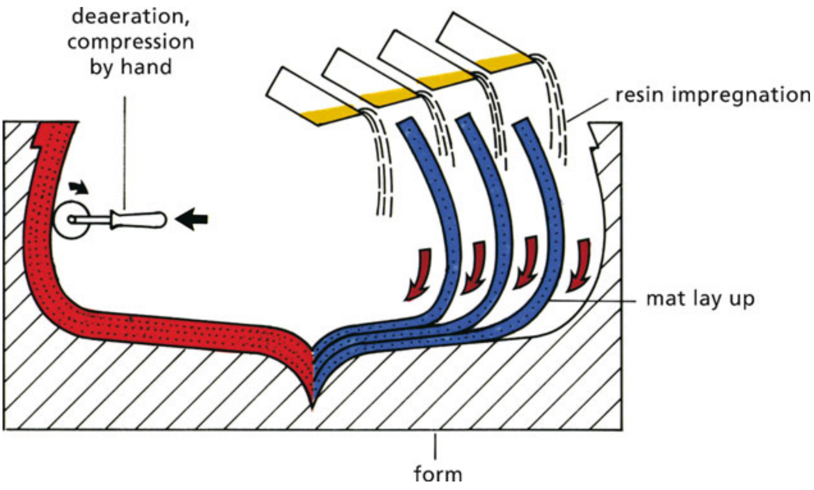


Fig. 52 Hand method (schematic)

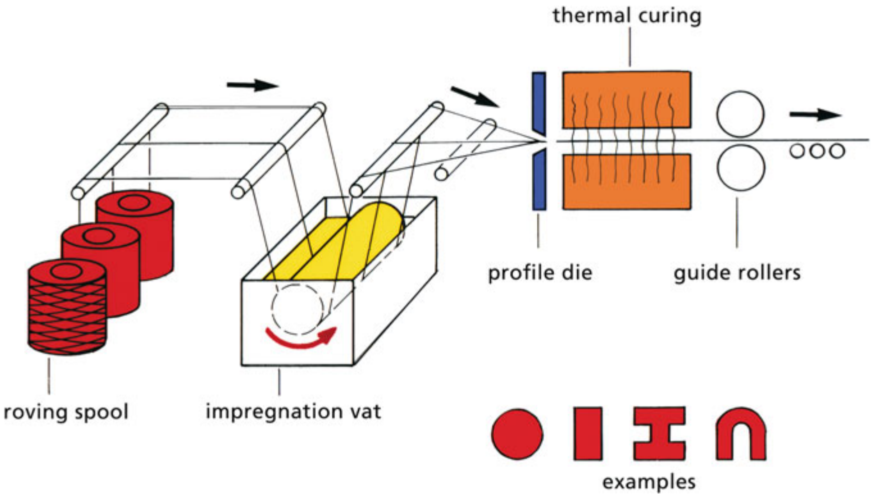


Fig. 53 Profile extrusion process (schematic)

A combination of profile extrusion and CM (pulforming) introduced in the US is a further development of this method. The reinforcing glass fiber rovings are drawn through compression molds after passing through the impregnation bath and formed into complex parts such as GRP springs or bumper mounts. Figure 53 illustrates the process principle.

7.3.7 Filament Winding

Filament winding can be used in rationalized processes to produce pipes, pressurized containers, drive shafts, and other cylindrical bodies. Endless fibers, glass mats, or rovings that have been through an impregnating bath are wound around a mandrel. The glass filament reinforcement can be adjusted with the help of the winder kinematics so that the strength of every segment of the molding can withstand the locally applied forces, Fig. 54.

7.3.8 Spray Layup

Instead of laying up textile glass mats, rovings are chopped continuously by a cutter to fiber lengths of 20–50 mm, then blown onto the mold surface covered with release agent or applied to the surface prepared for coating. Resin application is done at the same time. The preaccelerated resin is mixed with peroxide, either inside or outside of the gun, and sprayed. The spraying is done by hand or with automated spraying equipment designed accordingly. The wetting of the fibers is realized either during or after the calculated glass and resin volumes contact the mold or surface to be coated.

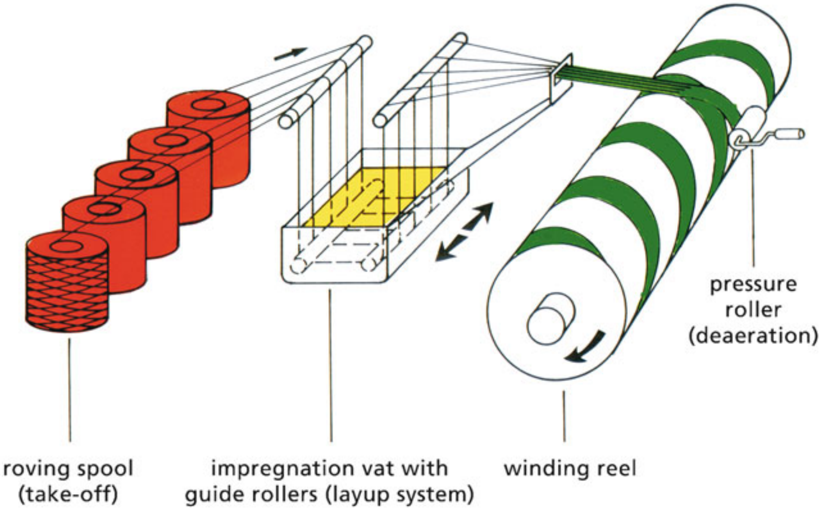


Fig. 54 Pipe production using the filament winding process (schematic)

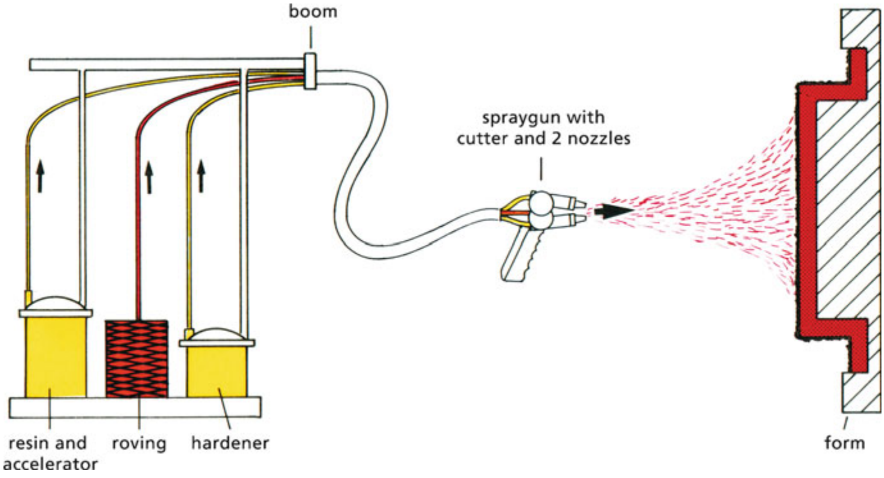


Fig. 55 Spray layup process (schematic)

In the spray layup process, Fig. 55, low-pressure and high-pressure methods are differentiated, thus predefining the roving specifications.

7.3.9 Vacuum Molding

Small series of moldings with smooth visible surfaces on both sides are made using the vacuum molding process, Fig. 56. Two mold halves are required. One half can

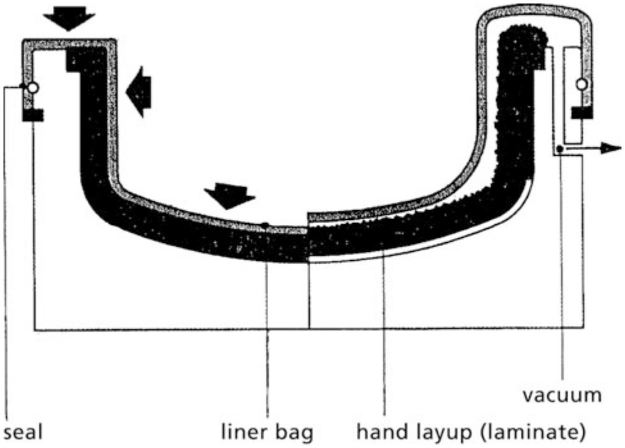


Fig. 56 Vacuum process (schematic)

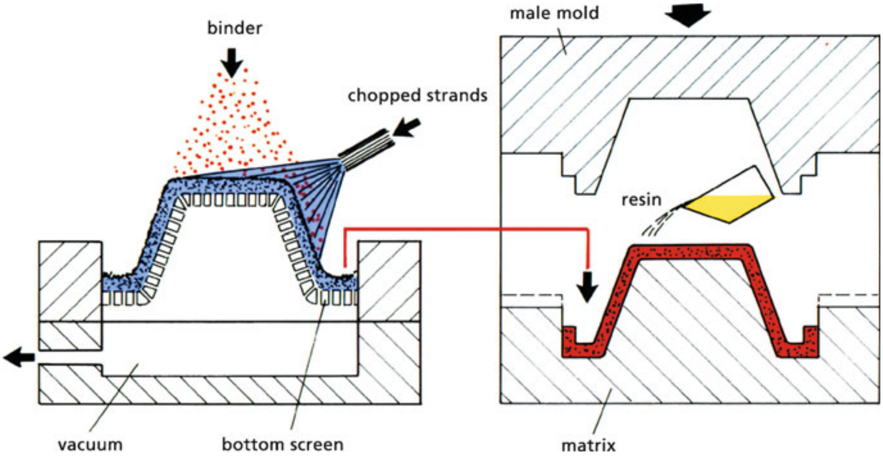


Fig. 57 Preform production and pressing (schematic) (e.g., motorcycle fenders)

consist of a flexible cloth. The fiber strips are placed in the solid lower half of the mold, impregnated with resin, then covered with the rubber sheet or upper mold half. The resin is distributed by connecting the mold cavity to a vacuum pump. Excess resin and air bubbles are sucked off.

7.3.10 Injection Forming

This method is suited to production of small and medium-sized series. Two mold halves are used. Before the mold is closed, the reinforcing material is usually placed in it as a preform (Fig. 57). Then thermosetting resin is injected into the mold cavity using the RTM method. Complex moldings with smooth, closed surfaces can be made such as engine hoods, etc.

7.3.11 Centrifugal Casting

The forming molds are lined with nonimpregnated reinforcing materials, which are then impregnated with thermosetting resin mass by means of the centrifugal force. The insertion of mats and textiles must be realized before rotation is begun, whereas addition of chopped glass and resin can be realized through a lance during rotation.

The centrifugal force presses the material against the outer wall of the rotation mold and impregnates it with resin. Curing is induced by blowing in hot air. The rate of rotation depends on the diameters and is around 500–3,000 rpm. Pipes made with the centrifugal casting method have a smooth outer surface (Figs. 58 and 59).

7.3.12 CM of Fiber-Reinforced Duroplastics

SMC (sheet molding compound) is the process used for large series, above all in the automotive and electrical industries. The interiors of the ICE train wagons are also made of SMC.

These molding compounds comprise essentially unsaturated, i.e. curable, polyester resins, curing agent, mineral fillers, glass fibers and auxiliary and loading materials. These latter include dyeing pigments, zinc stearate as a lubricant and release agent and magnesium oxide to thicken the resin mass. Table 13 shows three typical formulae. The LS (low-shrink) and LP (low-profile) formulae are molding

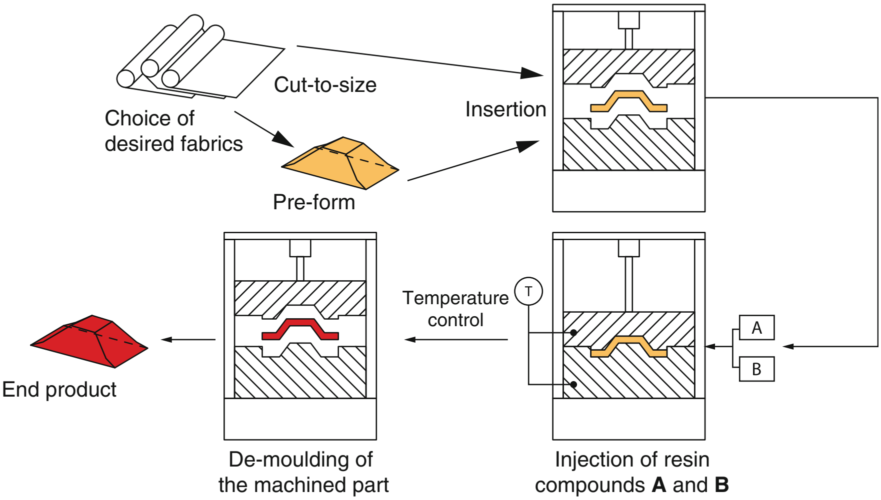


Fig. 58 RTM method (schematic)

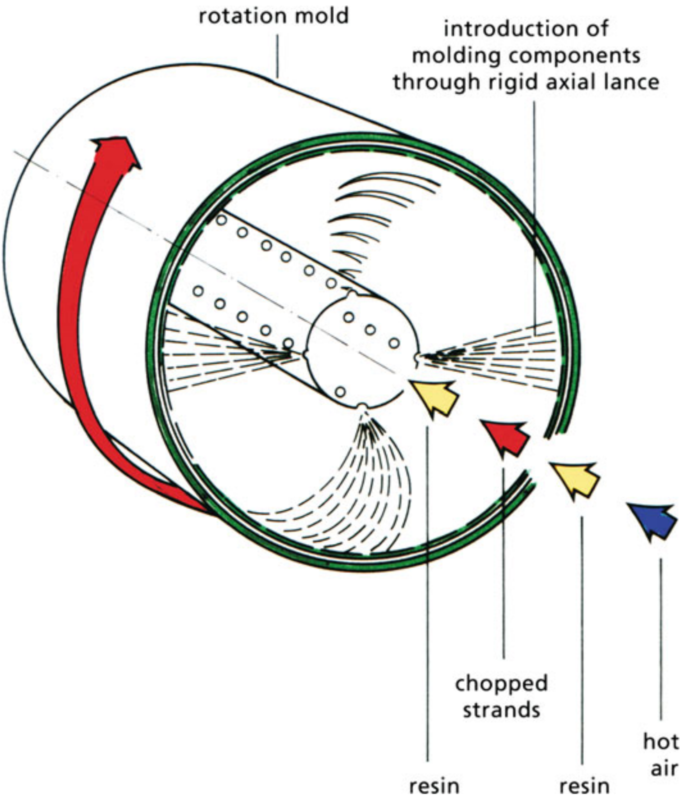


Fig. 59 Pipe production with the centrifugal casting method (schematic)

Table 13 Typical SMC formulae [6]

Type of component	Standard % by mass	LS % by mass	LP % by mass
1. Polyester resin	37.1	27.8	25.54
2. Thermoplastic component	–	9.3	14.60
3. Reactant	0.4	0.4	0.36
4. Release agent	1.5	1.5	1.50
5. Polyethylene powder	2.0	2.0	–
6. Fillers	55.6	55.6	56.50
7. Pigment dispersion	3.0	3.0	–
8. Thickening agent	0.4	0.4	1.50
Total	100.0	100.0	100.0

compounds that have been modified by addition of thermoplastic particles to improve the surface qualities of the structural components (e.g., waves or sink marks). The thermoplastic components contribute to compensation of the shrinkage of the resin mass during the curing process [6], see also Sect. “Duroplastics.”

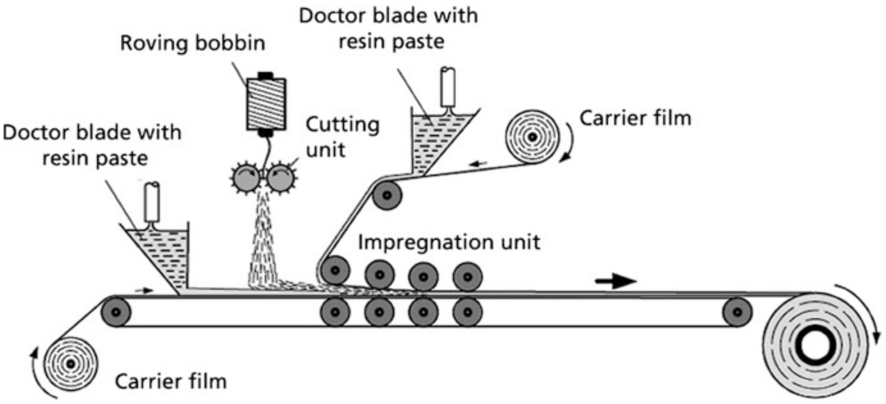


Fig. 60 Resin mat (SMC) process (schematic) [83]

In an SMC facility, an extra wide cutter is used to cut, for example, 40 rovings. The glass fibers, chopped to lengths of ~20–50 mm, fall onto a film doctored with resin filler paste, which is then covered with another film doctored in the same way and pressed together to form the actual resin mat. After going through a slightly compressing lamination line, the laminate is rolled up as the resin mat. This continuous process produced resin mats of differing widths. After the optimum degree of maturation is reached, the resin mat is cut and molded. Storage stability at room temperature can be enhanced by working suitable inhibitors into the resin mats. The term prepreg (preimpregnated material) is commonly used for the finished resin mat [80], Fig. 60.

Automakers demand "online" painting with series-quality paints for GFP body parts to ensure tone matching and lower costs. The temperatures and residence times involved do not damage the SMC moldings, although craters may be formed by the pores and voids located right under the surface in the heat. Although genuine progress has been made with the low-profile resins (see also Sect. "Plastics production (process engineering)" in Chap. "Synthesis (Manufacture, Production) of Plastics"), complete prevention of the voids and pores has not proven possible as yet.

Coating of the molding inside the compression mold, a method adopted from the US known as inmold coating (IMC) has provided a useful interim solution, albeit a complex one. The coating prevents the pores from rupturing. This method can also be used to render the surface conductive as a preparation for electrodeposition coating or electrostatic spraypainting.

Table 14 lists the SMC processing parameters.

8 Influences of Processing on Structural Component Properties

Every kind of working and processing of materials will influence the properties of the resulting products.

Table 14 Processing parameters (categories) for SMC structural components

Storage/time	-18 °C: 3 months, RT: 7 days
Maturation time, SMC mat	~4 days
Surface of the sandwich	<70 % of the mold surface
Processing temperature	130–160 °C
Viscosity at RT	30,000–50,000 Pa s
Viscosity at 160°C	5,000–10,000 Pa s
Molding pressure	80–120 bar
Pressing force per m^2	1,000–1,500 t
Curing time	1 min/mm thickness
Cycle time	30–90 s, depending on thickness of structural component
Post-curing	Cool in equipment
Shrinkage	0–0.2 % (thermoplast. mod. UP) 0.5–3 % (UP)
Insert	Metal possible
Surface	IMC (in-mold coating)
Material costs	~€3 kg^{-1} (€2.5–€5 kg^{-1})
Product forms	Short-fiber, mat, UD band prepreg
Glass content	30 % (25–50 possible)
Negative aspects	Sticky SMC mats, odor of styrene, problems with semifinished products in general (storage, logistics, i.e. higher costs compared to direct processing)

In the case of plastics, the influence of processing on the properties of the finished article is particularly great. For this reason, the designer of a structural component must keep the structural component dimensioning factors listed in Fig. 61 in mind.

In view of this variety and these multiple interactions, this chapter can only offer a brief version of the main aspects of this theme [88].

8.1 Structural Component Properties

Figure 61 lists a small number of general structural component properties. Each particular structural component has specific properties, making it practically impossible to provide a detailed description of properties for all structural components. They can be divided into groups, for instance body parts, seals, toys, electronics components, etc.

Within each group as well there are variations; a shockproof plug for example is required to exhibit properties quite different from those a plug connection in the engine room of a truck has to have.

Each structural component must therefore be considered separately, along the entire length of the product engineering chain as depicted in Fig. 62. In most cases,

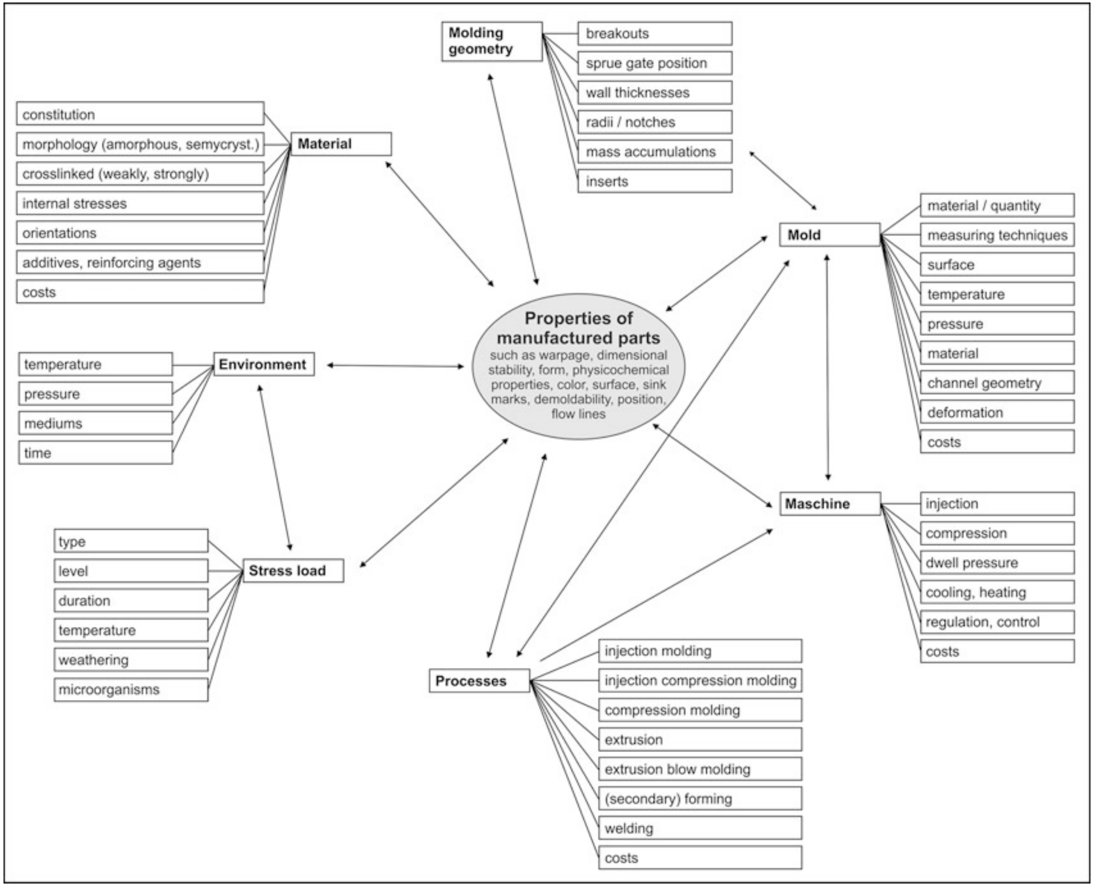


Fig. 61 Influences on structural component properties (a selection)

- Material production e.g. alloy or polymer chemistry, compounding technique
- materials, composites, material composites, materials fro, renewable raw materials

Software GaBi 4.0

Simultaneous Engineering (CAE)

- processing. process engineering
- design, structural component design (CAD),
- rapid tooling (RPT), rapid prototyping (RPT)
- surface engineering
- production engineering (CIM, PIUS), logistics, automation, economy, costs (LCC)
- quality management (CAQ, PPS, TQM, etc.)
- product utilization, maintenance, repair, useful life, reuse and continued use
- reuse / continued use, disposal, environment
- holistic balancing (CIB), lifecycle engineering (LCE)
- education and advanced training (TheoPrax) (CIL), e.g. plastic sciences on CD-ROM

Fig. 62 Environmentally compatible product engineering, interlocking of partial steps

product development and production are interlocked processes, a necessary arrangement if the right product is to be marketed on schedule.

8.2 *Influences of Process and Plastic on the Structural Component Properties*

The process parameters of the different methods and material parameters influence the properties of structural components decisively.

The process engineering material properties are

- Flow (orientations, mold filling)
- Solidification (crystallization, internal stress, dimensional stability, warpage . . .)
- Shrinkage (crystallization, internal stress, dimensional stability, warpage . . .)

The essential process parameters for molding formation, for example in injection molding, are

- Mass temperature
- Tool surface temperature
- Injection rate

- Dwell pressure (or cavity pressure)
- Dwell pressure time
- Cooling time (cycle time)
- Sprue gate system, sprue gate position.

The parameters apply in analogous or altered form to other processes such as extrusion, molding and secondary forming.

For example, molding of uncrosslinked crosslinking plastics:

- Temperature of preform or molding compound
- Mold surface temperature
- Flow rate
- Cavity pressure
- Cooling or crosslinking time

Many of the relationships described in detail below, in most cases for injection molding of thermoplastics, between the process parameters and the structural component properties are applicable to other processes when modified accordingly.

8.2.1 Thermoplastics and TPEs: Molecular Orientations

Injection Molding

Molecular Orientation During Primary Forming

Especially in injection molding with its high shear rates, molecular orientations are frozen as the result of rapid cooling at the cold mold wall. The orientation states observed in extrusion and calendering are less pronounced. In injection molding of thermoplastics, the melt wets the wall when gating is done properly and a thin layer adheres to the form wall. The inflowing melt then flows past this layer. As a rule, the mold is filled by laminar flow and not, as in metal casting, by an open jet, i.e. the melt front in geometrically simple sections can be described at any point in time during the mold filling process in terms of arcs with their center or centers at the gate.

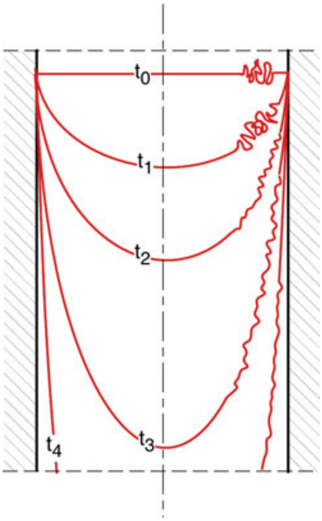
The molecular orientation in an injection-molded part depends on [84]:

- Constitution of macromolecules (influence viscosity and elasticity of the melts)
- Molar mass (influence viscosity and elasticity of the melts)
- Degree of entanglement
- Process parameters such as temperature of mass and mold, thickness of part, mold filling rate, dwell pressure level and dwell time.

Shearing, especially at the mold wall, orients the macromolecules, which are then frozen by solidification, Fig. 63.

Figure 64 demonstrates clearly that orientation effects can occur in two directions at right angles:

Fig. 63 Distortion of a circular element of surface in shear flow, according to M. Chatain. A single threadlike molecule indicates the orientation of the molecular structure t = flow time $t_0 < t_1 < t_2 < t_3 < t_4$



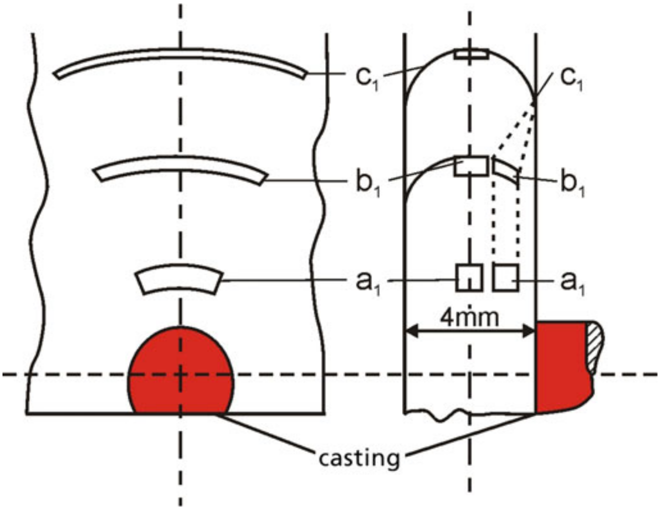


Fig. 64 Deformation of elements of volume in mass flow [85]

- In the direction of flow due to shear flow (resulting in normal stress),
- At right angles to the first effect due to elongation flow (resulting in shearing stress).

If both orientations are frozen, biaxial orientation states and corresponding solidification of the material can be achieved.

In the direction of flow, maximum orientation will normally lie near the surface of the molding, with minimum orientation in the middle of the wall.

The degree of orientation thus varies along a cross-section of the structural component wall. Variously oriented layers can be differentiated, resulting from the different flow states and cooling rates across the thickness of the structural component.

Expressed in simplified terms, three layers are present in the cooled molding [86–88]:

- A stretched outer skin (often with biaxial stretching near the sprue gate due to dwell pressure)
- A highly oriented layer resulting from shearing combined with rapid cooling
- A middle layer with a low orientation level (slower cooling and less shear)

The viscosity function is an important factor in the assessment of the flow of plastic melts in tools for both structural component designers and processors. It describes the dependence of flow behavior on shear rate for the plastic melt (melt stress).

Effects of Molecular Orientation

When the macromolecules show a preferred orientation direction, more primary valency bonds take effect in this direction, replacing part of the secondary valency bonds, which are lower by about one power of ten. This results in differing physical properties in both the direction of orientation and at right angles to it.

The material behaves anisotropically. The stress–strain diagrams show, in PMMA at various degrees of stretching, how much the strength parameters can change, Fig. 65.

As far as possible, the direction of the main orientation should coincide with the main direction of stress load, facilitating optimum utilization of the molding material in the structural component (Fig. 66).

Elimination of Molecular Orientations

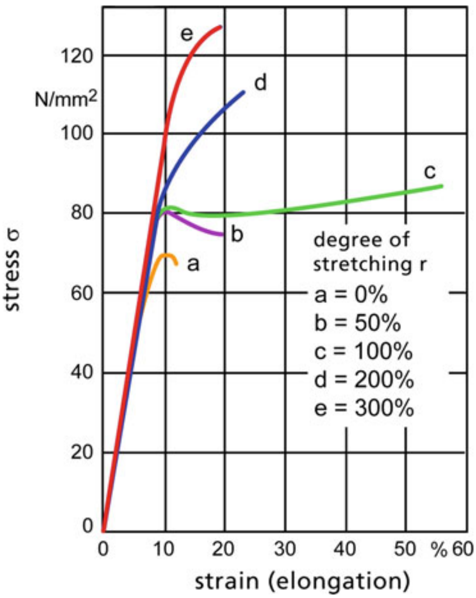
Reorientation processes occur parallel to the initiation of the orientations, i.e. die molecules tend to reassume a more favorable orientation in terms of energy – the statistically irregular coil form – thus acting to reverse the orientations [86].

Orientations in moldings can be specifically reduced or nearly completely eliminated in the following way:

Hot storage at $T > T_g$ for amorphous thermoplastics and $T \cong T_m$ for semicrystalline thermoplastics.

This results in a relaxation of the macromolecules (memory effect). The rate of relaxation is highly temperature-dependent. If the form of the part is to be retained, storage in forced molding must be used. Otherwise, a shape change takes place that is known as “back-shrinking.” In practice, forced molding storage can only be used in special cases because of the costs involved. In actual fact, there is no (affordable) method available to eliminate molecular orientations.

Fig. 65 Stress–strain diagrams of monoaxially stretched PMMA with different degrees of stretching [89]



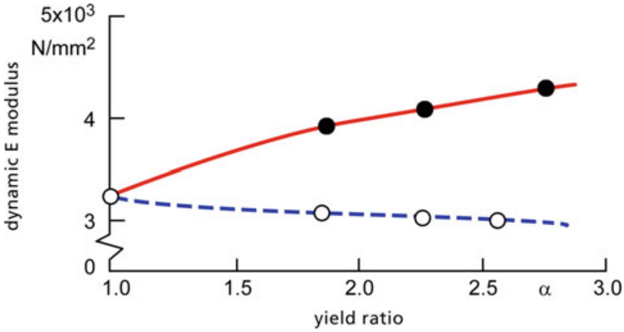


Fig. 66 Dynamic modulus of elasticity of stretched PVC as dependent on yield ratio ($T = 22\,°\text{C}$, $f = 320$ Hz)

Just reducing orientations "costs" cycle time, for instance because the mold temperature is raised by a considerable margin, resulting in increased relaxation of the macromolecules. What this amounts to is forced molding at higher temperatures. Partial success in this direction is possible by means of lower shear rates during the mold filling process, i.e. by heating the dies, increasing the gate cross-sections, raising the melt temperature. However, each of these measures has drawbacks such as partial filling or a reduction of molar mass, etc.

Secondary Forming

Molecular Orientation During Secondary Forming

Cold secondary forming: Cold secondary forming of amorphous thermoplastics is hardly used in practice (high-level molding forces; risk of mold damage; recovery effect upon reheating). Cold secondary forming is feasible with some semicrystalline thermoplastics; for instance, polypropylene can be nailed.

Hot secondary forming: Used for amorphous thermoplastics in the thermoelastic (entropy elastic) range above T_g or in semicrystalline thermoplastics ~30 °C below T_m (see cup experiment below).

Drawing: Hot drawing and cold drawing are differentiated, whereby dissipation (internal friction) results in temperatures in the flow zone of up to ~120 °C in cold drawing.

Extrusion

As was mentioned above, the degree of orientation is lower in extrusion due to lower shearing forces acting on the thermoplastic melt, but orientation is observed.

The die swell observed during extrusion and the swelling behavior in extrusion blow molding and spinning of textile fibers reflect the molecular orientations resulting from shearing forces applied when the material passes through the die, Fig. 67.

When a viscoelastic plastic melt exits freely from a die, the exiting strand has a greater diameter than the die. The shorter the die, the more pronounced this phenomenon is.

Explanatory Notes, Fig. 67

Shear forces applied during die passage *orient* molecular chains in the direction of shear force application. The macromolecules are forced from an unordered, coiled, state into a more highly ordered state.

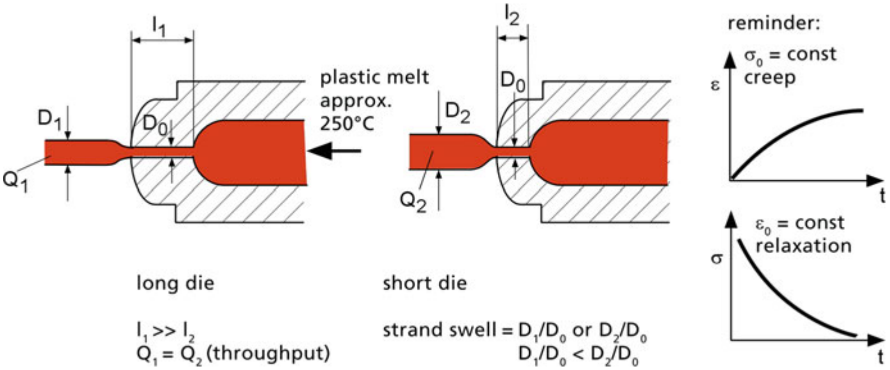


Fig. 67 Schematic view of the rheological behavior of plastic melts during die passage

According to the 2nd law of thermodynamics, all substances strive towards a state of greatest possible disorder (and the measure of this state of disorder is entropy).

Because of the viscoelastic behavior of plastics in general, and plastic melts in particular, this relaxation of the molecular chains is dependent on the factors time and temperature and is entropy elastic. The longer the die, the more time the molecules have to relax within a fixed die cross-section, so that the swell factor after the material exits from the die will be reduced.

The percentage of viscous flow within the die is large and the rubber elastic (entropy elastic) reverse deformation after exiting the die is small. Hardly any *relaxation* takes place during passage through a short die, entropy elastic predominates and the swell is large.

That described above can only take place at temperatures well above the glass transition point or melting point. When a plastic melt is injected into an injection mold, which is usually cold (~50–80 °C), the existing molecular orientations and local tension differentials are frozen and determine product properties to a great extent. This applies in a similar way to extrusion of, for example, pipes, since the melt strand for pipes enters the calibration and cooling zone as soon as it has passed through the die, whereby the influence of die length is not changed.

The description of the origin, effects and elimination of molecular orientations applies analogously to orientations of fibers (but not to their elimination). Glass fibers, for example, orient themselves in the direction of flow due to shearing forces in the plastic melt.

Therefore, under the influence of shear and elongation flow in injection molding or when melt flows come together (flow lines), there are molecular and fiber orientations at right angles to one another across the wall thickness of a molded part with molecular and fiber orientations at right angles to the directions of flow as well. The lower the melt temperature, the more pronounced this will be (viscosity-dependent higher shearing forces). The flow line becomes a weak point.

What this means for the design engineer is that he must be familiar with the directions of flow during the filling phase or use simulation programs that describe the filling image.

Orientations of molecules and fibers are therefore, as described above, to be understood as reinforcement of the active forces. On the other hand, they represent weak points at right angles to the directions of force due to the low level of secondary intermolecular bonding forces.

Experiment: Crushing break of a plastic cup, i.e. deep-drawn or injection-molded.

Influence of molecular orientations on properties

1. Why does the cup rupture lengthwise and not crosswise?
   Because the macromolecules are oriented by shearing in secondary forming (~120 °C) (Figs. 68 and 69) and this orientation is frozen during rapid cooling. And because the bonding forces within a macromolecule are ~20-times greater than those applying between the macromolecules.
2. How can this weak point be reduced?

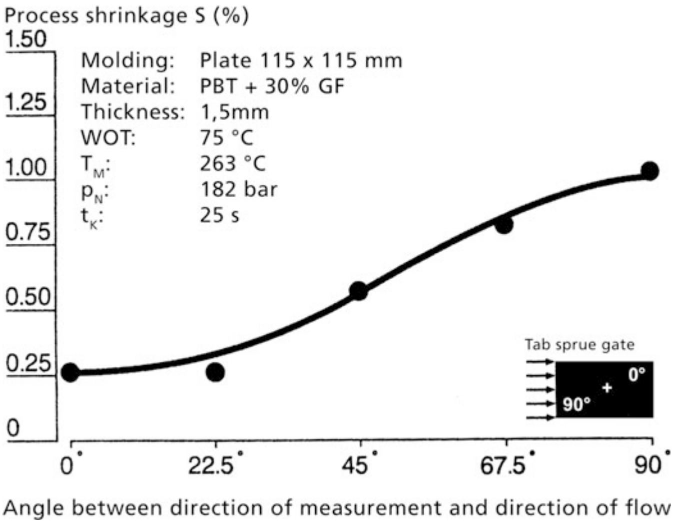


Fig. 68 Influence of orientation on shrinkage of glass fiber reinforced PBT [90], BASF AG

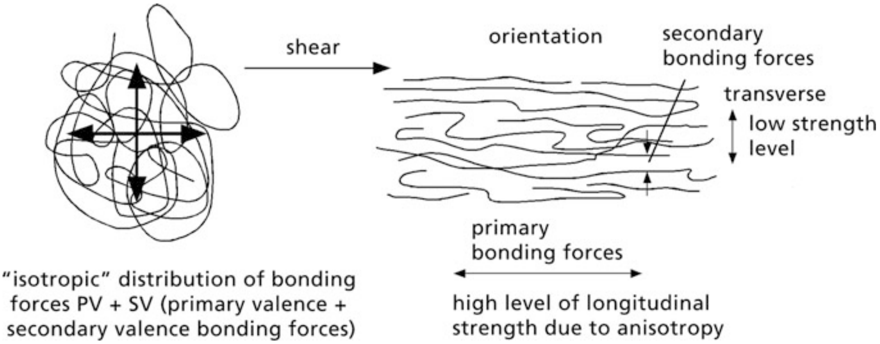


Fig. 69 Anisotropic molecular orientations result from an isotropic molecular coil due to shearing in primary or secondary forming

The problem can be reduced by selecting a different material or different injection or deep-drawing conditions.
Problem reduced – costs increased:
Example of injection molding: Raise melt temperature, raise molding tool temperature: reduces anisotropy, but lengthens cycle time.

3. What happens when the tumbler is heated to above T_g?
Deep-drawn tumbler, hot-molded from semifinished plate:
Memory of flat form of semifinished plate →
Oriented macromolecules reassume the most entropic form as soon as the mobility of the macromolecular chains allow (chain slippage) ($\gg$ above T_g) (seen particularly clearly in polystyrene)

Molecular orientations resulting from shearing forces applied during processing vary widely depending on the process. In injection molding of thermoplastics and TPEs, molecular and fiber orientations have a dominant influence on the structural component properties.

As the experiment with the plastic tumbler shows the orientations are also highly pronounced in hot secondary forming. As was mentioned above, this is less pronounced in extrusion and is less pronounced the lower the viscosity or shear rates and the shorter the flow paths are.

Compression Molding CM

In CM, for instance of GMT or LFT-D or of duroplastic SMC, the orientation of the macromolecules and fibers depends on the magnitude of the shearing forces.

Cuts that essentially fill the cavity, i.e. usually simple molding geometries, show little in the way of orientations.

The molecules and fibers of cuts with long CM flow paths, on the other hand, show pronounced orientations.

More recent results indicate this applies to long glass fibers as well, which unexpectedly fill out ribs as high as 40 mm, for example in the frontend of a car, when glass mat material is inserted to increase rigidity [41, 42].

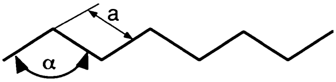
The influence of molecular and fiber orientations on structural component properties is significant. Internal stress in structural components as a result of processing constitute a further important influential factor.

8.2.2 Internal Stress in Moldings and Structural Components

Definition: Stresses present in bodies (moldings, structural components) independent of external forces are termed *internal stresses.*

Characteristic: The forces F and momentum M resulting from internal stress are practically *nil*; i.e. there is a static balance ($\Sigma F = 0$; $\Sigma M = 0$).

Origin: *Internal stresses* result from *inhibited* volume change in solid bodies (modulus of elasticity > 0).



Effect on macromolecules: In plastics, stresses result in deviations of the *internuclear distance* and *valency angles* from the respective statistically balanced state.

Causes of inhibition of volume change: The inhibition results from *local* differences in volume change resulting from local and/or temporally differing processes. According to Fig. 70, for example, local temperature differences result in changes in specific volume.

Examples of such locally differing processes, seen frequently in plastics engineering:

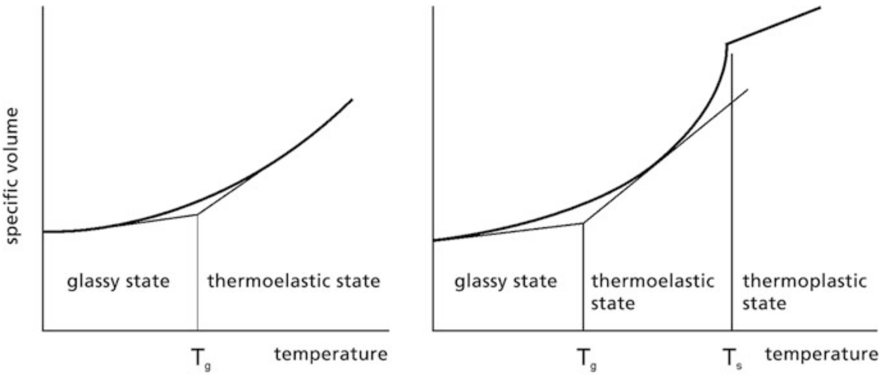


Fig. 70 Temperature dependence of specific volume of an amorphous polymer (*left*), and a semicrystalline polymer (*right*)

Cooling including cold inserts
Dwell pressure (injection molding)
Swelling
Crystallization (structural changes)
Polyreaction or polymerization including crosslinking (structural changes)

Applies, for example, to metals and ceramics as well

For the design engineer (structural component and mold) and above all for the processor, such interrelations are of basic importance for the structural component properties.

The specific volume and thus the shrinkage of the plastic – the moldmaker derives the overdimensions for the design from this parameter so as to achieve the specified structural component dimensions – must be matched up with the cavity pressures and corresponding mass temperature.

Local variations in process parameters result in local shrinkage differentials.

The different types of internal stress may certainly occur at the same time, for example due to cooling, dwell pressure, and crystallization during injection molding of semicrystalline thermoplastics. The different types of internal stress are also not sharply differentiated.

Cooling

Example of internal stress due to cooling: Parabolic temperature profiles form across the thickness of a warm, cooling sheet of amorphous plastic, Fig. 71. If the initial temperature is above the glass transition temperature and cooling is rapid (quenching), the internal stress distribution across the cross-section of the material is nearly parabolic as well.

Similar to sheet quenching, a temperature gradient is also registered in the mold during cooling from the melt. These processes are more complex in injection molding in particular, since not even mold filling is isothermic.

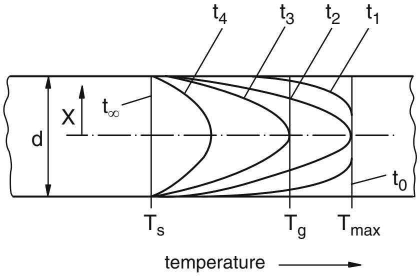


Fig. 71 Temperature profile $T(x,t)$ during quenching of a uniformly heated plate (T_{max}) at different times ($t_0 < t_1 < t_2 < ....$)

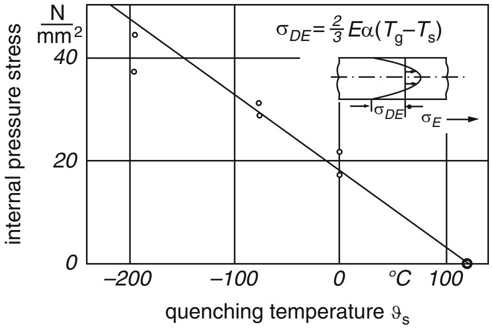


Fig. 72 Internal pressure stresses at the surface of quenched plates made of PMMA

Countermeasures

The magnitude of internal stress in the molding process can be reduced by *reducing the temperature differentials*, i.e. the melt temperature should be as low as possible and the mold wall temperature as high as possible. A *low cooling rate*, resulting in low temperature gradients in the wall cross-section, is the objective. These measures are only feasible within certain limits defined by other molding properties and production economics. A further possible measure is *early ejection (demolding)* before the temperature differentials are balanced over the wall cross-section. The temperature gradient, and therefore the stress level, are reduced. The core of the material is still hot and can heat up the surface again. This method, however, is often not possible due to *the lack of stability* in this state (Fig. 72).

- Slower cooling (heating of mold + insert)
- Reduction of insert mass
- Greater thickness of plastic wall around the insert

Effects of Internal Stress

Internal stresses in the molding can influence:

- Loadbearing capacity
- Dimensional stability.

Table 15 Stress cracking in plastics

Plastic	Examples of mediums that cause stress cracking
PS	*n*-Heptane (vapor or liquid), benzene, ether, methanol, oleic acid, vegetable oils
PE	Surfactants, alcohols, ether, silicone oils, ketones, esters
PP	Similar to PE
PVC	Methanol
PA	Most mediums do not cause cracking if the material is in a moisture balance with the environment
PMMA	20 % Soda lye, oil of paraffin, glycerol, water, hexane, heptane, various alcohols, NMA, benzole, acetone
PC	Methanol, terpentine, PVC plasticizers, isopropyl alcohol, *n*-hexane

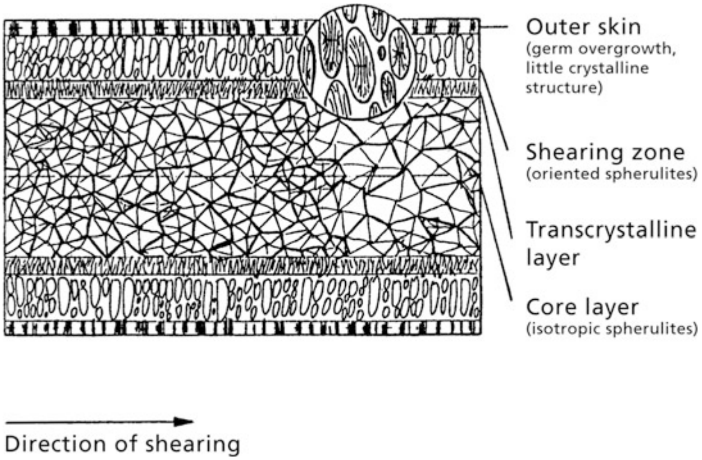


Fig. 73 Structure of a semicrystalline injection molded part (PP) [87] according to Backhaus [89]

Internal Compression Stress

Internal compression stress in the surface layer increases bending strength.

Internal tensile stress at the surface can lead to stress cracking without the influence of external forces, especially if mediums are also at work: *stress cracking*! (of course, external tensile stresses in combination with mediums can also lead to stress cracking.)

Particularly sensitive to these influences are:

Amorphous thermoplastics are among the materials that are particularly susceptible to stress cracking, Table 15. Therefore, always ask the raw material producer first or carry out tests under realistic conditions (Fig. 73).

Crystallization

Injection Molding

In semicrystalline thermoplastics, local temperature differences during the cooling process resulting in differences in the degree of crystallization across the wall thickness of a structural component (see Sect. “Structure of plastics” in Chap. “Properties of Plastics in Structural Components”). At the surfaces of the structural component, there is a low degree of crystallization (and even amorphous layers) due to rapid cooling at the “cold” mold wall, for example in injection molding; inside the structural component wall, especially in thick walls, the degree of crystallinity is high.

This structure influences the macroscopic properties.

Summary [88]

Outer skin: Excessive melt cooling, practically no formation of a crystalline structure

Shearing zone: Highly oriented layer with fine-grained crystalline structure

Core layer: Slower crystallization process after filling phase due to slower cooling rate than near wall, resulting in a coarse structure with large spherulites (crystalline regions)

In machine elements such as friction bearings with a tribological function, process-related influences are highly desirable. Heated molds are a possible solution, also in injection molding.

The crystallization from the melt exerts an influence in semicrystalline thermoplastics (Fig. 70). The significance of the dwell pressure becomes apparent.

Extrusion

On the basis of the example of pipe extrusion, Fig. 74 shows the influence of cooling on the density gradient across the pipe wall thickness. It is clear that this pipe production involved external water cooling and internal pressurized air. The result is low density on the outside (low degree of crystallization), maximum density in the middle of the wall, shifted somewhat toward the inside diameter

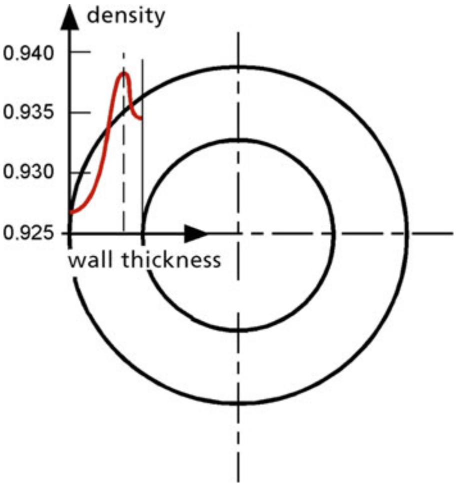


Fig. 74 Density (crystallinity) as a function of wall thickness in HDPE pipes (according to Stockmayer)

(highest degree of crystallization) and a dropoff in density at the inner pipe surface, which is however still greater than on the external surface of the pipe since air conducts heat less efficiently than water.

Density and degree of crystallization have a directly proportional (linear) relation.

Dimensional Stability

The dimensional stability of plastic structural components – especially when integrated with other parts to make up components or a system, and in particular in combination with different materials (steel, aluminum, magnesium, ceramic, fiber composites) – is often a factor of central importance in technical applications (Fig. 75) [16].

The parameters that influence the *dimensional stability* of plastic parts include: *mass distributions, grain structure, reinforcing materials, processing conditions, moisture content* (swelling) and *temperature variations* during operation.

Shrinkage

"Exact predetermination of shrinkage is not yet possible. The design engineer must estimate the dimensional difference between the mold and the molding based on various information sources (raw material manufacturer, experiential values, comparative measurements). Since values determined in this way often deviate from the real states, attempts are made to influence shrinkage within relatively wide ranges by controlling the process." [86]

Figure 76 shows the qualitative dependence of *process shrinkage* on process parameters.

Shrinkage also depends to a great extent on the position, type, and size of the *gate*. Shearing forces result in a pronounced longitudinal orientation of the macromolecules with small gates, resulting in pronounced *lengthwise shrinkage* compared to *crosswise shrinkage*: The result is *warpage* of the structural components (Fig. 77).

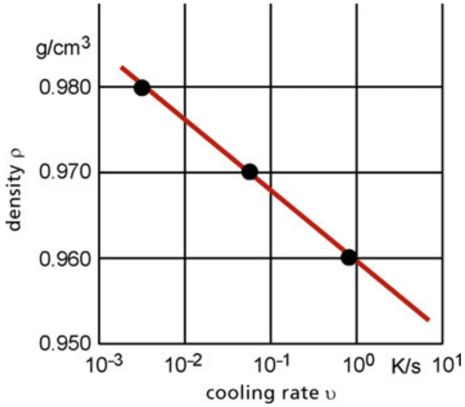


Fig. 75 $\rho = f/v$ in PE-HD wafers (60 × 10 × 1 mm)

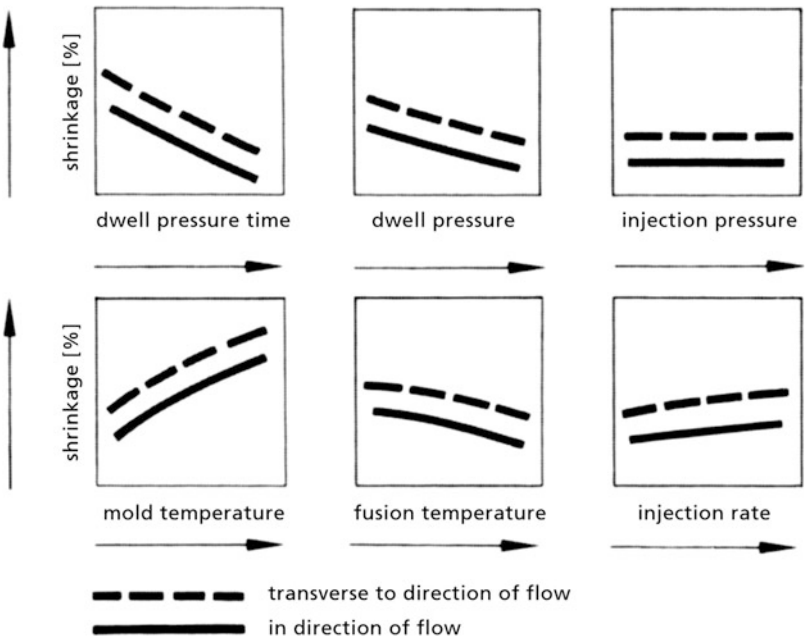


Fig. 76 Dependence of shrinkage on *process conditions* [84]

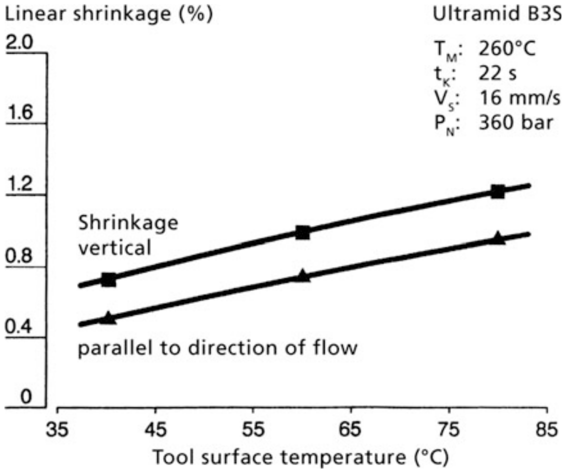


Fig. 77 Dependence of shrinkage on mold surface temperature [86]

"Amorphous materials show shrinkage levels of ~0.3–0.9 %, with a correspondingly low range of potential influence of process conditions. For ABS, for example, an increase in mass temperature of 10 °C reduces shrinkage by 0.01 %. The mold surface temperature has very little influence. Shrinkage can be reduced by 0.01 % per 10 bar increment of dwell pressure (ABS). Shrinkage ranges are much greater in semicrystalline plastics (0.4–3 %). This means the different process conditions have more potential influence on shrinkage levels." [86].

Aftershrinkage

In semicrystalline thermoplastics, especially under the influence of higher storage or application temperatures or water uptake (increased macromolecular mobility), aftershrinkage occurs, resulting in dimensional changes and warpage. The aftershrinkage is determined by cooling rate, tool temperature and wall thickness. At mold temperatures exceeding 90 °C (long cycle times), the aftershrinkage can be kept very low, and is further reduced the thicker the walls are (lower cooling rate).

Warpage

The dimensional deviations that occur in plastic parts are usually not the result of incorrect mold design or shrinkage accommodation, but rather result from *bending and deformation of the injection-molded parts*.

To obtain dimensionally correct parts, warpage must be estimated, then reduced as far as possible by means of structural design, material selection and processing.

8.2.3 Elastomers

Orientations

Molecular orientations result from shearing forces in rubber mixtures just as in processing of thermoplastic melts. The swell and relaxation phenomena in long dies are, in principle, comparable.

Extruded rubber profiles (uncrosslinked) show relaxation of orientations, and therefore dimensional changes, similar to what is observed in thermoplastic melts [7].

The decisive differences characteristic of elastomers (crosslinked) are

- Vulcanization in the mold and
- The glass transition temperature T_g at lower temperatures.

The former factor fixes orientations in a wide-meshed network.

The latter allows relaxation processes to continue even at room temperature.

- With *thin-walled molding* and short cycle times, orientations could be fixed by crosslinking. This possibility is not, however, treated in the published literature, according to which orientations, even in thin-walled structural components, relax during processing without anisotropy.
- In *thick-walled moldings*, the vulcanization time – even in injection moldings – is within the ≥ 3 min range, in $C \geq 6$ min. The relaxation of the orientations may be complete (requiring only seconds at higher temperatures).

Fibers are used only rarely as reinforcing materials in elastomer moldings, so that this type of orientation is of no relevance for the particle types used.

Internal Stresses

Generally speaking, the introductory remarks on orientation also apply to internal stresses. The decisive factors for anisotropy, particularly in *thick-walled moldings*, are the internal–external differences in degree of crosslinking. Röthemeyer and Sommer [7] provides details.

Internal aftervulcanization (temperature gradient during cooling) cannot compensate for the difference. In a rubber–metal damping element, the internal degree of crosslinking was ~75 % of the external level [7]. This does not result in internal stresses because the wide-meshed network allows for deformations. There are, however, differences between the internal and external properties.

During cooling to room temperature after demolding, no warpage will occur in the elastomers with glass transition temperatures below 0 °C, since internal stresses are reduced in the entropy elastic network. For instance, a sink mark is not to be expected in the middle of a thick plate until the molding is cooled to below its glass transition temperature due to the higher degree of crosslinking on the outer surface (greater modulus of elasticity) (T_g external $> T_g$ internal).

In rotary shaft lip seals, internal stresses are an important factor when it comes to calculating useful product life and demolding. Stresses resulting from various types of shrinkage may also complicate matters.

Dimensional Stability

The dimensional stability of elastomer structural components, particularly precision parts such as rotary shaft lip seals (O-rings), is often problematical. Little has been published on the subject. Internal company know-how plays a major role in elastomer engineering. For example, the range of variation of mixture ingredient ratios in the elastomer formula influences the dimensional stability of sealing rings.

Shrinkage

Shrinkage in (elastomeric) structural components is the amount by which mold and molding dimensions differ. The relevant reference parameters are the standardized mold dimensions.

The measuring methods used, for example to monitor O-rings, include optical CNC machines, mechanical scanning systems and plug gauges.

The following causes of shrinkage affect elastomer moldings:

- Thermal differentials (compression)
- Gas exhalations of low molecular formula components or cleavage products

- Vulcanization, whereby this factor causes greater shrinkage at right angles to the direction of rolling than in the direction of rolling (orientations).

Taking the example of O-ring moldings from nitrile butadiene elastomer (NBR), shrinkage of the inside diameter of the O-ring shows a number of qualitative dependencies:

- The smaller the O-ring diameter, the greater the shrinkage.
- Low cavity pressure (dwell pressure phase) results in greater shrinkage.
- The shrinkage (internal O-ring diameter) increases with the mass temperature.
- The same also applies to the mold temperature, although the effect is not as pronounced as for mass temperature.
- The cross section shrinkage of an O-ring decreases with increasing mold temperature.

Surface Characteristics

Surface defects in elastomer structural components include flow defects, air inclusions, specks in the material and many others (see Sect. "Duroplastics").

As a rule, the surface of the mold is completely reproduced, i.e. its roughness corresponds to the roughness of the elastomer structural component. Slight deviations are possible with some material compositions due to surface stress [91].

8.2.4 Duroplastics

Orientations

When processing (CM, injection molding, extrusion, ICM, etc.) from uncrosslinked (A state) or crosslinked (B state) duroplastic molding compounds, the shearing forces applied upon injection through dies impose orientations upon the macromolecules and, if any are present, upon the reinforcing fibers as well. Because of the low viscosities of uncrosslinked masses such as phenolic, melamine, UP and epoxy resins and the hot mold wall, relaxation of the molecular orientations sets in quickly. As a rule, duroplastics show little or no orientation. Crosslinking fixes this state.

Reinforcing fibers react differently: They remain oriented, resulting in the familiar disadvantages and advantages in thermoplastics: reinforcement in the direction of load application, weaknesses at right angles, flow line weaknesses, warpage.

For example, in direct injection molding of lid-like, thin-walled structural components (e.g., headlight reflectors), pronounced circular orientations of the short glass fibers are observed in the BMC (bulk molding compound) UP resins around the sprue gate. The solution is usually ICM or push–pull injection molding.

Internal Stress

Local differences in degree of crosslinking, for example in thick-walled moldings between the inside of the wall and the outer skin, result in shrinkage differentials and thus to internal stresses. This is observed when the temperature falls below the glass transition temperature – i.e. in duroplastics usually on or above 100°C.

Until that point is reached however, one has plenty of time to relieve these stresses.

Another specific countermeasure is curing in stages, as has been practiced for some time now for example in disk brake linings and grinding wheels.

The systems covered up to this point crosslink endothermically, i.e. the energy required for crosslinking must be supplied from outside the system. In systems characterized by exothermic reactions, for example epoxy resins, UP resins and polyurethanes, unfavorable wall thickness distribution resulting from differences in degree of crosslinking can result in high levels of internal stress in the structural component. Insufficient heat application results in pronounced internal crosslinking, even to the point of decomposition and cracks extending from inside to outside.

In adhesive joints, for example with epoxy resin adhesives, internal stress in the adhesive layer may result from different coefficients of expansion in the glued materials, whereby their moduli of elasticity are important factors. The glass transition temperature, and thus the curing temperature, also play a role. The reaction shrinkage of the resin is another source of internal stress. Suitable formulations with added fillers, oligomers or copolymers are among the measures taken to reduce these influences.

Among the filling and reinforcing materials, microglass beads take up advantageous positions between fibers and sharp-edged additives. They compensate for orientational shrinkage differences and reduce the radial-symmetrical internal stress observed with sharp-edged particles.

For instance, the epoxy resins highly filled with microglass beads that are used in mold design show shrinkage levels of only 0.15% [79].

Dimensional Stability, Tolerances

Tolerance is defined as the difference between dimensional maximum and minimum.

In parts made of curable molding compounds, deviations are influenced mainly by the following four factors [79]:

- Mold structure and production tolerances,
- Choice of process and precise reproducibility of production conditions once fixed,
- Mold wear and
- Type of molding compound used and its batch-to-batch uniformity.

In terms of reproducible *dimensional stability* of the molding compound, the following criteria are decisive [79]:

- Processing shrinkage (DIN 53464),
- Any anisotropy,
- Aftershrinkage (DIN 53464),
- Swelling of moldings.

DIN 16901 classifies plastic molding compounds in four groups according to shrinkage parameters. Among the groups 0–1, 1–2, 2–3, and 3–4, group 0–1 shows the finest tolerances and group 3–4 the least favorable values.

Shrinkage

DIN 53464 differentiates between processing shrinkage (often just called shrinkage) and aftershrinkage. Swelling must also be considered when looking at molding utilization. Processing shrinkage is measured in % of cold mold dimensions, aftershrinkage in % of molding dimension before aftertreatment.

Low processing shrinkage levels in epoxy resin structural components reflect both low EP mass shrinkage and postgelling rubber elastic compressibility. When the mold is opened, the EP molding is still hot and, in some cases, will spring back. This effect runs counter to chemical shrinkage, so that intentional control of these phenomena can be applied to produce parts without shrinkage or with negative shrinkage. The cavity pressure during crosslinking is an important factor.

The low level of shrinkage resulting from epoxy resin crosslinking results in the narrowest possible dimensional tolerances. In combination with optimum electrical properties, this makes the material suitable for applications such as printed circuit boards, plug-in connections, ignition distributors, ignition coil covers, sparkplug sockets, power switch rods, etc.

The dimensional stability of PCBs is highly complex in all three directions (x, y, and z) throughout both the production and utilization phases.

K. Borchard in Woebcken [79] provides details on the dimensional stability of this material under the heading “Basic material for printed circuits.”

Analogously to thermoplastic injection molding, metallic inserts should be preheated to 120–150 °C before being placed in the mold for duroplastics as well. This applies less to small threaded sockets and more to larger magnetic coils encased in epoxy resin. A positive factor in this connection is the high level of crack resistance of EP resins.

Shrinkage and aftershrinkage may be directional in polymers with oriented fibers [92]. Low shrinkage molding compounds are potential remedies.

Aftershrinkage may also result from hot storage in use. Dimensional changes, warpage, or even cracks are among the possible consequences, for instance at ribs and engraving metals.

Processing of SMC is described briefly in Sect. “Processing methods.”

The nearly shrinkage-free SMC qualities are used to produce class A surfaces in automobiles. On the other hand, future use of such SMC applications is being called into question at present due to extremely stringent surface quality specifications and the amount of afterprocessing required. An undeniable advantage of SMC is its combination of a high level of rigidity with freedom of structural design and transparency for electromagnetic waves (hidden antennas).

The shrinkage of BMC can be tailored within a range of ~0.25 % up to a maximum of 0.05 %. Reflectors are an example of an application of BMC types with an elongation of 0.05 % (cooled molding larger than cold mold).

The aftershrinkage of structural components made from dry-compounded polyester resin molding mass is minimal, with excellent dimensional stability.

Warpage

Warpage, usually of plate-like structural components, of course correlates closely with shrinkage. Whenever shrinkage is asymmetrical, i.e. anisotropic, warpage occurs in moldings with frozen internal stresses.

The nature of the process influences warpage. CM, for instance, produces moldings with homogeneous mechanical properties (little anisotropy) and minimum warpage, even in long glass fiber-reinforced parts (short flow paths, low fiber damage levels due to low shear rates).

Injection-molded structural components, especially flat ones, often present nearly insurmountable warpage problems.

The warpage of structural components made of low profile SMC (LP-SMC) is lowest compared to the other SMC qualities with higher shrinkage levels.

When the SMC PCBs to be placed in the compression mold are cut to size, whereby they cover 30–70 % of the mold surface depending on the desired flow processes, warpage of the later structural components can be influenced by way of glass fiber orientations. Calculation of the melt front is an important element in these considerations.

Printed circuit boards, already mentioned under shrinkage, also warp occasionally. Glass mat-epoxy resin laminates are less critical than paper–phenolic resin laminates. Curing shrinkage is more pronounced in PF resins. As one would expect, laminates copper-clad on one side show more warpage (linear expansion differential). Plasticized PF resins can be forced to bend in the opposite direction with a calender (keeping T_g in mind). In glass textile laminates, the textile thread length may also be a factor in sheet warpage. In textile production, the filling threads (weft) are never at exactly right angles to the warp and sometimes form arches [79].

Surface Characteristics

Many duroplastic structural components are surface-treated like moldings made of thermoplastics.

Examples include:

Engraving of printed films, painting, printing, metallizing, embossing [79]. The processing parameters for CM, ICM, injection molding, extrusion, winding, spray layup, pultrusion, etc.

The individual processes, with their specific framework conditions, influence surface quality to varying degrees.

Examples of surface characteristics of structural components made of different duroplastic molding compounds are presented below as results of specific processing influences:

Phenolic resin molding compounds can also be processed as resins using liquid resin processing methods.

Encapsulated solvent residues result in surface disturbances if insufficiently dried during CM.

As in injection molding of thermoplastics, the location of the sprue also influences the surface quality of injection-molded structural components made from phenolic resin molding compounds.

Surface quality is usually better in ICM of PF – analogous to thermoplastics.

Duroplastic moldings usually have a highly resinous (low-filler) mold skin. Care must be taken not to damage this mold skin when treating, for example polishing the surface.

High content levels of lubricants and release agents are frequently deleterious as regards the surface gloss.

These additives are not uniformly distributed, resulting in matte spots. The lubricants also act as mold release agents, an effect that is desirable for demolding. When the part is to be painted, on the other hand, additional washing and drying procedures are required to achieve paint adhesion.

In vapor deposition of metals (metallizing) of moldings, the problem of gas discharge from duroplastics under high vacuum is observed. Pretreatments (tempering) and protective painting before the metallizing process reduce the gas discharge.

Urea moldings are often used as visible parts with technical functions, for example switch caps, electric plugs, toilet seats, and screw closures. The important surface quality features include color tone, lightfastness, freedom from streaking, gloss and smoothness. Typical defects in UF moldings are overcuring or undercuring. Light spots are typical of overcuring and dull areas are produced by undercuring.

The influence of the formulation of SMC structural components (unsaturated polyesters) on shrinkage is described above. The main effect of these measures is to prevent surface voids. LP–UP resins show almost no shrinkage at all, but the whiting effect often seen in the cured material makes uniform coloration impossible, making spraypainting necessary. The addition of finely ground polyethylene powder not only improves the flow properties and reduces the shrinkage of the LP–UP resin, but also improves the surface smoothness of the molding.

In painted SMC in particular (as well as in RIM or RRIM – reinforced reaction injection molding – of polyurethane), mold release agents (zinc or calcium stearates) are used that exudate at the molding surface during curing/crosslinking and make for efficient demolding.

However, as described above, these substances prevent paint from adhering properly.

SMC or RRIM moldings are given a priming coat by the raw part producer. To achieve this, the producer must first remove the mold release agents. This priming procedure may turn up adhesion problems, air inclusion (pores) or craters in the SMC parts, leading to increased afterworking [79].

The IMC method is used to reduce defects in the cover-coated surface [79].

A silver coating chemically precipitated in the laboratory helps render surface molding defects visible (mirror surface).

In principle, the same methods can be used to finish the surface of BMC moldings as in SMC production.

Painting and metallizing (for reflectors and car headlights) are the predominant methods of surface finishing used for BMC structural components.

In dry-compounded polyester resin molding compounds and the moldings made out of them, modification with melamine resins results in a reduced processing rate similar to what is seen with phenoplasts and aminoplasts. It is possible to improve the surface quality [79].

Wear-resistant surfaces can be achieved by means of high filling with microglass beads. The shrinkage of the UP resin during curing causes the beads to come out of the surface. Decorative laminates and coated wood materials (plywood) are treated in detail by Woebcken ([79]).

9 Rapid Prototyping

Because of an increasing demand from industrial companies for shorter product development cycles considering increasing quality aspects fast available prototypes can be used for accelerating the development process and a shorter *time to market* of a product. Figure 78 shows a comparison between a linear classical product development chain and *Rapid Product Development*. The most important factor

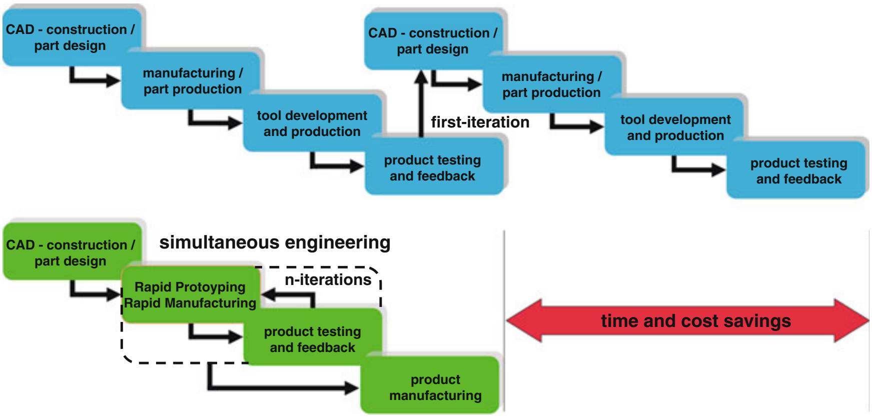


Fig. 78 Comparison of classical product development and rapid product development

in *Simultaneous Engineering* is the possibility to use fast iterations within the conception and construction period and in consequence a fast feedback of product testing [95].

Rapid Prototyping (RP) is the designation for a group of primary shaping technologies without the need for building costly molds known for example from injection molding, so called *solid free-form manufacturing*. With the appearance of more powerful computer and laser systems, in 1987 the first commercial RP-system, the SLA-1 by 3D-Systems, was available, followed by Electro Optical Systems (EOS) in Germany with the Mark 1000 SLA system in 1990. DTM (now a part of 3D-Systems) and Teijin Seiki (now a part of CMET Inc.) presented the first selective laser sintering (SLS) system in 1992. RP-technologies have now grown out of the development phase of generating *three-dimensional pictures* and are used for building physical models (Concept Modeling), tooling components (Rapid Tooling) or small series production (Rapid Manufacturing). The market for these technologies grewto a turnover of $9,837 million in 2006 with more than 4,000 sold systems [115].

9.1 Generative Production Processes

Unlike other subtractive machining processes, *Generative Processes* build parts by a layer-by-layer technique using form neutral substances like fluids, powders, foil- or wire-shaped materials by chemical and or physical reactions. In general the process, as shown in Fig. 79, results directly from a 3D model, which is sliced into thin cross-sections; typically with a thickness of 0.1–0.4 mm. Depending on the kind of process, parts that may be difficult or even impossible to fabricate by conventional methods, can be produced out of polymers, metal, ceramic or composite materials [101]. A selection of RP-processes is described below, but due to the complexity of the processes readers are referred to the cited references.

9.2 Stereolithography

The fundamental process of SLA is the solidification process of a liquid photopolymer, for example an epoxy resin. It is interspersed with suitable photoinitiators and exposed to ultraviolet (laser-) radiation, which initiates polymerization in those areas where the resin is heated by the laser beam according to the cross-sections. The beam deflection is realized by a scanner system consisting of two movable mirrors [102]. The curing is limited in the horizontal direction by the diameter of the laser beam and in the vertical direction by the optical penetration depth of the used resin. After completion of a layer the platform moves down according to the layer thickness and new resin is coated. After finishing the build process the model requires post-processing, in which the model is cleaned, the support removed and post-cured in a UV-light chamber.

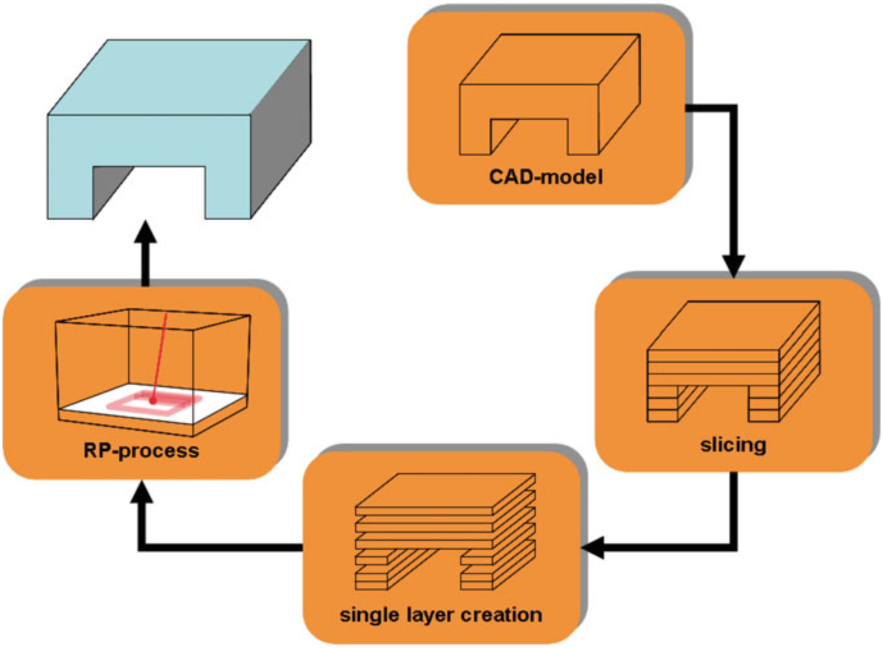


Fig. 79 Principle of model generation by rapid prototyping techniques

The advantages of SLA are a large build area, very good accuracy and surface quality. But prototypes possess limited specific thermo-mechanical properties according to the used resin. During the building process the parts are of a relatively low stability (gelatine-like), and as a consequence overhangs need support constructions.

9.3 Laminated Object Manufacturing

The laminated object manufacturing (LOM)-technique was invented by M. Feygin in 1985 and marketed by Helisys as LOM 1015 and LOM 2030. Profiles of object cross-sections are cut from foils of paper or other web material. The foil is unwound from a feed roll onto the stack and first bonded to the previous layer using a heated roller which melts a plastic coating on the bottom side of the foil. The profiles are then traced by a laser. After cutting of the layer is complete, excess paper is cut away to separate the layer from the web [110].

The advantages of LOM lie in no chemical changes and minimal heating, so shrinkage and stress-induced deformation is very small. The process runs at room temperature so a “developing time” is not required. The laser only has to cut the part contour and hatching, not all the internal area. Moreover, no support structures are needed for overhangs. The system is inexpensive to maintain, no toxic materials are used, and these machines are well suited to desktop operation. But the surface is rough and there is a time-consuming need for removing the tiles and finishing. Complex parts can be damaged while removing tiles and enclosed volumes will trap the support material. There is a substantial risk of delamination in case of machining, due to dependence of material properties on the direction for the laminate, and a high loss of material.

9.4 Three-Dimensional Printing

Three-dimensional printing (3DP) was developed at MIT and often used as an RM-process. 3DP starts by depositing a layer of powder material at the top of a fabrication chamber. To accomplish this, a measured quantity of powder is first dispensed from a similar supply chamber by moving a piston upward incrementally. A roller then distributes and compresses the powder at the top of the fabrication chamber. The multi-channel jetting head subsequently deposits a liquid adhesive in a two-dimensional pattern onto the layer of the powder which becomes bonded in the areas where the adhesive is deposited, to form a layer of the object. Once a layer is completed, the fabrication piston moves down according to the thickness of a layer, and the process is repeated until the entire object is formed within the powder bed. After completion, the object is elevated and the extra powder brushed away leaving a "green" object. No external supports are required during fabrication since the powder bed supports overhangs.

3DP is probably the fastest RP method by low material costs. Color output is also possible, but there are limitations concerning resolution, surface finish, part fragility, and available materials.

9.5 Fused Deposition Modeling

A plastic filament is unwound from a coil and supplies material to an extrusion nozzle, which is mounted to a mechanical stage movable in the *x*–*y* direction. The nozzle is heated to melt the plastic and regulates the melt flow. As the nozzle is moved over the table in the desired geometry, it deposits a thin band of extruded plastic to form each layer. The plastic hardens immediately after being squirted from the nozzle and bonds to the layer below. The entire system is placed in a chamber where temperature can be regulated just below the melting point of the plastic. Several materials are available for the process including ABS and investment casting wax. Recently, PC and PPS materials have been introduced which extend the capabilities of the method in terms of strength and temperature range. Support structures are fabricated for overhangs and later removed by breaking away from the object.

The method is office-friendly and quiet. Fused deposition modeling is fairly fast for small parts (several cubic centimeters) or those that have tall, thin form-factors, but is very slow for parts with wide cross-sections. The surface quality depends on the geometry of the extruded line.

9.6 Selective Laser Sintering (SLS)

SLS was developed and patented by C. Deckard at the University of Texas, Austin in the mid-1980s [99]. As shown in Fig. 80, a thermoplastic, metal, or ceramic powder is spread in a layer of typical 0.1–0.3 mm thickness by a roller or wiper over the surface of a building platform.

A laser beam is then traced over the surface of this tightly compacted powder to selectively melt and bond it to form a layer of the object. The platform moves down a layer thickness to accommodate the new layer of powder. A piston in the powder reservoir moves upward incrementally to supply a measured quantity of powder for each layer. The powder bed is maintained at a temperature just below the melting point of the powder so that low laser energy is needed to elevate the temperature slightly to cause sintering and to speed up the process. In the case of polymers this so called *quasi-isothermal laser sintering* reduces or avoids warpage ("*curl*") [94]. The process is repeated until the entire object is fabricated, followed by a considerable length of cool-down time up to several days before the part can be removed from the machine. After the object is fully formed, the building platform is raised to elevate it. Excess powder is simply brushed away and final manual finishing may

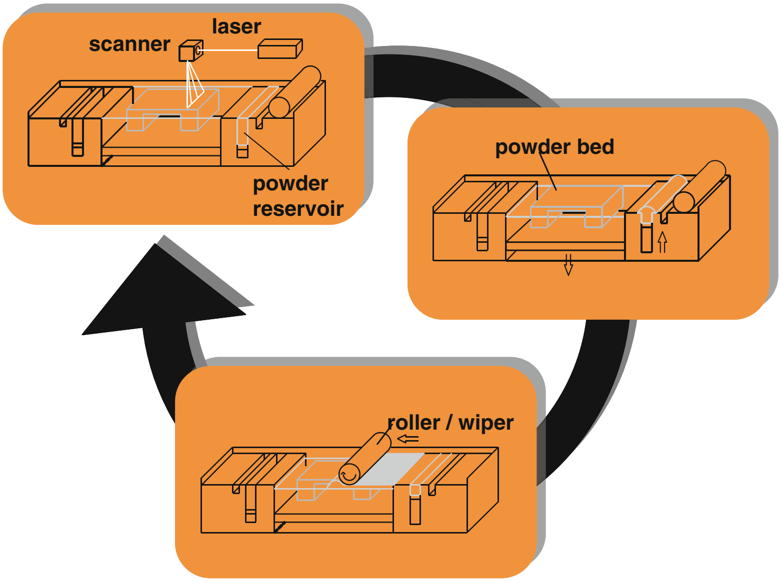


Fig. 80 Schematic illustration of a laser sintering process

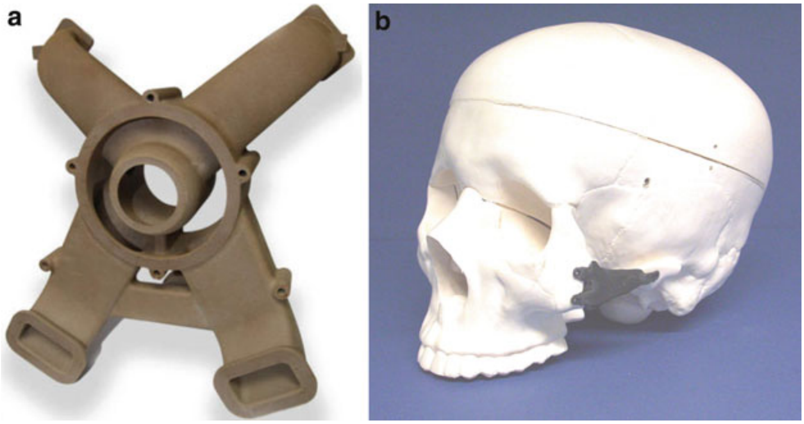


Fig. 81 (**a**) Laser sintered air duct of PEEK®HP3 for application in aeronautics (Victrex/eos GmbH, Germany), (**b**) laser sintered implant of PEEK in Human cranium (blz, Germany, [113]

be carried out. No supports are required since overhangs and undercuts are supported by the solid powder bed.

The most important advantage of SLS compared to other RP-processes is the wide range of usable materials and making functional parts in essentially final materials. There are several well investigated and commercially available thermoplastic materials [94, 98] such as nylon (PA 12) and PS. Going along with an optimization of SLS materials and the demand of the consumer market there is an increasing interest in the development of new materials for SLS.

There is a demand for more powerful polymers like for example PEEK [103, 107, 111], which enables new application areas in the automobile industry and medical fields, as shown in Fig. 81 and underlines the increasing potential of SLS-technologies. Because of this EOS GmbH recently presented a high temperature system, EOSINT P 800, along with PEEK®HP3 for SLS. There is a further interest in qualification of bulk polymers like polypropylene [100]. 3D Systems Inc. recently presented DuraForm PP 100 for SLS. Further more there is an interest in some technical polymers like Polyoxymethylene [112].

Current research studies deal with an additive-assisted SLS process using carbon black as the IR absorber to enable an adjustable optical absorption behavior of the polymer powder [105–107]. Related to SLS is the recently introduced selective mask sintering [108, 109]. Hereby a negative mask of the slice is printed onto a glass plate using toner and a thermoplastic powder, applied in layers, is then melted through that mask by an IR emitter. With comparable freedoms of design the construction time can be shortened and hence the residence time of the powder decreases significantly at high temperatures. This results in a more efficient manufacturing and a reduction of polymer degradation while processing and thus in improved mechanical properties of the parts. Because of the energy-insertion by broadband infrared emitters, new materials can be processed more easily compared to conventional SLS. Another related process is Direct Metal-Laser-Sintering

(DMLS). The technology fuses metal powder, which is mostly based on bronze or nickel, into a solid part by melting it locally using a focussed laser beam. It is a net-shape process, producing parts with high accuracy and detail resolution, good surface quality and excellent mechanical properties, for example tooling inserts. Moreover for the processing of metals, laser-engineered net shaping (LENS^{TM}), direct light fabrication and selective laser melting has been developed [97]. Further methods allow fabricating green-parts of powder-based ceramics for example by Liquid Silicon Infiltration [114] or ceramic slurries [104]. Subsequent to greenpart generation the parts are treated in a thermic cycle to create relatively dense ceramic parts. The part properties can be quite close or equal to those of the intrinsic materials, so the method has also been extended to provide direct fabrication of metal and ceramic parts.

SLS processes are more complex than most other RP-technologies. Because of its pressureless characteristic, the only driving force for densification of powder is a reduction in total surface area [96]. So there is a high influence of the initial density of the powder layer on the resulting part density and contour accuracy depending on the properties of the used powder materials, for example grain size distribution. Therefore, surface properties are not quite as good as with SLA.

9.7 Opportunities and Risks of Rapid Prototyping and Rapid Manufacturing-Systems

The most important benefit of RP-systems is the reduced *time to market* for models or parts. These models are used for several purposes; testing of form, fit and function, avoiding the high costs of prototype tooling, and allowing more freedom of design and iterations (Table 16). The ability to fabricate products more economically arises from several links in the RM process chain: One of the largest savings, as mentioned, is manufacturing parts without the need for tooling. Additional savings arise from lowered inventory requirements and from the ability to fabricate complete operational assemblies. Generative fabrication offers also the potential to use multiple materials as well as to control the local geometric meso- and micro-structure of a part, for example by variation of the deposited materials or incorporated mean energy in SLS to achieve anisotropic part properties. Thus, the functionality of a part can be optimized in ways that are impossible with conventional manufacturing methods. In the near future one major field of application for RM-parts will be highly specialized or customized products, especially for the human–machine interface. There is significant potential for the use of RP-methods for medical applications like individual implants or specially designed scaffolds for tissue engineering [116].

But it will be a long time before the choice of materials available for RM is even remotely comparable to those available for standard manufacturing technologies. There are just a few processable materials commercially available today. In addition, recycling of complex materials may be difficult or impossible. The actual speed

Table 16 Overview of opportunities and risks for RP-technologies

Evaluation segment	Opportunities (advantages)	Risks (disadvantages)
Technical	– No tooling needed, thus high freedom of design and product customization – Opening up to new applications areas (medical environment) – Latest developments offer more and powerful materials/RM-products	– Process control is sensitive and available materials are limited – Scientific understanding of processes to some extent insufficient – Layer characteristic of parts and postprocessing necessary (removal of support; infiltration of green parts)
Economic	– Simultaneous engineering minimizes "time to market" – High potential for reduction of development costs	– High processing costs (equipment, supplies) – Small order quantity and slow speed of fabrication of part
Environment	– Depends heavily on the use of the part(s) involved (concept model or e.g., individual customized product) – New developments offer office friendly systems	Safety equipment necessary because of laser technology
Social	– Increasing demand for jobs because of high annual increment of estimated revenues for RM-products and services	– Much more time and know how pressure on suppliers

of fabrication compared to standard manufacturing methods is much slower, and can be ~10–1,000-fold slower than building parts for example by injection molding. The finishes and accuracy are also not on a par with conventional technology due to the layer-wise generation and depending on the used materials and system. Secondary operations are also required, such as support removal and hand-finishing. There are also part size limitations at present which are more restrictive than those of standard methods. CAD directly drives all additive fabrication processes, making it theoretically possible to avoid the use of tooling altogether. In the majority of practical cases, it may often still not be possible to do that because of process and materials limitations, but complementary rapid tooling technology might offer a beneficial compromise for example DMLS allows fabrication of highly dense and stressable parts. When feasible, as shown by the latest developments of SLS, the complete elimination of tooling results in enormous savings in time and money. It makes it possible to fabricate parts and products in small quantities, or allows the use of materials and design parameters that might not be conceivable.

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Secondary Forming of Plastics Structural Components: Thermoforming

Fabian Beilharz

Abstract Primary forming techniques such as injection molding or extrusion use melts at about 250 °C. This chapter on secondary forming describes the shaping of thermoplastic semi-finished products like foils or sheets above their softening temperature of about 120–180 °C to form three-dimensional moldings.

Keyword Thermoforming

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1 Introduction

Thermoforming generally describes the shaping of thermoplastic semi-finished products above its softening temperature to three-dimensional moldings [1–3]. The process differs from the deep-drawing of metals, where the blank is not entirely

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P. Eyerer (ed.), *Polymers – Opportunities and Risks I: General and Environmental Aspects,*
Hdb Env Chem (2010) 11,
DOI 10.1007/978-3-540-88417-0_5,

fixed in the clamping and material can be fed continuously into the process during the deformation. The fixed clamping of the semi-finished product in thermoforming results in an approximately constant volume along with an enlargement of the surface, resulting in a reduction of thickness [1]. Thermoforming involves semi-finished products with a range of 100 μm–12 mm in thickness.

2 Thermoforming: Process Steps

Process steps for plug-assisted negative pressure forming are exemplarily shown in Fig. 1. Relevant process steps are described subsequently in more detail.

2.1 Heating

Dependent on the material and thickness of the semi-finished product, different heating methods can be applied [3]:

- Contact heating: Homogenous heating through thermal conduction, used for thin sheets
- Convection heating: Heating through thermal conduction, used for thick sheets

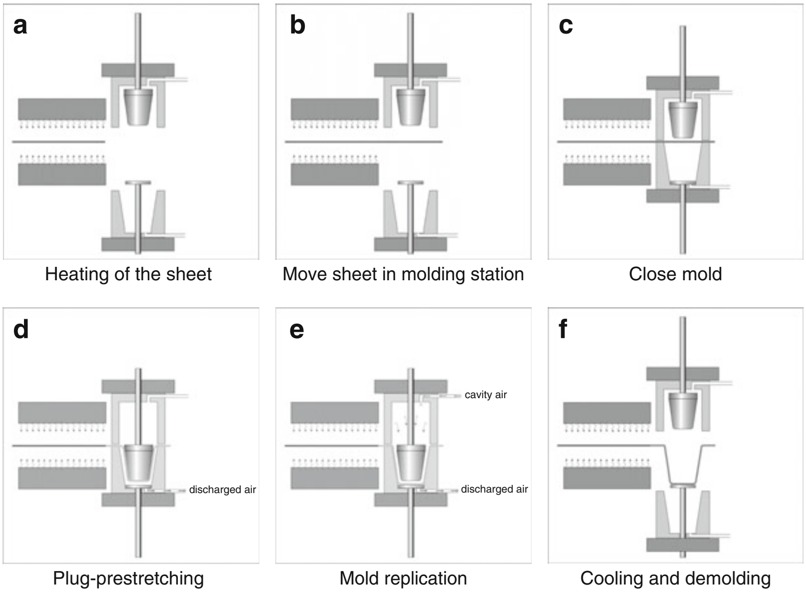

Fig. 1 Process steps for plug-assisted negative pressure forming [4]

- High-frequency or microwave heating: Inhomogeneous heating, materials must have high loss factor, therefore not applicable to polyolefines.
- Infrared heating: Universal heating method and therefore widely spread. Ceramic-, quartz- and halogen-radiators are used.

2.2 Shaping

The shaping of semi-finished products takes place in the rubbery-elastic stage [1]. Strain energy is applied by means of mechanical energy, pressure difference or a combination of both [3]. Mechanical energy is applied by the use of pre-stretching plugs to obtain a better material distribution into the mold. The shape of the part, which is normally given by a single side mold, is finally reproduced by pressure or vacuum. After shaping the sheet is cooled down to maintain its contour.

2.3 Demolding

Demolding of the part can be followed by further process steps, for example edge trimming by cutting or milling.

Many process variants for thermoforming are known, differing in the types of tools used and the process conduction. For further details please refer to the literature [5, 6].

3 Thermoforming: Plastics

Generally all thermoplastic polymers can be processed by thermoforming, but there are significant differences regarding process windows. Amorphous polymers show a wider softening temperature range than semi-crystalline polymers, which results in a wider process window and a more stable process [7]. For this reason only few semi-crystalline polymers are used in thermoforming, for example PP, PE, C-PET and polyester. The most commonly used amorphous polymers are PVC, PS, ABS, SAN, PMMA, PC and A-PET.

Furthermore, multilayer and fibre-reinforced composites as well as foamed semi-finished products (e.g. PVC slush skin for dashboards) are used in thermoforming.

Thermoforming normally involves trimming of the final product, which leads to a significant amount of recyclable material. This material is reused for the extrusion of semi-finished products. For thick sheets it is common to extrude multilayer materials with a core from regrind, while the top layer is virgin in order to obtain a good surface quality.

Fig. 2 Thermoformed panel with electroluminescence ambient light (*Source*: Manfred Jacob Kunststofftechnik GmbH)

4 Examples of Thermoformed Products

One of the main application areas of the thermoforming process is the production of packaging trays, for example for the food industry (yoghurt-cups, salad bowls, etc.). The packaging sector normally uses thin sheets fed to the machines from a roll. For such products the material costs of the sheet can be up to 60–70 % of the whole production costs [8].

The production of technical parts is the other main application for thermoforming. Vehicle dashboards and interior parts, fridge inner liners, bath tubs, sanitary modules, swimming pools, and surfboards can be produced by thermoforming. For large-scale products and products with a significant wall thickness mainly sheet material is used.

One example of an innovative thermoformed product is the application of new semi-finished products to the thermoforming process, like an interior panel with ambient light for automotive or aviation applications (Fig. 2). The semi-finished product is made of polycarbonate with an electroluminescence layer on the back. In order to protect the electroluminescence layer, the panel is partly back injection molded with PC/ABS.

5 Advantages and Disadvantages of Thermoforming

5.1 Advantages

Thermoforming shows several advantages compared to the competing injection molding process [3]. Machine and tool-costs are generally less expensive in thermoforming due to the low pressure forming and the use of mostly single side molds. This allows the production of large-scale parts with inexpensive machine and tool equipment. The use of semi-finished products allows the instant change of materials for small lot productions. Multilayer materials can be used to improve product properties (barrier properties, surface quality, etc.) without any extra costs for tooling.

Furthermore, thermoforming is used to produce thin wall parts economically. The required force to deform a semi-finished product in the thermoforming process is reduced with decreasing thickness, while the shear force in the competing injection molding process increases.

Thermoforming as a discontinuous process is often used for Form Fill Seal (FFS) applications. New machine developments allow a continuous output of thermoformed products which can ease the production control of inline FFS machines.

5.2 Disadvantages

Thermoforming is an open process, which means the process is sensitive to environmental changes and therefore sometimes unstable and difficult to control. Because of its instability, the thermoforming process has developed more like an art than a science [9]. The settings of process parameters and the development of new thermoformed products is only based on experience [10]. Little attention has been paid to thermoforming in terms of scientific understanding, which makes the process critical for complex applications compared to injection molding.

Table 1 Opportunities and risks of thermoforming

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Mass products – Large-scale parts – Fast material changes – Multilayer parts with simple molds – Integration in FFS production lines	– Process control sometimes unstable – Scientific understanding of processes insufficient – Irregular wall thickness – Little freedom of design – Properties of semi-finished products are unknown – Temperature control difficult
Economic	– Low costs for machine and molds – Short cycle times – More economical for mass products and large-scale parts	– More investment in research and technology necessary to increase process repeatability and to open the market for new applications
Environment	– All thermoplastic sheet material can be recycled and extruded to new semi-finished products	– High energy consumption for off-line thermoforming – High amounts of waste material from trimming to be transported for recycling, except thermoformer has own extrusion facilities
Social	– Jobs in Germany due to market leadership in the field of thermoforming machine manufacturing	– Most thermoforming companies in the EU are small- and medium sized – Competitive global pressure, resulting in risk of outsourcing due to high labour costs in Germany

Types of polymers suitable for thermoforming are limited and there is generally very little knowledge about the properties of purchased semi-finished products. The properties of a semi-finished product significantly influence its processibility [11] and the final part properties [10]. This phenomenon is often not under control of the thermoformers. Opportunities and risks are summarised in Table 1.

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Further Reading

Elías Cueto et al (eds); spons org (2007) 10th ESAFORM Conference on Material Forming: Zaragoza, Spain, 18–20 April 2007. European Scientific Association for Material Forming (ESAFORM), American Institute of Physics

Opportunities and Risks Involved in Designing Structural Components Made of Polymers

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Abstract In the introduction to this book, and to this chapter in particular, the polymer engineering process is presented from a holistic point of view, i.e., with all of its material sources and ramifications. In the sections that follow, this point of view will be demonstrated on the basis of a number of examples of structural component development from the recent past; some of these projects extend into the future as well. Following an introductory text, each example of component development will be supplemented by a qualitative evaluation table with explanations as required. These tables are also qualitative checklists for avoiding future errors based on the example of the specific application considered in each case.

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P. Eyerer (ed.), *Polymers – Opportunities and Risks I: General and Environmental Aspects*, Hdb Env Chem (2010) 11,
DOI 10.1007/978-3-540-88417-0_6,

Keywords CAE in plastics processing, Car door sills, Child seat, Dashboard, Drinking cups, Explosively embossed mold surface, Foaming with microwaves, Foaming with steam, Fuel cell, GMT vs. LFT-D, Halogen-free flameproofing agents, Inmold assembly, Inmold lamination, Material selection, Microwaves in extrusion, Mold design, Nanocomposites, Opportunities, Polymer testing, Polyurethane RRIM, Risks, Simulation, Thin-wall injection molding, Toothed gear, Ventilator vane

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1 Introduction

In the introduction to this book, and to this chapter in particular, the polymer engineering process is presented from the point of view of holistic considerations, i.e., with all of its sources and ramifications. In the sections that follow, this point of view will be demonstrated on the basis of a number of examples of structural component development from the recent past; some of these projects extend into the future as well.

Following an introductory text, each example of component development will be supplemented by a qualitative evaluation table with explanations as required. These tables are also qualitative checklists for avoiding future errors based on the example of the specific application considered in each case.

2 Opportunities and Risks of Material Selection

The selection of a material for a product cannot be isolated from the overall product engineering. Many plastic toys, for example, break prematurely, much to the chagrin of children, because the design, construction, and tooling techniques have simply been adapted one-to-one from metal engineering. Sharp-edged radii are a frequent cause of rupturing in plastics.

Material selection must go hand-in-hand with design, processing, and tooling techniques that harmonize with the material used, not to mention suitable surface processing techniques.

These relationships are reflected in the following three examples with a view to opportunities and risks.

2.1 Automobile Frontend

The frontend is the structural component that integrates the engine compartment and the front bumper. It provides the attachment framework for the headlights, fan shroud, and towing hook (optional). Up to about 10 years ago, this structural component, in large-series middle-class cars, was made entirely of sheet metal and comprised about 15–20 individual parts.

Metal–plastic hybrid constructions have been around for about 5 years now. The upper seatbelt tensioner construction consists of about five to ten sheet metal elements. A plastic fan blade shroud has been installed at the bottom.

A fully plastic prototype made of long fiber-reinforced polypropylene (PP) GF 30 with locally integrated glass textile reinforcement in the belt area was developed about 1 year ago. The manufacturing technique used is hot pressing, developed in a vertical scheme involving many partners in a 3-year project funded by the Federal German Education and Research Ministry (BMBF).

The participating carmakers are now considering integration of the new development in series production, one other carmaker is now converting.

Table 1 compares their opportunities and risks, Fig. 1 shows the frontend plastic element in an LFT-D version (direct long fiber-reinforced thermoplastics). For detailed descriptions see [5, 11]).

Table 1 Opportunities and risks involved in an automobile frontend made of long fiber-reinforced polypropylene with locally integrated glass textile inserts (LFT GF PP-D)

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– 40 % weight reduction if all specifications are met	– Series trials not yet completed. Causes of some processing phenomena not completely scientifically explicable
	– New technology with potential – Intermediate semifinished product step eliminated	
Economic	– 50 % cost savings for structural component – Small and medium-sized businesses more lean production	– None
Environmental	– Reduced fuel consumption during product life	– Not known as compared to metal or metal hybrid version
	– Fully recyclable in the form of similar structural components (middle layer)	– Market for secondary raw materials still very small
	– Lightweight construction: potential for reduced fuel consumption during product life	
Social	– Will sustain high-tech jobs in Germany	– None

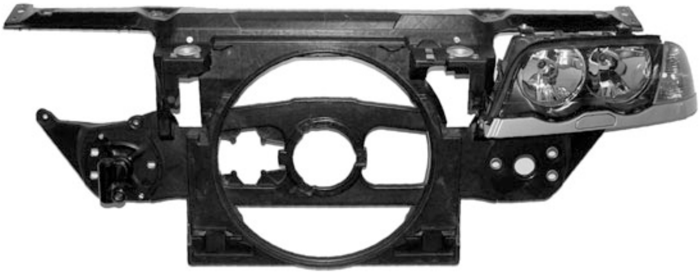


Fig. 1 Fully plastic frontend with locally integrated glass textile reinforcement (Fraunhofer ICT)

2.2 Arboform® (Injection moldable wood)

Future product design requires innovative approaches in material development. The predominant issues are variability in properties and functionality, light weight, low costs, and environmental compatibility in all stages of the product lifecycle.

Wood, a traditional engineering material, is still competitive due to its high impact resistance, thermal loading, and high-grade styling potentials.

Disadvantages include the high costs and environmentally harmful adhesives used to realize complex geometries with layered constructions. Wood is one of the few inexhaustible natural resources, assuming proper management, and has been one of the most important products in the human economy since earliest times. From the material point of view, wood is a composite consisting mainly of lignin, cellulose fibers, and hemicellulose.

Lignin is a natural polymer formed in woody plants by polymerization of three phenyl propanoid monomers. After polysaccharides, it is the most abundant organic polymer in the plant world. In terms of properties, it acts as a binder between the wood cells, creating a composite material that is resistant to impact and compression.

Recent basic research has turned up new approaches for innovative materials combining elements of, and integrating the advantages of, wood and synthetic plastics. Lignin is one of the main components of this new class of plastic-like, wood-like biocomposites. The resulting mixture of lignin, natural fibers, and additives is a compound processable as a thermoplastic. The processed materials are short fiber composites. Arboform is a trade name for this class of compounds.

Although Arboform exhibits wood-like properties, it can be processed like a thermoplastic material and used in product engineering. Mixing and compounding of granules of this material is based on standard technologies of polymer engineering. It can be injection molded and pressed like a thermoplastic raw material. The relatively low processing temperature is one of the advantages of this compound. Lower temperature means lower energy consumption and low machine stress loading levels. It is a good alternative as a substrate for wood veneer elements because its thermal expansion coefficient is similar to that of wood. Substantial differences between expansion coefficients make application of wood veneers to plastic substrates difficult (Fig. 2) (Table 2).

2.3 Plastic Fuel Tank

The history of the plastic fuel tank (PFT) provides a perfect example of competition among different materials to meet product requirements.

Fuel tanks have been made of steel since automotive production began. One of the major disadvantages of this material has proven to be corrosivity. This became an issue mainly from inside the product, since underbody sealing (e.g., with PVC plastisols) helped cope with corrosion from the outside. Moreover, as more and more additional technical features were incorporated into cars, space for the fuel tank became limited. Early concepts identified spaces in the car trunk or behind the rear seat row, but it became common practice to place the fuel tank under the car body in the rear section. This meant additional forming requirements to accommodate various requirements such as maximization of trunk volume, safety features, and provision of sufficient space for the rear axle and muffler. It became increasingly difficult to realize the complex geometries of fuel tanks based on metal stampings. Moreover,

Fig. 2 Watch frame made of arboform (Fraunhofer ICT)

numerous additional joining steps were necessary: to join the two metal halves of the tank as well as the tube connections to the filling opening and motor fuel supply.

Polymers seemed to offer sufficient advantages over the conventional metal products. They were lightweight and definitely corrosion-proof. Forming of connections became easier. Although wall thickness was higher than in metal tanks, using up the entire available underbody space, additional filling volume was also created. This was due to the moldability of the polymers, making possible optimized tank geometries with little interference from processing limitations as seen in saddle tanks for four-wheel-drive cars.

HDPE blow molding was not identified as the technology of choice for serial production of fuel tanks until the mid-1970s. Earlier, other production

Table 2 Opportunities and risks involved in use of Arboform

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– High level of stiffness	– Causes of some processing phenomena not completely scientifically explicable
	– High dimensional stability, little shrinkage (max. 0.5 %)	– No data on real-time material behavior
	– Reduced expansion coefficient (max. $50 \times 10^{-6} \frac{1}{K}$), optimum for multilayered materials, e.g., wooden veneer	
	– Acoustic attributes like wood	
Economic	– Lower processing temperatures	– New material type, therefore production quantities as yet insufficient for competitive pricing compared to conventional materials
	– Crude oil substitution	
Environmental	– Positive environmental behavior	– No data as yet
	– Reduction of a waste problem	
	– Degradability similar to wood	
Social	– Promising alternative nonfood application of agricultural products	– Still unknown

technologies such as injection molding of halves with subsequent joining (the exact technology of metals application, merely transferred to polymer processing) and rotational forming were under assessment, but did not yield satisfactory results. Moreover, the identification of the material of choice in combination with the forming technology was a lengthy process. Polyolefins were easy to process and available at low cost, but they were highly permeable to fuels due to their nonpolar nature. Polyamide or POM offered enhanced hydrocarbon barrier properties, but costs and other properties restricted their use in series production. Processing technology for forming large hollow bodies was in its early stages. In particular, constant wall thicknesses over the entire tank structure, the shape of which had grown increasingly complex, took years to achieve. In the mid-1960s, Ford Motor Company had tested polyamide fuel tank prototypes, but when series production of PFTs started, polyethylene was the chosen material. Nevertheless, little difference between the simple geometries of cuboid metal tanks and PFTs was seen at the time.

To tackle the problem of fuel loss through the tank walls, polar barrier layers were tested. Among the methods tried were fluorination and sulfonation, as well as epoxy resin or polyamide powder coatings on the fuel tank walls. Again, cost and process safety were the issues begging for solutions, and fluorination and sulfonation proved to be the processes of choice for enhancing barrier properties. Both inline and offline processing approaches were tested, and fluorination with fluorine gas as a component of the blowing gas was eventually the choice of most European PFT producers, although fluorine gas required additional safety measures to facilitate application in blow-molding facilities.

The first PFT on the street was installed in a Porsche rally car at the end of the 1960s. Series production was implemented in 1973 in the Volkswagen Passat model. In the US, series production of PFTs started up in 1989. The plastic market share in new cars in the US is about 40 % for this component, whereas in the EU about 75 % of all new cars are equipped with PFTs. Complex shapes can indeed be produced with polymers, although some limitations apply: Because of swelling processes, it is necessary to leave larger gaps between the tank and car body compared to metal tanks, detracting from the volume gain of PFTs over metal fuel tanks to some extent. Moreover, aluminum heat shields have to be installed around the PFTs in the muffler and catalytic converter areas and the complex geometries require elaborate fuel management and pumping techniques. Common rail technology with heated fuel reflux into the PFT creates additional thermal stress on PFTs made of HDPE; this material has an expected long-term temperature load capacity of about 90 °C. Multilayer PFTs with up to six different layers represent proven technology for permeation minimization.

In recent years, automobile hydrocarbon emission controls have come into force, mainly in the US. Especially in the state of California, the hydrocarbon emission restrictions were originally intended as a means of promoting the use of electric cars. The California Air Resources Board (CARB) issued a classification for car emissions together with stepwise increase of the requirements for new cars. On the technology side, fuel cell cars became an alternative, and PFT manufacturers started up efforts to minimize fuel emissions. They were so successful at meeting the partly zero emission vehicle (PZEV) standards that now hydrocarbon emission sources such as polymer interior trim, adhesives, sealants, or tires are the objects of new emission minimization requirements. Hydrocarbon emission minimization improvements applied to PFTs covered the minimization of communication between the PFT body and the environment, use of additional “hoods” over some connection areas and use of improved barrier layers combining proven EVOH and PA barrier technologies. One recent approach involved the revival of the well-known method of joining two halves to make a PFT, but based on a polymer co-extruded multilayer sheet, which was thermoformed. This technology offered the advantage of easy mounting of internal pumps and tubing, although the joining proved to be the weak point, as in blow-molded PFTs. Metal fuel tank producers have also improved their products by using lighter steel varieties and improving their processing technologies, for example with hydro forming, making possible similarly complex product structures as are realized in PFTs and satisfying the same requirements.

Thus material and process development for production of fuel tanks in recent decades reflects the competition between metals and polymers as forced by technical, economic and – more recently – legal requirements. In years to come, fuel cell

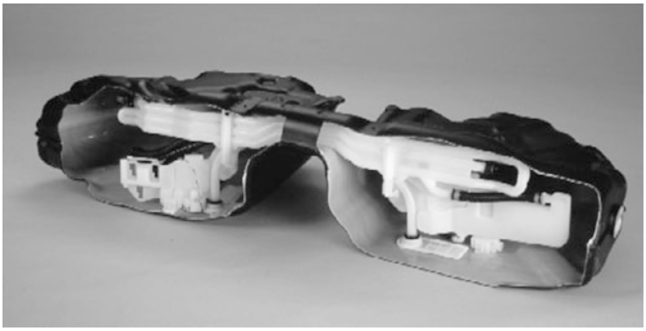


Fig. 3 Multilayer PFT with ship-in-the-bottle technology for fuel management components (photo courtesy of TI Automotive)

applications based on fuels such as hydrogen and methanol will require innovative fuel storage solutions for cars (Fig. 3).

2.4 Soft PVC Vs. Thermoplastic Elastomers in Toys

The pallet of materials for children's toys is as varied as the spectrum of products. In addition to metals and wood, plastics have proven to be excellent materials for many different articles for children and babies. Important properties such as good ergonomics, attractive design, high level of functionality, low risk of injury, and low weight are all satisfied by plastics along with the reasonable raw material and production costs for these materials (Fig. 4).

Among the most economical and durable plastics is PVC. By addition of plasticizers, the hardness of this material can be adjusted within broad limits so it can be adapted in an optimum manner to specific product property requirements.

2.4.1 Plasticizer Problems with Soft PVC

On the other hand, the material PVC is also the subject of drawn-out controversial discussions. Soft PVC in particular, with the commonly used phthalate-based plasticizer types, has been the object of criticism. Investigations by the German Federal Environmental Office, WWF Germany, Greenpeace, and the US EPA indicate a potential health hazard arising from certain plasticizers containing phthalate. These studies express suspicions concerning genetic damage, fertility reduction, carcinogenicity, damage to liver and kidneys, and irritation of skin and respiratory organs. Whether these harmful properties can be extrapolated to human

Fig. 4 Toys made of different plastic materials

exposure – they were recorded only at very high concentration levels in animal experiments – still remains to be determined.

2.4.2 Legal Framework

Understandably, this information has resulted in the enactment of various regulatory laws. Since 1999, the EU Commission has not allowed EU member countries to market toys or baby articles containing certain phthalate-based plasticizers that are to be put in the mouths of children under 3 years of age. These regulations have now been significantly expanded.

The toymaking branch has responded both by turning to alternative plasticizer systems, for example based on citric acid esters, or to different types of plastics altogether, mainly so-called thermoplastic elastomers (TPEs).

2.4.3 TPE as an Alternative

The market for TPE has shown an unbroken dynamism in recent years. Characteristics desirable for many applications have certainly contributed to this trend:

- High level of elasticity, flexible
- Elastomeric character with the advantage of thermoplastic processing
- The Shore hardness of many TPEs is adjustable over a wide range
- Simple, low-cost recycling

Table 3 TPE families

Material abbreviation	Designation	Structural type
TPE-O	Thermoplastic olefin elastomer, uncross-linked	Blend
TPE-V	Thermoplastic olefin elastomer, (partially) cross-linked	Blend
TPE-S	Thermoplastic styrene block copolymer	Block copolymer
TPE-E	Thermoplastic polyether ester elastomer	Block copolymer
TPE-A	Thermoplastic polyamide elastomer	Block copolymer
TPE-U	Thermoplastic polyurethane elastomer	Block copolymer

Table 3 shows the TPE families.

This property profile has led to substitution of TPE in a wide variety of applications for which elastomers had previously been used. For highly sensitive areas of application such as the food and toy industries, harmless TPE materials are available which, for example, comply with the rigid Food and Drug Administration (FDA) guidelines.

The following criteria must be considered when selecting suitable TPEs for toys:

- No health risk
- Compliance with legal regulations
- Good processability
- Surface must take paint well, good paint adhesion
- Good dyeing properties
- Soft setting (Shore A 60–95)
- High level of elongation at break
- Good demolding qualities
- Temperatures during use up to 60 °C
- Good gluing qualities
- For outdoor toys in particular: weather-resistant, UV-resistant
- Recyclable

Depending on the application of the toys (e.g., teething rings for babies or toy figures for small children) the proper TPE must be selected from the many different types. Wholesale replacement of soft PVC by a single TPE class is not yet feasible since none of the TPE materials can match PVC's universal properties (Fig. 5).

Table 4 summarizes opportunities and risks involved in replacement of soft PVC with TPE.

2.5 Fuel Cells: Polymer Electrolyte Membranes (PEMs)

Fuel cells are currently considered to be among the most significant future technologies. Their use in the automotive sector has been an object of intensive efforts for some years now. Another potential future use is as an energy source for portable electronic devices (laptop, handy, etc.). Both of these application sectors address mass markets in which the system price also influences market entry. The simpler

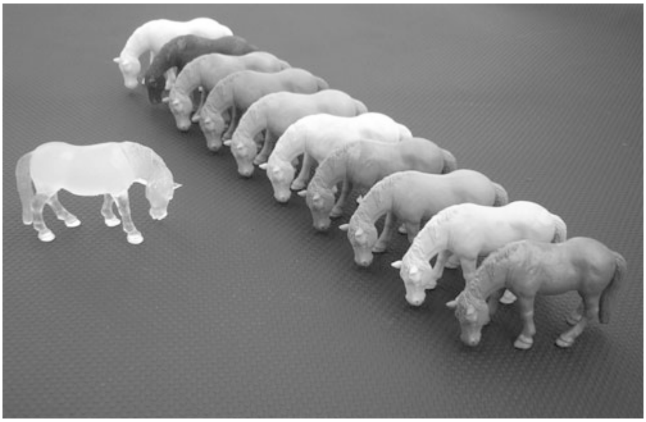


Fig. 5 Toy figures made of new TPE materials

handling and storage of liquid methanol has given the trend in development of fuel cells for microenergy supplies a push in the direction of the direct methanol fuel cell (DMFC). In the automotive sector as well, the discussion of potential energy carrying substances does not appear to be over by any means.

Polymeric functional materials are of central importance for the polymer electrolyte membrane fuel cell (PEMFC) and DMFC technologies in particular. In addition to the expected cost reduction due to low-cost mass production, for example of polymeric bipolar plates (see Sect. 2.1), the polymeric membranes are irreplaceable in the PEMFC and DMFC technologies.

The structure of PEMFCs and DMFCs does not differ in principle. Figure 6 shows the schematic structure of a DMFC. Oxidation of the fuel to CO_2, in this case methanol, takes place at the electrical catalytic converters (anode) along with the reduction of oxygen to water (cathode). In the process, protons produced at the anode migrate through a proton-conductive membrane (fixed electrolyte) to the cathode, where they react with oxygen to make water.

The proton-conducting polymer membranes fulfill a number of functions, which clearly influences the choice of materials:

- High level of electrical resistance
- Impermeability to the fuel used
- Thermal and chemical stability
- High level of proton conductivity
- Low cost (20–50 €/m^2)

The membrane material most often used in fuel cells today is Nafion®, made by DuPont. Nafion® is the product name of a perfluorosulfonic acid/polyethylene copolymer (PFSA/PTFE) that clearly meets the specifications for thermal and chemical stability and high levels of proton conductivity and electrical resistance. Other perfluorinated membranes are now commercially available in addition to Nafion®: DOW® Membrane from Dow Chemical Corp. and a membrane made by

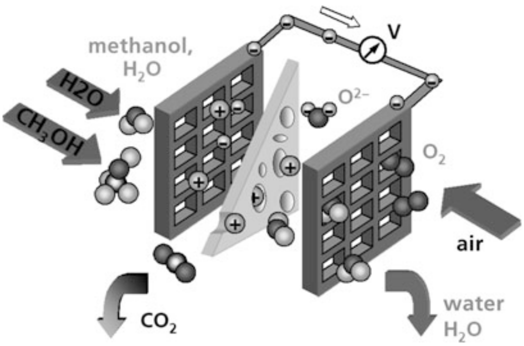
Table 4 Opportunities and risks of replacing soft PVC with TPE

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Good processability	– Thick-walled toys critical due to increased shrinkage potential
	– Processing on standard machines, increased corrosion protection (PVC-coating) not required	– Paint adhesion limited (TPE-O)
	– Density less than PVC in some types	– Less elongation at break than PVC in some types
	– Short cycle times with TPE-S	– TPU systems tend to adhere to mold surface
	– Ready compatibility with other plastics (2C injection molding)	– Products adhere to one another, especially with TPE-S types (SBS)
	– No corrosive substances in processing, particularly with TPE-O types	– Limited UV resistance in TPE-S and TPE-U types – Lower level of temperature resistance (TPE-O, TPE-S) – Special processing methods such as film production for blow-up figures, rotational molds only usable to a limited extent with TPE materials
Economic	– Cycle times in some cases shorter than for soft PVC	– Higher raw material price than for soft PVC – Greater expense for wide product spectrum due to necessity of using different TPE types (higher logistics and employee training costs)
Environmental	– Less critical recycling situation – Less formation of critical substances in case of fire	– PVC has been discussed at length in many studies. This level of extensive knowledge has not been reached as yet for many TPE materials. Risk of as yet unrecognized problems with TPEs.
Social	– Early reaction to laws creates competitive advantage over soft PVC imports	– Risk that end consumers will not accept raised product price
	– Know-how advantage in TPE processing – Preventive health care – Future security assuming laws become more stringent	– Competitive disadvantage

Gore based on a microporous, stretched Teflon film the pores of which are filled with a perfluorinated polymer.

A precondition for proton conductivity in Nafion® is uptake of sufficient water into the membrane and prevention of its drying out during operation. The protons diffuse through "water channels" in the membrane to the cathode or are transported

Fig. 6 Schematic structure of a single DMFC



through the membrane by the so-called “Grotthus mechanism.” Because of its similar chemical properties, the methanol is also transported through the membrane by means of diffusion and permeation. In addition to a loss of capacity, i.e., of methanol itself, this methanol crossover also reduces the performance of the fuel cell system due to processes taking place at the cathode. In addition to diffusion and permeation, a third effect, so-called electroosmotic drag, transports methanol to the cathode, whereby the methanol is entrained within the solvate shell of the migrating protons. This effect increases with the current load of the fuel cells. The methanol crossover is still an unsolved problem in DMFC operation.

Therefore, intensive international R&D efforts are underway to find new membrane materials and/or to suppress methanol crossover. The main focus of this work is not only to suppress the methanol crossover, but at the same time to achieve high levels of proton conductivity. Extensive tests have been run with sulfonated polysulfone, polyethersulfone, polyimide, polystyrene, and many other materials with both PVdF-based membranes and polypyrroles or with block copolymers, for example polyarylene polyether. A composite membrane made of polybenzimidazole with phosphoric acid as the proton conductor was also tested. The use of phosphoric acid has the additional advantage that these membranes are still efficient proton conductors at temperatures between 130 and 150 °C. By contrast, Nafion is only functional at temperatures below 100 °C because it tends to dry out. The higher temperature has a favorable influence on the reactivity kinetics of the methanol in the electric catalytic converters available today and is therefore a desirable factor. On the other hand, some of the phosphoric acid leaves the system during fuel cell operation or reacts with the methanol to create volatile compounds. Both lead to a reduction of proton conductivity and thus to increased membrane resistance. More recent approaches aim at a synthesis creating inorganic–organic composite membranes that would reduce methanol crossover. Some improvements have been achieved, they have often entailed a reduction of proton conductivity. The search for a suitable membrane material for the DMFC that meets these demands for a reasonable price is still ongoing (see also Table 5).

Table 5 Opportunities and risks of membranes for PEMFCs and DMFCs

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Central functional element of PEMFC and DMFC – Mass production	Membranes that meet the required specifications: – High level of electrical resistance – Impermeability to the fuel used – Thermal and chemical stability – High level of proton conductivity – Low price membranes are still in the development stage
Economic	– Low-cost production	– Production to date: complex and expensive – Not competitive in the medium term due to high price (for instance of the membranes required)
Environmental	– Environmentally compatible production – Recyclable materials – DMFC afford future sustainable use of regenerative energy sources and are, from an ecological and economical point of view, a significant element in future methods of supplying humanity with sufficient energy	– Fluorination still problematical
Social	– Ensures and creates jobs as a significant future technology	– Hydrogen-based technology harbors safety risks for humans and animals

2.6 Plastic Oil Module

The use of plastic instead of metal in technical parts has increased due to the higher performance of new polymers as well as advanced engineering methodologies for development of technical components. The driving forces behind this trend are the enormous advantages expected with these materials as for example weight reduction. The substitution of metal by plastic poses however some technical challenges due to the special properties of plastics and their processing methods.

The next example describes the advantages and challenges raised by the substitution of metal by plastic in the manufacturing of an oil module housing integrated in a petrol engine. While in the past the standard solution for oil filter modules was aluminum processed by die casting nowadays the use of plastic has become a successful alternative for this product. Such a fully plastic oil module was first developed for mass production in 2003 by Mann+Hummel in co-operation with Audi AG [9]. Today there are further solutions of fully plastic oil modules on the market. This contribution summarizes the function and requirements of such an oil module, the opportunities and risks to be expected with a fully plastic housing and the results obtained.

The oil module controls and protects the oil system and ensures the correct function of the engine oil as a lubricant and heat dissipator. It combines different functions such as oil filtration, oil pressure control, cooling and crankcase ventilation. An indispensable technical requirement is that the module withstands high pressures and temperature fluctuations and is resistant to motor oil. In order to be economically justifiable, the module must be suitable for mass production.

Die cast aluminum, the former standard material for this part, satisfies the criteria mentioned above. The different functions were performed by separate components integrated in the engine.

The motivation to replace the aluminum with a plastic module arose from a number of expected advantages such as considerable weight reduction, parts integration, energy absorption, and feasibility for automated, high-volume processing with a potential for rapid and low-cost production.

However, the main reason why aluminum had been used for oil module housings is its rigidity – even at high pressures and temperatures. Replacing aluminum with plastic involves the risk of insufficient sealing due to greater deformation under extreme loads, potentially resulting in internal leakage affecting the entire oil system and possibly damaging the engine as well. Moreover, the dimensional tolerances of plastic parts are greater due to the production methods employed.

To cope with these risks when substituting metal by plastic in technical parts the right polymer has to be chosen and furthermore the part design has often to be modified to reduce deformation and meet the requirements of a plastic-compatible construction. The design can be optimized by using simulation tools in order to identify the regions of high stresses and strains under operating critical conditions. Nevertheless, the final prototype has to be subjected to exhaustive experimental testing to ensure the right functionality.

A thermoplastic widely used in technical parts due to its high stiffness and strength is glass fiber-reinforced polyamide (PA 66 GF35). Figure 7 shows an oil module made completely of this material except for the valves and sockets, which was produced by Mann+Hummel.

In this example the construction of the module had to be modified with respect to the aluminum alternative to eliminate the risk of poor sealing. Special sealing concepts were developed, involving a special seal geometry for the screw cap and others for the heat exchanger and engine flange [9]. A new valve concept was also developed that achieves the holding and sealing functions with separate design features in order to avoid leakage that might occur with the standard valves if the bored diameter in the plastic housing increased under operating conditions. To reduce the part deformation meeting the requirements of a plastic-compatible design, ribs were placed at critical positions. The function of the seal to the engine block flange was simulated under all potentially critical conditions, such as cold start and very high temperatures, to ensure the correct mode of operation. The deformation of the connections within the plastic was also simulated so that geometry changes to achieve a stable construction could be realized before the prototype phase. The final construction was then subjected to a number of pressure load tests.

Fig. 7 Worldwide first plastic oil module for mass production in 2003 by Mann+Hummel GmbH, Ludwigsburg, Germany

With regard to processing, the die-cast aluminum housing required further machining processes such as turning, drilling, and milling. These steps are avoided with the plastic housing, since it is injection-molded. This technology produces a finished part and permits easy realization of complex geometries.

The plastic oil module integrates diverse functions such as filtration and engine oil cooling, overall oil system control, oil pressure regulation and part of the oil separation for crankcase ventilation in one component. This reduces assembly costs considerably. Moreover, the module has a lower mass compared to its aluminum counterpart. By taking into account the lifecycle from raw material to reutilization of the component, the weight difference results in a fuel saving with reduced CO_2 emissions. An example of a holistic balance for various oil filter housings for automobile engines is provided by [2] for data available at that time and for certain framework conditions. Table 6 summarizes the opportunities and risks of a fully plastic oil module.

2.7 Lithium Ion Batteries: Polymeric Electrolytes Vs. Liquid Electrolytes

Since its introduction in 1992 by SONY, the lithium accumulator has become a widely used battery system for portable devices (e.g., mobile radios, notebook PCs).

Table 6 Opportunities and risks of fully plastic oil module housing vs. metallic solution

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Complex geometry easily produced – No further machining, i.e., turning, drilling, or milling – Function integration – Weight reduction	Sealing requires improvement – Current lack of experience
Economic	– Low-cost production and assembly	– Investment in research and development is needed
Ecological	– Polyamide is well suited to the recycling methods used in the automotive sector – Fuel savings and reduced CO_2 emissions over the lifetime of the car due to weight reduction	– Unknown compared to aluminum version
Social	– High-tech saves jobs – Higher level of consumer awareness due to ecological advantages	– No social risk

Compared to other battery systems on the market, the lithium accumulator sports the best ratios of stored energy volume to material weight.

One of the main contributors to the remaining safety risk involved in the use of rechargeable lithium batteries is the use of liquid, organic electrolytes. These electrolytes having high vapor pressures at temperatures as low as 60–80 °C are flammable. When plastic-coated metal foils are used as housings for the lithium batteries (so-called coffee bags) the increasing internal pressure at higher temperatures may tear open the foil housing, as a result of which the opening lithium battery can then become a source of explosion or fire. On the other hand, use of a foil housing is a desirable factor due to the low price and flexibility of this concept.

With the use of solid to gelatinous, polymeric electrolyte layers that ensure electrical separation of the electrodes and the unity of the cell components combined with good conductivity for lithium ions, it is not necessary to employ liquid electrolytes in lithium batteries. This simplifies the production of lithium polymer batteries, which are also safer in operation because the electrolyte is polymeric, not liquid. This battery cell structure facilitates production of thin foil batteries, a favorable form for use in portable devices. The expected performance data correspond to what is obtained with other lithium ion systems.

The desirable characteristics of polymeric electrolytes for lithium batteries are high levels of ionic conductivity, no electronic conductivity at all if possible, a high dielectricity constant, good electrochemical compatibility with the anode and cathode material, and good mechanical properties to fulfill the separator function. Since Wright et al. reported for the first time in 1973 on ionic conductivity of poly (ethylene oxide) salt complexes there have been a number of attempts to modify this property to achieve higher levels of conductivity and better mechanical properties. Poly(ethylene oxide) salt complexes are in crystalline form at room temperature, greatly restricting chain and ionic mobility. However, high levels of ionic conductivity require good ionic mobility. For this reason, the poly(ethylene oxide) salt complexes, for instance, must undergo a transition to the amorphous form, for instance by heating them to temperatures above 60 °C.

Other strategies aim to restrict formation of the crystalline phases of the polymeric electrolytes based on polyethylene oxide (PEO):

- PEO as a component of copolymers
- PEO as side chains in comb polymers
- PEO as a network component

The problem of a lack of dimensional stability in linear copolymers and comb polymers can be solved by means of networking of the polyether chains. This type of networking reaction can be achieved, for example, with the help of diisocyanates or methacrylates.

A polymeric electrolyte film ensures mechanical separation of the electrodes so that no additional separator material is required. A number of established techniques are available for processing polymeric materials (Fig. 8) (Table 7).

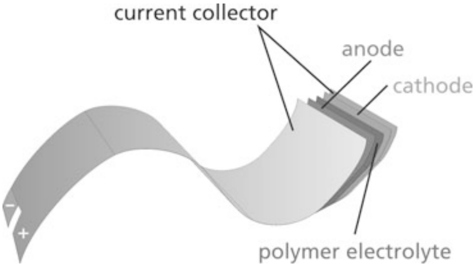


Fig. 8 Schematic structure of a flexible lithium polymer battery

Table 7 Opportunities and risks of polymeric electrolytes for lithium ion batteries compared to liquid electrolytes

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Very low vapor pressure at higher temperatures – Higher energy densities of lithium ion battery – High degree of form flexibility – Higher operating temperatures	– Low level of ionic conductivity at temperatures below 0 °C – High level of temperature dependence of ionic conductivity
Economic	– Lower cost of production process – Opening up of new markets	– Production process not yet developed to the point of market maturity
Environmental	– No solvents required in production process – Better recyclability	
Social	– Higher level of operating safety and reliability	

3 Opportunities and Risks of Plastic Process Engineering

As has been mentioned repeatedly, process engineering is integrally bound up with material selection, molding technology, design, construction, and further engineering steps. The more completely these steps are integrated and the more continuous the flow of feedback into the product development is, the smaller the number of subsequent manufacturer alterations and recalls during the product utilization phase will be.

The major opportunities of most plastic engineering techniques lie in their low-cost:

- Combination of different methods
- Combination of different polymers
- Integration of functions during processing and
- Integration of processing steps in primary forming processes (inmold assembly of structural components)

as well as in

- Simplified material recycling with granulation and remelting
- Tailor-made properties by means of synthesis and, above all, specific compounding
- Differentiated molding tool techniques with an emphasis on know-how and
- Advanced simulation technique that affords predictions of rheology, processing steps, mold filling processes and finished part properties under loads

The risks involved in plastics processing, as in other material technologies, frequently involve poorly planned structural component designs leading to high-cost mold manufacturing and alterations. The choice of the wrong material usually means the molds have to be remade from scratch. In addition to the direct costs involved, there is the risk that a considerable amount of – costly – time will also be lost.

The following examples elucidate these opportunities and risks.

3.1 Polymer-Components for Fuel Cells

3.1.1 State of the Art

Fuel cells represent an energy system with excellent economical and environmental potential and there has been an enormous acceleration in the development and commercialization of fuel cell systems for portable, mobile, and stationary systems.

The characteristic of fuel cells is the ability to convert chemical energy directly into electrical energy without the need for combustion, giving much higher conversion efficiencies than conventional thermo-mechanical methods and the absence of any environmentally hazardous exhausts.

In principle there are five different fuel cell types, mainly differentiated by the used electrolyte and the working temperature (Table 8).

The proton exchange membrane fuel cell (PEMFC) also known as polymer electrolyte fuel cell (PEFC) is the leading candidate for commercialization.

Because of the low processing temperature of the PEMFC it is also predestined for the implementation of polymeric components.

The basic principle of a proton exchange membrane (PEM) fuel cell is shown in Fig. 9.

The PEM fuel cell is principally built up by the bipolar plates and the gas diffusion layers with the membrane-electrode assembly (MEA). Located on both

Table 8 Fuel cell types

Fuel cell type	Electrolyte	Processing temperature	Applications
Solid oxide fuel cell (SOFC)	Y stabilized ZrO_2, conducting O^{2-} ions at high temperatures	800–1,000 °C	Industrial applications, power stations, buildings and heating systems
Molten carbonate fuel cell (MCFC)	Li/KCO_3 as molten salt, that conducts CO_3^{2-} ions	650 °C	Industrial applications, power stations, ships
Phosphoric acid fuel cell (PAFC)	Concentrated phosphoric acid, proton-conducting	200 °C	Power stations
Alkaline fuel cell (AFC)	Aqueous KOH, OH^- ion-conducting	80 °C	Aerospace, military
Proton exchange membrane fuel cell (PEMFC)	Proton-conducting ion-exchange membrane	80 °C	Stationary, mobile, portable

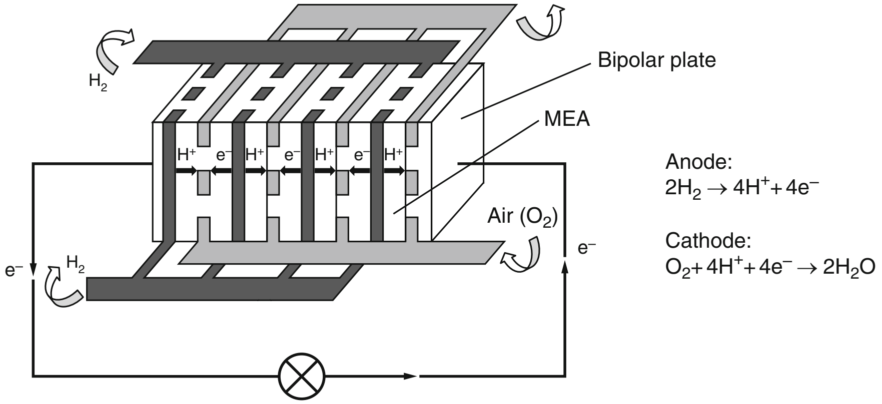


Fig. 9 Basic principle of PEM fuel cells (PEMFC)

sides of the MEA the bipolar plates serve to collect the electrons on the external surface of the electrode (anode side) and to distribute them to the external surface of the cathode.

In this arrangement, hydrogen is supplied to the negative electrode (anode) where it dissociates into protons and electrons ($2H_2 \rightarrow 4H^+ + 4e^-$). Protons pass through the membrane to the positive electrode (cathode) while the electrons are conducted through the bipolar plates externally creating an electric current. At the positive electrode, the protons and electrons recombine in the presence of oxygen (normally from the atmosphere) to form water ($4H^+ + 4e^- + O_2 \rightarrow 2H_2O$). The by-products of the PEM fuel cell reaction are water and heat.

3.1.2 Opportunities and Risks for the Use of Polymers in PEMFC

The most important components in a fuel cell are the Membrane Electrolyte Assembly (MEA) and the bipolar plates. The MEA usually consists of an electrolyte membrane, which is coated with catalytically active platinum-electrodes and a gas diffusion layer of hydrophobic graphite. As the electrolyte membrane cation exchange polymers are used. A crucial break-through was reached here by the employment of fluoridated polymers. The market leader here is Nafion® developed by the company Dupont.

Currently many developments in relation to the use of polymers are focused on the bipolar plates, therefore some new possibilities for the use of polymers for bipolar plates are shown below. Furthermore, peripheral components like the housing are predestined for the use of polymers and in the following an example is given.

3.1.3 Bipolar Plate

Beside the MEA the bipolar plates are the key components in a PEMFC stack in terms of their contribution to weight, volume, and costs. Bipolar plates contain a fine mesh of gas channels called the flow-field, to ensure a uniform distribution of the process gasses (hydrogen and oxygen) of fuel and air across both sides of the MEA and the removal of the reaction products. Furthermore, the bipolar plates in PEM fuel cells separate the individual cells from each other and guarantee an electrical connection between them in series. Substantial requirements for the bipolar plates are a high electrical conductivity and corrosion resistance.

At present these bipolar plates are made of metallic materials or graphite plates. Graphite has acceptable electrical, thermal, and mechanical properties, but the flow-field of graphite plates is actually produced by machining which is too expensive for mass production. Metal plates are of interest because of their toughness and versatile fabrication options, but corrosion is a significant difficulty. The traditional materials, high-density electro graphite and stainless steel, are being replaced to a greater and greater extent by conductive polymers like graphite-filled thermoplastic for moldable plates.

Below the development and employment of high-filled thermoplastics is examined, which represent an economical alternative for the production of bipolar plates with lower processing costs and more affordable raw materials for the following reasons:

- Relatively cheap materials (graphite and standard thermoplastics)
- Excellent corrosion resistance
- Acceptable electrical and thermal conductivity
- Potential for economical and ecological mass production

3.1.4 Material Development for Polymer Bipolar Plates

The technological challenge for the material is to on one hand achieve the necessary material properties like electrical conductivity and on the other hand have sufficient flow characteristics which allows for processing by extrusion, compression molding, and injection molding.

This requirement can be fulfilled by an ideal combination of polymers and fillers, with different particle sizes and distributions.

As matrix polymers for the bipolar plate standard thermoplastic and technical polymers can be considered. For the developments at the Fraunhofer ICT polypropylene (PP) was used as a suitable polymer because of its material properties and also its low material price. With a service temperature of 100 °C PP is in the uncritical temperature range for the operating conditions in a PEMFC.

In order to increase the conductivity from polymers, a variety of conductive fillers like carbon black and graphite is available for use in plastics. Because of the structure of carbon black, which contains many pores with small mass, conductive paths in the polymer can be obtained with low critical concentration. Graphite as a filler has a laminated structure and similar electrical characteristics as carbon black.

- Highly conductive carbon black: specific surface 1,000–1,500 m^2/g, particle size 15–30 nm, electrical conductivity 10^1–10^2 S/cm
- Graphite: specific surface 5–15 m^2/g, particle size 1–20 μm, electrical conductivity 10^2–10^3 S/cm

The developments at Fraunhofer ICT focus on the combination of graphites and carbon black with different particle geometry and size distribution, to obtain as many contacts as possible between the conductive fillers, and thus produce conductive paths. The polymer serves in the material mixture as a binder to achieve a mechanically stable gas-tight system and to make a thermoplastic processing of the material compounds possible (Fig. 10).

By combination of electrically conductive fillers of different particle sizes and size distributions, thermoplastic processable polymer compounds with 80 mass

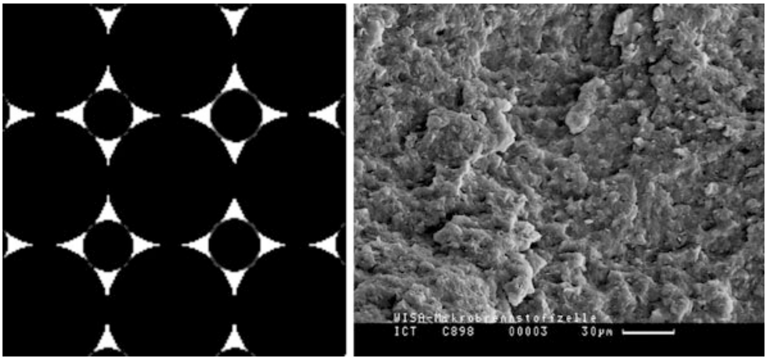


Fig. 10 Idealized arrangement of fillers (*left*), PP-graphite mixture (SEM) (*right*)

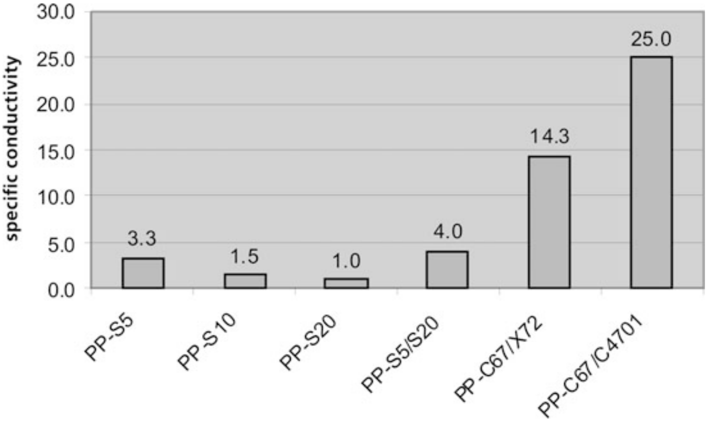


Fig. 11 Polymer compounds with 80% filler and a conductivity up to 25 S/cm

percent of filler and an electrical conductivity up to 25 S/cm have already been developed at Fraunhofer ICT (Fig. 11).

3.1.5 Production of Bipolar Plates from High-Filled Polymers

Regarding procedures for an economical mass production of bipolar plates, compression molding and injection molding are the favored production technologies. The application of these technologies is not unproblematic due to the high filling degrees and the resulting high viscosity of the polymer compounds. For the manufacturing of large bipolar plates for stationary or mobile systems a uniform filled mold and high processing pressures to reach a sufficient dimension accuracy are very important.

Small fuel cells for portable applications require bipolar plates with surface textures (flow-fields) with partial cross-sections <1.0 mm. This requires a tool technology that allows a complete filling of the mold and the transmission of the structures of the tool onto the bipolar plate material.

3.1.6 Compression Molding of Structured Bipolar Plates

Compression molding is a relatively simple and inexpensive procedure for the manufacture of moderate piece counts. For the production of bipolar plates compression molds with surface structured inserts were designed and manufactured. For the molding, the granulate can directly be molded in a heated mold under high pressure. Another way is the direct extrusion of a profile (semifinished material) into the structured mold, forming the plates from this plasticized polymer. In this variant the tool temperature is kept constant. With a multicavity-mold the cycle time can accordingly be shortened, and the output quantity of plates per cycle increased (Fig. 12).

3.1.7 Injection Molding of Structured Bipolar Plates

With extremely high piece counts injection molding is superior in polymer processing to all other manufacturing processes. The advantage of injection molding is the possibility for a fully automatic production of structured bipolar plates in one step.

To form fine structures and to support the filling stage of high viscosity materials, the use of a mold with a vertical flash face for injection compression molding is useful. Figure 13 shows a mold with a molding with two surface structured cavities for the production of bipolar plates over a gap filling the mold.

3.1.8 Fuel Cell Casing

Especially for smaller portable fuel cell systems the use of polymers for the casing exhibits numerous advantages. Using thermoplastic materials in combination with

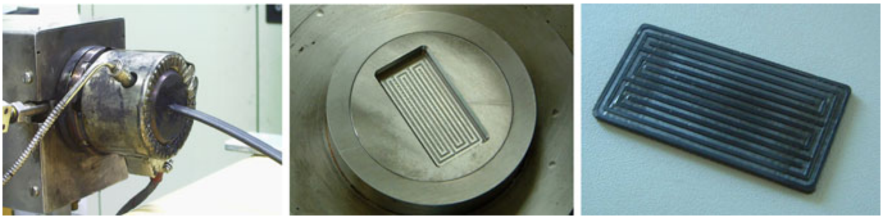


Fig. 12 Production of bipolar plates by extruding and compression molding

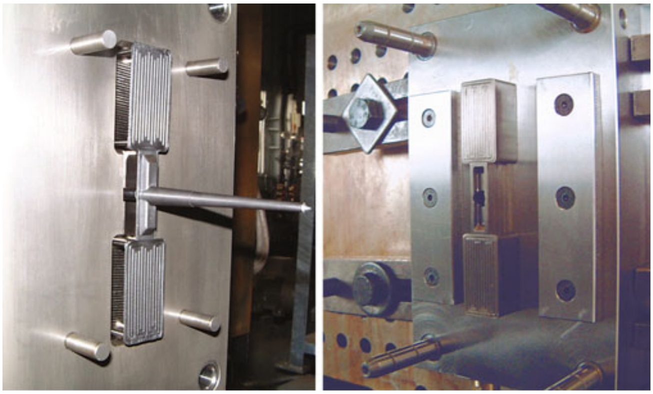


Fig. 13 Injection mold tool with two cavities for bipolar plate production

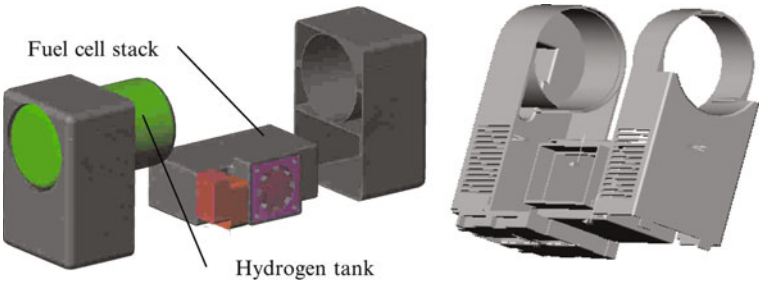


Fig. 14 Design of casings for a portable fuel cell

injection molding for the processing allows design liberty, economical processing of large numbers of items, and complete recycling after use (Fig. 14).

Furthermore, a functional integration of the various components of the fuel cell system into the casing is provided.

3.1.9 Conclusion

There is significant potential for the use of polymers in fuel cells. Polymer properties allow for an economical and ecological manufacturing of components such as bipolar plates and also peripheral parts. For bipolar plates the focus is on the achievement of high conductivity and improved heat resistance. For peripheral components like the casing, the use of polymers can contribute to new design possibilities and enable a high integration of functions (Table 9).

Table 9 Opportunities and risks of injection-molded polymer bipolar plates compared to metal plates

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages, open points)
Technical	– Freely moldable material, high molding accuracy – Chemical resistance – Low weight – Simplified, wear-resistant mold technology	– High viscosity of materials, difficult processing – Electrical conductivity and temperature stability: problem solved for PEM cells
Economic	– Automated mass production – Economical process, low mold wear – More economical materials (PP, graphite)	– Higher investment and mold costs – Suitable for high-count production series only
Ecological	– Materials can be remelted and recycled	
Social	– New processes (innovations) secure existing jobs and create new ones	

3.2 Passenger Car Door Sills Made by the Polyurethane RRIM Technique (Reinforced Reaction Injection Molding) Compared to Injection Molded PC/ABS Blend

The PUR-RRIM (Reinforced Reaction Injection Molding) technique, used in making external car parts, is particularly useful for small to medium piece counts, specifically in door sill sheathings up to 3 m in length. Demands for best surface quality (class A) in high piece counts, on the other hand, raise production expenditures for processes, the molding tool technique, trimming, surface precleaning, and positioning devices to very high levels.

Furthermore, the polymerization of polyol and isocyanate and the attendant cross-linking reaction in the mold are not suited to all processors. Maximum quality discipline must be contributed by all parties to the process. The chemical recycling process (alcoholysis) has been technically solved, but is not yet economically feasible. Online painting free of warpage is not possible with either the PUR-RRIM process or polycarbonate blend. Because PUR adheres well to metals, an internal mold release agent is used that tends to accumulate at the integral skin in the cross-linking process and achieves a sufficient mold release effect. It can then be removed by prewashing for the following painting step.

Table 10 summarizes the opportunities and risks of PUR-RRIM compared to PC/ABS.

PUR-RRIM has a lower viscosity than thermoplastics by a factor of approx. 100, so that the liquid PUR monomer fills complex geometrical mold cavities with reduced wall thicknesses and long flow paths.

For external parts with high or maximum surface quality requirements, these good flow properties are significant in terms of prevention of flow lines.

Table 10 Opportunities and risks of polyurethane RRIM compared to PC/ABS injection moldings

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Slight undercuts demoldable	– Lateral waste requires afterworking or expensive molds or machine technology (stable mold brackets)
	– Wall thickness up to 1.6 mm	– Class A surface difficult to realize due to pores
	– One external sprue, so there is no flow line	– High risk of warpage during storage and transport
	– Long flow paths (low viscosity)	
	– Good paint adhesion (PUR on PUR, if mold release agent has no contrary effect)	
	– High level of cold impact strength	
Economic	– Low level of mold-closing forces	– High afterworking requirements unless production and QM are excellent
	– High level of operational efficiency for customer – tolerates damage very well	– Complex, expensive transport containers
		– Expensive basic material
Environmental	– None	– Disadvantageous tendency, but depends on part geometry and concrete application (see Chapter 8, 3.1 Holistic balancing)
		– Recycling expensive
Social	– None	– Chemistry (isocyanate, amines) in production
		– Employees must be willing to participate in advanced training courses (critical process)

3.3 Foaming with Steam and Microwaves

The production of molded articles made of particle foams such as expanded polypropylene (EPP) or expanded polystyrene (EPS, also known under the brand name Styropore) is carried out by welding individual foam particles together into a formed part or molding. In the conventional steam chest molding process the source of energy used is steam, which heats and welds the foam particles in the mold into a formed part (Fig. 15).

Current development efforts aim to reduce or replace the less efficient energy source steam with microwaves as an alternative for energy-efficient welding of the foam particles. The use of high-frequency microwaves in combination with the use of microwave-active materials offers the possibility of constant and uniform energy transmission and welding, for example in large-volume structural components. Microwave technology also provides a means of partial heating of inactive materials by adding microwave-active materials in the welding zone heated by the waves and transferring the heat to the surrounding inactive material. As shown in Fig. 16,

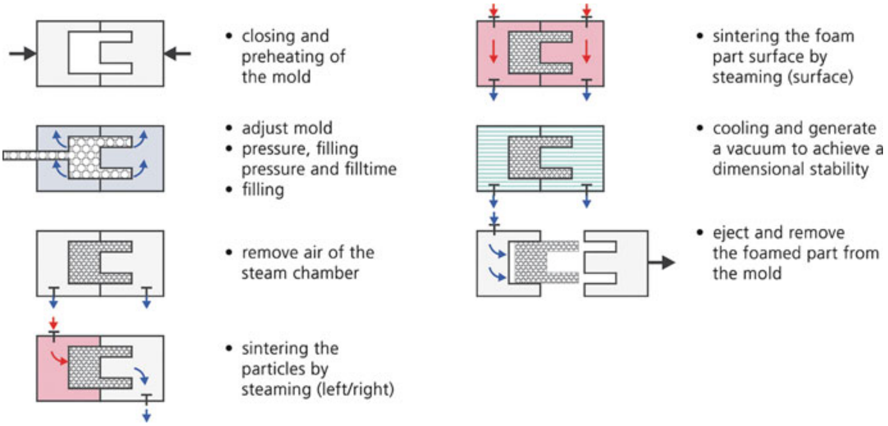


Fig. 15 Steam chest molding process for processing EPP

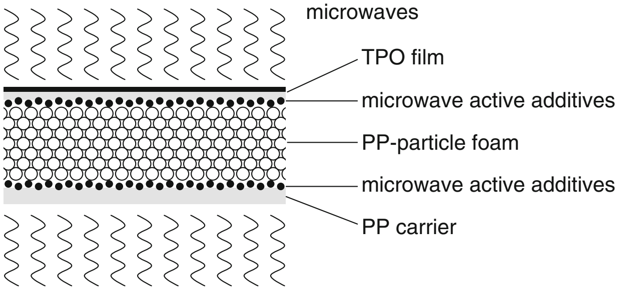


Fig. 16 Foam composite material made by means of microwave welding

an additional field of application for the use of microwaves in foam processing could be in welded integration of foamed parts with surface coatings.

Because of the high energy requirements of conventional welding of foam particles with hot steam, more energy-efficient processing methods are at a premium. Microwave processing is a potential solution for energy-efficient welding of foam particles. Application of this high-frequency radiation in connection with materials that absorb microwaves can afford a controlled application of energy. The foam particles can be coated with a microwave-absorbing material, resulting in a heating up of the particle surface and sintering of the individual particles in the microwave field without heating up the entire material or mold. One type of application would be even energy application to weld the particles in large parts. Another conceivable application would be partial heatup achieved by use of microwave-active materials, for example between a foam surface and a coating material to build material composites.

Figure 16 shows an example of realization of material composites by heating up the connection surfaces with microwaves. A composite material is built up from a

Table 11 Opportunities and risks in use of microwaves for foam processing

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages, open points)
Technical	– Low-pressure manufacturing feasible – Both volumetric and selective heating possible	– Areas with inhomogeneous melting/welding of foam – Molding technology still in development stage – Work to be done in the area of microwave engineering
Economic	– Enormous energy economization – Shorter process times – More compact systems technology without steam equipment	– Considerable investment in “high-tech equipment” necessary
Ecological	– Enormous energy economization	
Social	– New developments (innovations) secure existing jobs and create new ones	– Advanced employee training required!

carrier material, a foam corpus, and a coating of the same material. Between the contact surfaces to be heated up, a microwave-absorbing substance is applied and heated with microwave radiation to melt the contact surfaces, resulting in a continuous material connection in the composite (Table 11).

3.4 Handle for a Child’s Seat

Integral-molded children’s car seats feature handles for manual carrying. The entire seat construction is made of a thermoplastic material (PP or ABS). The opportunities and risks of standard plastic injection-molding vs. the gas injection technique (GIT) are explained using the example of the child’s seat handle.

Earlier handle versions for these children’s seats were U-shaped constructions with large numbers of ribs to lend them rigidity; the handles in the GIT injection moldings are closed tubes, Fig. 17.

This new injection molding process step, compared to the standard IM method first developed about 15 years ago (see Sects. 3.1 and 5.2.4 in Chapter “Processing (Primary Forming) of Plastics into Structural Components”), involves opportunities and risks as illustrated in Table 12, whereby the opportunities predominate by a long shot and the risks have now been practically nullified by a new processing method.

3.5 Comparison of GMT Process with LFT-D Process

Long fiber-reinforced thermoplastics are becoming increasingly important as materials, in the automotive sector in particular. The light construction aspect of

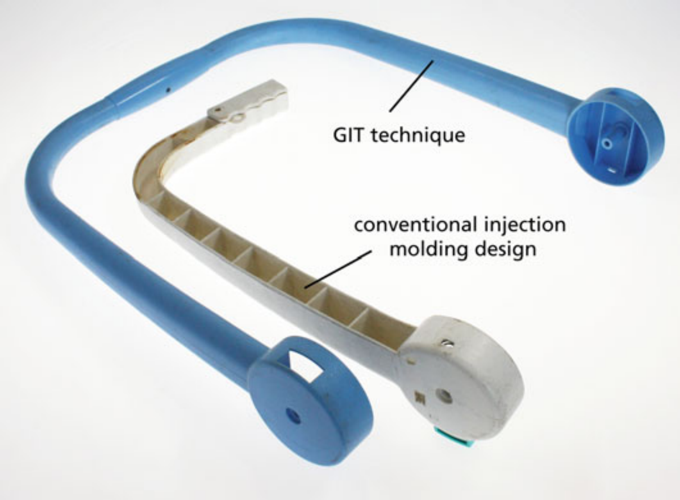


Fig. 17 Schematic presentation of two different injection-molded child's seat handles (Photo: Fraunhofer ICT)

Table 12 Opportunities and risks – child's seat handle manufactured using GIT IM process vs. standard injection molding

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages, open points)
Technical	– Greater rigidity (tube vs. U-profile) – No surface sink marks due to ribs – Simplified mold technology (no demolding draft, no sliders) – Simplified mold filling – Minimum warpage	For this example: – None
Economic	– Lower mold costs	– Supplementary investments required for injection molding machines (approx. 100 T€)
	– More economical material (PP as opposed to ABS)	– Patent situation critical
Environmental	– PP more environmentally compatible in the production phase than ABS; however, overall effect depends on part geometry and application phase (see Chapter 8, 3.1 Holistic balancing)	– Monomer-loaded gas in GIT process must be treated separately
Social	– Much better in terms of hygiene (soiling in ribbed open back side) – New process developments (innovations) secure existing jobs and create new ones	– Advanced employee training required!

this group of materials is the driving force behind this development to replace heavier metal parts. The molding process also offers the possibility of integrating functional elements – a considerable potential for production cost reduction.

This trend began at the end of the 1980s with the processing of glass mat-reinforced thermoplastics (GMT). Processing of GMT semifinished goods involves straightforward pressing. The properties of the resulting parts are, however, limited by the properties of the semifinished goods available on the market. Applications for GMT include parts such as dashboard frames, underbody moldings, front-end installation brackets, and others.

So-called direct processes (LFT-D) are increasingly becoming established in the market, i.e., processes in which the parts are molded directly from the components glass fibers, polymers and additives by the extrusion method, thus circumventing the semifinished production step entirely.

As to the choice of materials, the Dieffenbacher long fiber thermoplastic direct method with inline compounding of the matrix polymer (LFT-D-ILC) offers increased flexibility.

In this process, the matrix polymer is modified by additives to tailor properties such as long-term temperature resistance or mechanical endurance for specific applications. This means development of a material for each specific application, resulting in improved material properties as well as in cost savings with further consequences (Table 13) [12].

Figure 18 shows a number of applications of fiber composite materials in the automotive industry [11].

3.6 Inmold Assembly Vs. Individual Assembly

3.6.1 Hard–Hard Combinations

Multicomponent injection molding opens up a considerable potential for inmold assembly. At first, the emphasis in this technique was on plastic components of different color in fixed composites, for example vehicle tail lights.

At the beginning of the 1980s, the company Fickenscher in Selb developed a suitable molding technique in combination with plastics that were not mutually compatible (different melting temperatures, shrinkage potentials, or chemical incompatibility) to produce mobile parts that were solidly connected – a significant innovation. This made it possible, for instance, to mold toy figures in a single mold with movable arms and legs. The desire to produce toy figures with movable arms and legs that were permanently connected to the trunk of the figures so that small children could not possibly swallow the small parts was the initial impetus for this development. Additional applications include adjustable air vents in instrument panels and gearbox components.

Figure 19 shows the injection-molded, inmold-assembled planetary gear made of the material PBT/POM. In the mold, which is used in a two-component

Table 13 Risks and opportunities of parts made with the LFT-D process compared to parts made using the GMT process

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technological	– Reduced thermal load applied to matrix polymer – Less screw wear and greater throughput volume because the fibers are added to the melted matrix material – Considerable flexibility regarding individual material adaptations to determine parts properties. Fiber-mass proportions are possible within a range of 10–50%, comparable to GMT – Adaptation of fiber length to application. A length of 20–25 mm has proven favorable for many different applications – Very low level of mass deviations in plastic material – comparable to GMT – Very good flow properties due to good dye dispersion and compact plastic materials – Reduced extrusion pressure requirement due to adaptation of plastic material geometry to application	Producer of parts is responsible for the material and the process used
Economic	– Low material costs, semifinished goods production is rendered unnecessary – Flexibility for automation for production of so-called "tailored LFT" – combination of long and endless fibers – Short cycle times	Relatively high level of investment requires full equipment usage
Renewability	– Resource savings by means of in-house recycling of materials – Lower energy consumption due to elimination of a production step	
Social	– Preservation of high-tech jobs in Europe	

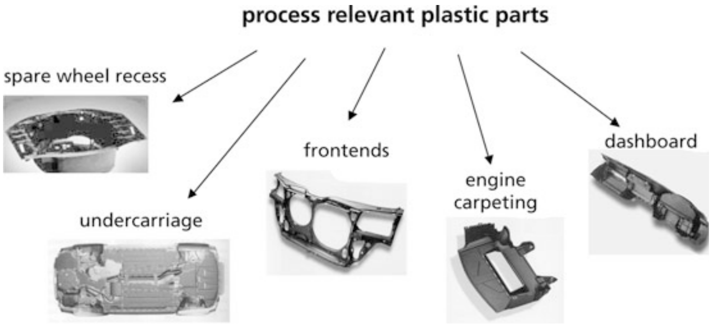


Fig. 18 Applications of fiber composites produced by means of the GMT or LFT-D process [11]

Fig. 19 Injection-molded inmold assembly of a planetary gear made of PBT/POM (Oechsler AG)

injection molding machine, the so-called sun gear of the planetary gear system is molded first. At a second mold station, the planetary gears are then molded out of a plastic material that is not adhesion-compatible to the sun gear. The planetary and sun gears are juxtaposed in the exact positions desired by means of internal movements inside the mold. In the third step, the cover plates and axes are insert-molded around the interlocking gear wheels. The gear wheels remain movable on the axes due to the molded part geometry and the shrinkage behavior of the components inserted last. All process steps are performed simultaneously at the individual molding stations. The planetary gear assembly is thus completely assembled when it is ejected from the mold and can be put to use right away.

This process principle can also be used to produce detachable connector elements in a single run (see Fig. 20).

By means of extreme cooling of the prior injection unit, inter-movable parts made of only one plastic type are feasible. Such monosystems are preferable from the point of view of recycling. Drawbacks, on the other hand, include the long cycle times required for cooling to low temperatures so as to prevent the contact sites with the second component from remelting. This single component overmolding process is used to make the out-of-mold hinge produced as in Fig. 21.

The two wings have the same injection volume so that a single hot runner distributes the melt from the injection cylinder between the two mold cavities. The prior injection unit and the finished part are produced at the same time, whereby

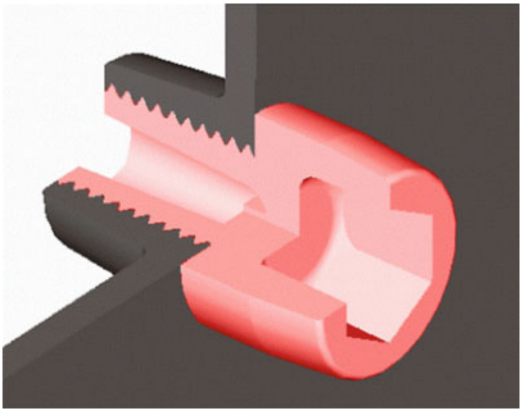


Fig. 20 Detachable threaded connection in 2C process

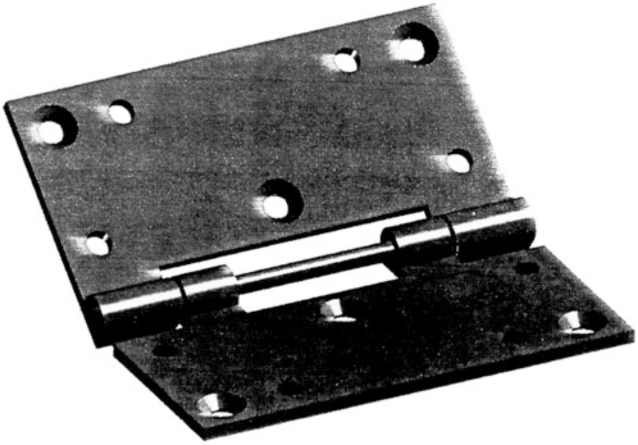


Fig. 21 Out-of-mold hinge made of PA (Image: Ferromatik)

transport of the prior injection unit into the second cavity is realized according to the rotating mold principle.

3.6.2 Hard–Soft Combinations

In addition to hard–hard combinations, hard–soft combinations hold a special position in multiple-component engineering. Soft, sealant, insulating, or damping TPEs are injected over a base corpus of hard thermoplastic. Familiar parts on the market made with this process include complex plastic housings with integrated seals (pump casings) and soft-touch grips (toothbrushes, razors, electrical appliances).

Another challenge in terms of molding and process technique is presented by hard–soft composites pairing thermoplastics with elastomers. Elastomers are superior to the thermoplastics when it comes to dynamic sealing qualities, temperature resistance, and useful life. The injection molds used in this process are cooled in the area of the thermoplastic cavity, whereas the cavities into which the elastomer is injected have to be kept within the cross-linking temperature range of 180–200°C.

The advantages of the process derive from the reduced assembly expenditures (no seal insertion, no joining of soft grips). Also, the components are solidly attached to one another, so that for instance the seal is less likely to be incorrectly positioned for the following production steps.

Less advantageous are the increased expenditures for molds, investments costs for a multiple-component system, highly trained machine operators, and the risk of limitation of control potentials that would otherwise be available in the form of interference in individual production steps if the value added were not produced to such a large extent in a single combined process step.

The opportunities and risks are summarized in Table 14.

Table 14 Opportunities and risks of inmold assembly

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Reduced number of working steps	– Complex process requiring good know-how regarding materials, mold and machine technologies
	– Exact positioning of joining units established by mold	– Matching of the material combinations requires a thorough knowledge of the materials
	– Minimized logistic planning (purchasing, storage, and handling of the individual components	– Complex and demanding molding techniques and technology
	– High level of functional integration	– Shrinkage can lead to tolerance problems
	– Light construction potential	– Increased maintenance requirements
Economic	– Reduced production time	– Investment costs for multiple-component system
		– Concentration of value added in a single working step
		– High repair costs for undetachable connections
		– Trained staff must be available
Environmental	– Monocomposites are readily recyclable	– Dismantling more difficult with undetachable connections, so that different materials may not be separable
	– No additional adhesives required	
Social	– Competitive advantage with low-cost production – ensures preservation of operational locations	– Lack of skilled labor

3.7 Microwaves in Extrusion of Plastics

Extrusion is a traditional process in plastics processing, one that is characterized by a wide range of product types, continuous processes, and a high level of economy. Extrusion of hard PVC is a special case of this method, since processing of this material type usually requires a special extruder construction, the so-called counter-rotating twin-screw extruder. This type of extruder is characterized by a chamber-like conveyance mode and a narrow spectrum of residence times.

Since plastics are, generally speaking, poor conductors of heat, most of the plastification energy required in extrusion processes is transferred by means of mechanical energy dissipation. Since hard PVC mixtures are normally highly viscous and also very limited as to temperature stability, screw rpm levels for plastification are very low in order to avoid temperature peaks in particular. The energy transfer at low rpm results in high torque levels accordingly, which cause considerable wear and narrow the process window in a pronounced manner, especially when processing mixtures containing high proportions of mineral fillers.

Another drawback in this connection is the low level of flexibility of these processing aggregates. Changes in material formula, particularly in the lubricant balance, frequently result in pronounced changes in the plastification behavior of the PVC melt, reduced production volumes, or quality problems. Since cylinder heating affords only a narrow range of influence, either the entire system must be substituted, or at the very least the plastification screw will have to be adapted accordingly.

Microwaves offer an interesting solution to these process engineering problems and thus to improvement of the economy and flexibility of the extrusion technique. Transfer of energy with microwaves can for the most part be controlled independently of the mechanical and thermal energy supply situation inside the extruder, so that they can not only potentially increase the total amount of transferable energy but also render process control much more flexible.

The number of different PVC mixtures used in PVC extrusion is very large, geared to satisfaction of varying customer requirements. The attendant processing problems can be managed effectively by making the energy supply to the extruder more flexible.

The extrusion of PVC is a field well adapted to use of microwave technology. Use of the chemically polar basic polymer means that microwave absorption within the polymer is possible. Nonpolar polyolefins, on the other hand, cannot be heated directly by microwaves. Since, however, the counter-rotating twin-screw extruders used in PVC extrusion process practically nothing besides PVC, use of the microwave does not amount to a loss of flexibility as far as the range of materials an aggregate is designed to handle.

The design of the plastification cylinder must be altered significantly in the adaptation process to allow the microwave energy to penetrate through the cylinder jacket from the outside and reach the product to be heated. Microwave-transparent windows must be installed on the cylinder that can withstand the heavy mechanical loads the extruder is exposed to and still provide for a high level of microwave transmission efficiency. Microwave-transparent materials suitable for use in extruders include plastic, glass, and ceramic materials. Of the three, only ceramics can withstand the high temperatures and mechanical loads in long-term use. Just how the ceramic windows are to be built into the cylinder wall presents a major engineering challenge, since the different heat expansion coefficients of steel and ceramic must be taken into account along with the low tensile strength of the ceramic materials.

Basic studies on microwave absorption levels in PVC and the additives used for PVC processing have demonstrated that different mixture components and the resulting mixtures certainly do absorb microwaves at different levels of efficiency. Among processable mixtures, however, the differences in absorption behavior are so small that this factor is not likely to affect the processability of the material in a microwave-supported extrusion process.

Initial tests of microwave-supported plastification run in a test kneader, the kneading chamber of which has the same geometry as the counter-rotating twin-screw extruder, showed very good microwave transmission to the PVC to be plasticized. These tests also demonstrated that plastification is possible even at a clearly reduced kneading chamber temperature and that this clearly reduces the plastification time.

Table 15 summarizes the opportunities and risks of the use of microwaves in plastic extrusion.

Table 15 Opportunities and risks of microwave use in plastic extrusion

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Greater output due to increased level of transmissible energy – Reduced wear due to lower proportion of mechanical energy – Greater process flexibility due to third, independently controlled, energy source – More rapid process control with no-delay control of microwave energy supply	– Narrowed selection of processable basic polymers. Nonpolar plastics cannot be heated with microwaves – Not yet known how much energy can be transmitted by microwaves – Microwave-transparent inserts required in extruder
Economic	– Lower energy costs – More economical – Fewer mischarges – Shorter runup times – Higher product quality	– Higher investment costs – Higher maintenance costs – Higher training requirements
Environmental	– Lower level of energy consumption – Smaller mischarges and fewer rejects – Lower heat radiation load at workplace	– Health risk of microwave radiation leakage
Social	– Preservation and creation of jobs – Construction of high-tech facilities	

3.8 Thermoforming Vs. Injection Molding: Drinking Cups

See Chapter "Secondary Forming of Plastics Structural Components: Thermoforming".

Thermoforming has, in addition to production of technical parts, a large application field in packaging articles like trays, drinking cups and yogurt cups, in which areas this processing technology presents the greatest challenge to conventional injection molding. The thermoforming process is completely different from what is generally familiar from injection molding and toolmaking. Big differences in process control, temperature control, ejection, and stacking of the produced parts make much of the experience gained from injection molding obsolete [10]. The opportunities and risks are discussed based on a simple drinking cup made of plastic material.

First of all the process scheme with all thermoforming steps is shown in Fig. 1 in Chapter "Secondary Forming of Plastics Structural Components: Thermoforming." In most cases, the provision of the sheet material, and demolding and stacking in particular, constitute additional production steps that require an experienced hand. The forming step is only a small part of the whole production chain.

Generally speaking, thermoforming is an open process with one forming mold half, whereas injection molding is a closed process with two mold elements that provide the form, actively shape the plastic and close to mold it [6]. The open thermoforming process requires considerable caution, especially the polymer processing temperature. With amorphous polymers, the forming range is above the glass transition temperature and a generous temperature window for forming is possible. With semicrystalline materials the forming window is narrow, usually starting above the softening point and remaining within the melting range [4].

From the production side, the number of cycles in thermoforming is much higher and the number of cavities per mold almost three times higher due to the low closing forces of the mold. Usually a very thin-walled product with about 0.1–0.2 mm can be achieved easily and due to the high stretched side wall areas, the straightened molecules lead to a very high stiffness. Thin-wall injection molding is still a problem and to get enough stiffness, the wall thickness needs to be much higher. In thermoforming, less material is needed for some stiffness.

In the production stage, ejection and stacking are easy in thermoforming, whereas injection molding needs robots to get the cups. Material waste levels are higher in thermoforming, where 30 % of the raw material is lost. Running the machines inline makes it possible to regrind the waste material and feed it back into the extruder. Seventy percent of the part costs in thermoforming are material costs, so that saving material (regrinding, thin walls, etc.) leads directly to lower part prices. Higher machine start-up times in thermoforming due to temperature heating profiles do cost more time and energy in comparison to the mostly successful second shot in injection molding.

Multilayer materials specially developed for longer "best before" dates and better barrier properties can be processed by means of thermoforming in one

Fig. 22 Cups produced by forming and by injection molding

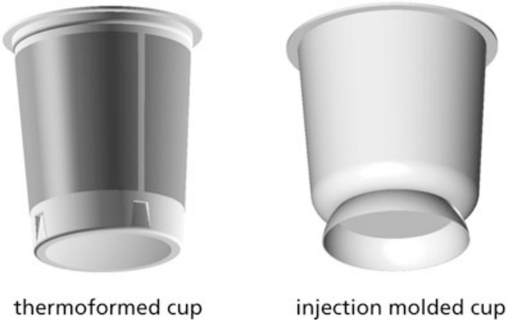


Table 16 Opportunities and risks of a thermoformed cup vs. an injection molded cup

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Greater stiffness with thinner walls – Higher output rate	– Less transparency – Design limitations – Open process
Economic	– Lower tooling costs – Part price dominated by material cost – Longer start-up phase	– Higher fixed costs – Short start-up phase
Environmental	– Less material for same stiffness – Lower forming temperature – Inline use of waste material	– More waste material at start-up – Higher energy consumption
Social	– Process new and unfamiliar – Empirical experience – Niche market	– No skilled personnel available

forming step. The original multilayer structure remains, even in constructions with thinner walls.

In terms of design, injection molded cups make for easier and more flexible designing. Especially undercuts, and so-called cup designs, are not possible with thermoforming. Customers sometimes prefer the transparency of a molded PET or PS cup or the higher form definition.

In injection molding, the number of cavities is normally limited to about 48 cups per mold, whereas in thermoforming up to 148 cavities are standard. Therefore, the closing force is the process criterion, even for large products. Figure 22 shows the main design differences in the two cups.

The opportunities and risks are summarized in Table 16.

3.9 Experience with Compounding of Halogen-Free Flameproofing Agents

See Section “Fire Protection Agents” in Chapter “Properties of Plastics in Structural Components.”

Halogen-free flameproofing agents have the following *advantages* over halogenated systems [8]:

- Much lower levels of smoke gas development in a fire
- Better electrical values, e.g., creep resistance
- Less corrosive
- Lower compound material density in many cases
- Positive market image
- Much better environmental compatibility in some cases, e.g., regarding ozone degradation potential

However, there are also *disadvantages* to halogen-free vs. halogenated systems [8]:

- Charge volume usually has to be increased
- Price in some cases still high
- Few universally usable systems available to date

The following halogen-free flameproofing agents are currently important [8]:

- Phosphoric flameproofing agents
  - Organic phosphorus compounds
  - Ammonium polyphosphate
  - Red phosphorus
- Nitrogenated flameproofing agents
  - Melamine cyanurate
  - Melamine polyphosphate
- Inorganic flameproofing agents
  - $Al(OH)_3$
  - $Mg(OH)_2$
  - Phyllosilicates

How do the different flameproofing agents work?

Halogenated systems in the gas phase act by interrupting the radical chain mechanism that sustains the flame, whereby they are highly efficient. The different halogen-free systems, on the other hand, work like this:

- The site of action of phosphoric flameproofing agents is the solid phase. They withdraw water/oxygen from the matrix and form a hard layer, e.g., of polyphosphates.
- Nitrogenated flameproofing agents (melamine derivate) work by a mechanism combining energy withdrawal, formation of flame-retardant gasses (e.g., NH_3) and a nonflammable protective layer.
- Intumescent systems (APP) have a similar mode of action in that they also form flame-retardant gasses (e.g., NH_3, H_2O) and a nonflammable, expandable protective layer.
- Metal hydroxides ($Al(OH)_3$, $Mg(OH)_2$) function by means of endothermic water cleavage, resulting in an inert metal oxide and water.

Table 17 provides information on use of halogen-free flameproofing agents in thermoplastics [8].

Some limitations must be observed when compounding flameproofed plastics – whether halogenated or halogen-free:

- All flameproofing agents are sensitive to temperature and shearing forces and therefore influence processing.
- The degrees of filling often required require special mixing techniques. For example, a special screw design is required for compounding.
- Special safety regulations apply to handling of flameproofing agents, as is the case with all hazardous or aquatoxic substances.

Table 18 compares the opportunities and risks of halogenated and halogen-free flameproofing agents in thermoplastics.

Table 17 Use of halogen-free flameproofing agents in thermoplastics [8]

	PA	PP	PE	EVA	PS	ABS	PBT	PET	PU
P_{red}	X								X
APP		X							
Organic P compounds					X	X	X		
Melamine cyanurate	X								
Melamine polyphosphate	X								
Melamine									X
$Al(OH)_3$			X	X					X
$Mg(OH)_2$	X	X							X
Phyllosilicates				X					

Table 18 Opportunities and risks of halogen-free, as compared to halogenated, flameproofing agents

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Less smoke gas is produced in a fire – Material properties often better – Lighter in many cases – Less corrosive – Processing in most cases unproblematic	– Higher degrees of filling required (less effective at same volume) – Systems are less universal – Handling of red phosphorus critical
Economic	– Restrictive legal situation	– More expensive, therefore not yet competitive in some applications
Environmental	– Potentially more environmentally compatible (reduced ozone degradation potential), but this depends on the specific flameproofing agents and their concrete applications	– Somewhat less efficient than halogenated flameproofing agents, which is why larger amounts are required – necessary to analyze overall effects throughout product life (incl. utilization and disposal; see Chapter 8, 3.1 Holistic balancing)
Social	– Opportunities in worldwide market due to leading-edge innovation – Consumers feel better about products	

3.10 Nanocomposites

3.10.1 Definition of Nanomaterials

In the recent years, nanosized materials have attained a certain attention. The reason for this was the observation that the properties of many materials change dramatically compared to macroscopic bulk materials when they exist as particles in the dimension of several nanometers, which corresponds to an amount of a few atoms. For instance, the color of gold changes to red when it exists as a powder whose particles have a diameter of less than 100 nm. At even smaller particle sizes, the visible light does not interact with the particles any more – they are becoming invisible. In order to be a nanostructured material, at least one dimension of the structure must be smaller than 100 nm.

Fillers and reinforcements for polymeric materials are widely in use in order to optimize the properties of polymers in different respects, one of which are the mechanical properties. The stiffness and strength of polymers are commonly improved upon by the use of glass fibers. This improvement is based on the adhesion of the polymer matrix to the reinforcement in a way that external loads acting on the material can be transferred from the matrix to the reinforcing material. For this purpose, a high surface to volume fraction of the reinforcing materials is mandatory. Nanoparticles fulfill this prerequisite to a significant extent and so exhibit a high potential in view of the improvement of the mechanical properties of polymers.

Other very promising nanosized fillers have been developed, of which carbon nanotubes are amongst the most promising ones due to their high stiffness and strength as well as their outstanding electrical conductivity.

Against this background, attempts were made to improve the properties of produced polymeric composite materials by use of the new nanosized materials.

The use of nanoparticles is not free of risks regarding human health and impact on the environment. Nanosized particles are able to penetrate through the skin and can be accumulated in different organs of the human body and of other creatures. Research is continuing and has not yet provided a definitive conclusion to this matter. It can be regarded as common sense, that the danger arising from nanoparticles is directly coupled to their appearance as free particles. As soon as they are incorporated into a composite their hazardous potential is negated as they can no longer move freely. So safety issues are most important during the production process of the particles and the composites.

3.10.2 Nanostructured Fillers and their Functionalities

Nanostructured filler materials can originate from natural sources like clays or silicates and are mainly used as reinforcements for polymers leading to a much higher stiffness of the compound than through use of a traditional reinforcement material such as glass fibers if equal filler contents are applied.

Artificial nanostructured fillers are carbon nanofibers or nanotubes (CNT) and carbon black, which can act as reinforcements and which lead to an improved electrical conductivity of the compound. Nanostructured silica can be used as an antistick additive and nanosized silver particles exhibit an antibacterial effect when added to polymeric compounds.

3.10.3 Production of Nanocomposites

For the production of polymeric nanocomposites, in many cases a pretreatment and a functionalization of the nanomaterials are necessary [13] in order to allow a break up of agglomerates of nanoparticles and to gain adhesion to the matrix and distinct improvement of mechanical properties. This is achieved through various means such as plasma treatment in the presence of certain gasses, which is a well known and widely used process. Various treatments in the liquid phase are also known and applied [7].

For the processing of thermoplastic polymeric nanocomposites, standard equipment for the preparation of high viscosity thermoplastic compounds can be used: the co-rotating twin-screw extruder with its flexible processing unit which allows for controlled dispersing shear and elongational flow. In the case of low viscosity components for the production of thermoset compounds, common mixing and dispersion techniques can be used.

However, in both cases – thermoplastics and thermosets – the equipment and the processes need to be adapted to the nanosized fillers. The most crucial point in the production of polymer–nanofiller dispersions is the proper separation of the CNTs from each other, the deagglomeration of agglomerates, and their coupling to the polymeric matrix material. For this purpose, dispersion aids, stabilizers, and compatibilizers, used for other filler particles, need to be adapted in many cases specifically for nanosized fillers with their different surface treatments for the different matrix materials. This is a very complicated issue, and makes a close co-operation between the different scientific disciplines necessary [1].

The high potential of the nanostructured fillers for the achievement of certain functionalities or certain mechanical properties in polymeric composites can often not be fully exploited today. Nanocomposites exhibit improvements in their properties but in most cases they still remain behind expectations: their strength and stiffness or their electrical conductivity are much lower than the theoretically calculated values. The reason for this often lies in the nonoptimized compounding of the nanoparticles and a reagglomeration during further processing steps of the compound on the way to forming a part, for example injection molding (Table 19).

Table 19 Opportunities and risks of nanocomposites

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	Huge potential for new functionalities	Little experience with nanocomposites
Economical	Large predicted rise of turnover	Investments
Environmental	Improved materials are available	There is little known about the environmental impact of nanoparticles
Social	New and secured jobs	There is little known about the effect of nanoparticles on health

4 Opportunities and Risks of Structural Component Design and Mold Engineering

The principles that apply to material selection and process engineering, i.e., those of "simultaneous engineering," apply most particularly to structural component design and mold engineering.

A design engineer must be thoroughly familiar with the material plastic, both reinforced and unreinforced, in all of its possible variants and nuances, must be well-versed in the use of modern aids such as databases and must know when to consult external experts. Decades of practice are needed to dimension molding designs so as to accommodate all material parameters.

Professional schools and universities bear a large burden of responsibility. In Germany, the universities still concentrate mainly on metals, either ignoring plastics/polymers entirely in basic studies or having metal specialists cover them as themes of secondary importance. In view of the enormous worldwide increase in the technical, economic and environmental significance of plastics, this is an irresponsible attitude and a hindrance to the healthy development of national economies.

In this section as well, examples provide insights into the opportunities and risks involved in structural component design and mold engineering.

4.1 Inmold-Assembled Dashboard

Modern dashboard constructions are based on a supporting structure made of sheet metal, a plastic–metal hybrid, fiber-reinforced thermoplastics (GMT [PP]) or duroplastics (SMC [UP], SRIM [PUR]).

The middle layer usually consists of polyurethane foam covered by a film (ABS, PVC, PUR). Normally, three different molds are required to manufacture such a three-part dashboard. Material separation to obtain unmixed wastes at the end of the dashboard product cycle is not economically feasible.

Table 20 Opportunities and risks of an inmold-assembled monoplastic car dashboard vs. the standard modern three-part dashboard

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages, open points)
Technical	– See Fig. 23	– Supporting structure: problem solved
	– Supporting structure: LFT-D-PP technique	– Foaming PP particles with MW – problem solved
	– Replacement of upper mold half	– PP integral skin foam still a long way from satisfying current standards
	– Incorporation of foamable PP particles via extruder	– Some problems solved, but the entire vision, with all the risks attendant upon an invention, requires some additional problem-solving
	– Close mold, foam with microwaves	– Foaming PP particles with MW – problem solved
	– Integral PP skin foam forms on upper side of mold	
	– Instruments and electronic components are inserted and surrounded by foam	
	– Dashboard falls assembled out of mold	
Economic	– Large cost reduction potential	– Much time and money will still have to be invested in further developments
Environmental	– Clear environmental advantages in processing and recycling (confirmed by holistic balancing)	– Unknown
Social	– If successful: major innovations (creating new jobs)	– If not successful: poor resource utilization

Monoplastic dashboards ejected fully assembled from one and a half mold sets (inmold-assembled) represent a vision involving both opportunities and risks, Table 20.

Figure 23 shows the basic principle of the product vision under discussion here.

An LFT-D technique is applied in a compression mold with glass mat reinforcement to produce the supporting structure for the dashboard in large series, i.e., with cycle times of approx. 30 s. This is in keeping with the state of the art.

The compression-molded dashboard supporting structure remains in the lower half of the mold. The upper half is replaced with a new mold half containing instruments and electronic components as inserts. An extruder fills PP granulate treated with inactivated blowing agent into the opened mold. The mold closes, whereupon inductively coupled microwaves (2.45 GHz) activate the blowing agent so that the PP beads are foamed and sintered. The foam front arriving at the upper mold half forms a dense integral PP skin foam. The mold opens and the assembled dashboard structure can be taken out.

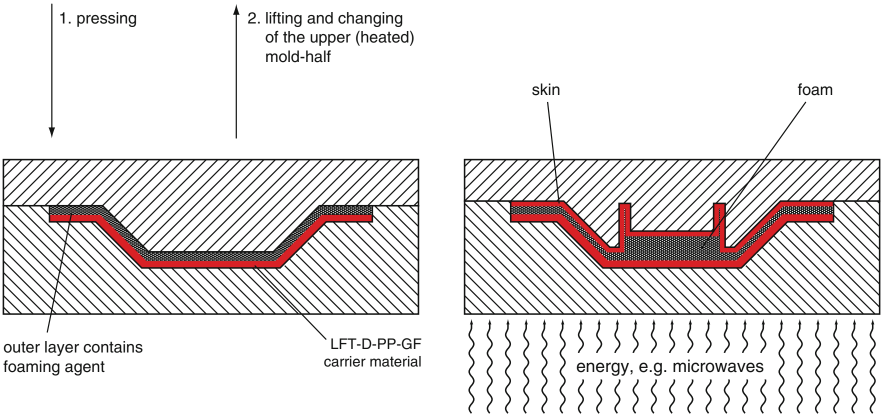


Fig. 23 Inmold-assembled monoplastic dashboard – steps involved in production

4.2 Location of Flow Line Influences Part Life, For Example in a Ventilator Vane

In the process of injection molding of plastics, so-called flow lines are produced where melt flows come together during the mold-filling procedure, e.g., behind breaches. If the viscosity of the melt fronts rises due to cooling on long flow paths, a mechanical weak point results where the melt flows come together behind the breach which may lead to early failure of the part in the utilization period.

When simulating the mold-filling process, the designer of a plastic part must therefore select the feed points such that the flow lines are not within regions of maximum stress load.

Figure 24 illustrates the main opportunities (correct) and risks (false) involved in designing a ventilator vane in terms of flow line location.

4.3 Injection Molding of a Plastic Toothed Gear: Type and Position of Sprue

Toothed gears for small and medium-sized watch motions and gears for automobiles and toys, in a few cases even for vehicle gears, are injection-molded or pressed out of thermoplastics and occasionally duroplastics as well. Dimensional accuracy is the key to production quality, and it must be sustained throughout the useful life of the part.

The sprue type and its position in the part mold are important factors besides the processing conditions (process parameters) and material selection. Memory

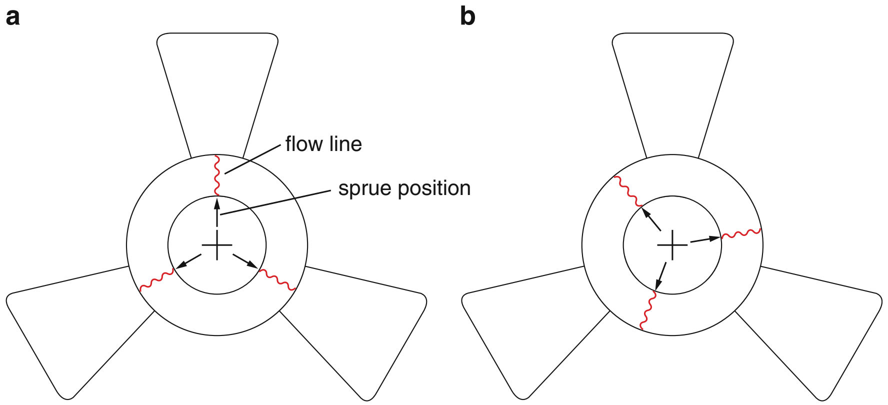


Fig. 24 Sprue position results in flow line at midth of vane (a) / tension peak of binding weld lies between vanes (b) as a weak point

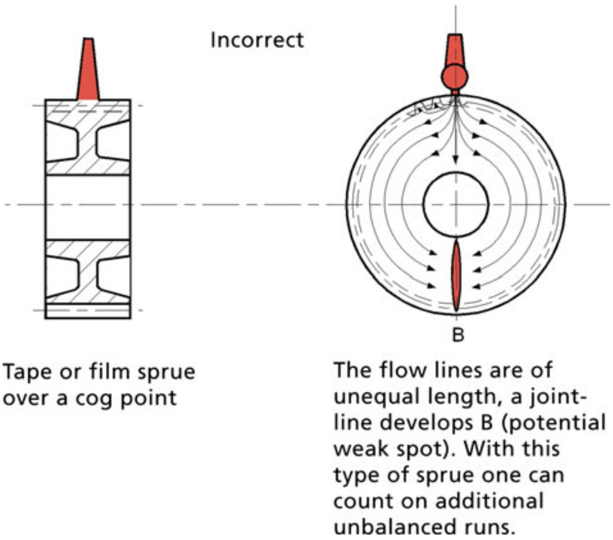


Fig. 25 Film or pin gate for a plastic toothed wheel [3] (incorrect resp. reduced properties)

effect (a potential factor at higher application temperatures), shrinkage (due to postcrystallization, postcross-linking, or drying) and warpage must be prevented.

In injection molding of semicrystalline thermoplastics, for example polyamide, polyoxymethylene, ultrahigh molecular polyethylene (very high melt viscosity), linear polyesters (PET, PBT), local variations in molecular orientation result in dimensional variations in the part (warpage, memory effect), especially if the toothed gear is exposed to a thermal stress load.

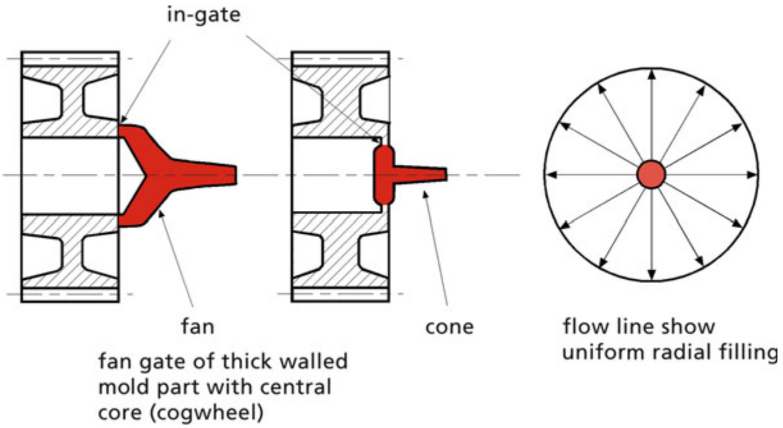


Fig. 26 Cone or sprue gate for a plastic toothed wheel [3] (correct; optimized properties)

For this reason, a pin gate, as shown schematically in Fig. 25 with the melt flow direction for filling drawn in, is useless. Besides, this would also mean an additional weak point at the resulting flow line.

A cone or sprue gate, Fig. 26, on the other hand, results in a radially balanced, inside-to-outside filling process with point-symmetric orientations.

Dimensional constancy (no warpage) is ensured. Local differences in degree of crystallization can be avoided by means of a balanced and controlled process (higher mold temperature means longer cooling, and cycle, time) and temperature constancy of all components through which melt flows. This also reduces the effect of local variations in postcrystallization and any resulting inhomogeneous internal stresses.

Table 21 lists the opportunities and risks involved in making a toothed wheel out of plastic compared with a toothed wheel made of metal.

4.4 Thin-Wall Injection Molding

4.4.1 Introduction

The production of thin-walled parts is one of the major challenges of the plastic-processing industry today. Thin-wall applications are found mainly in packaging, casings and housings, but also in technical devices and articles (medical, optical, electronic, and telecommunications technologies).

Reasons for reducing wall thickness can vary. In packaging, the main reason is to save on costs: The material represents a greater portion of the production costs and waste disposal fees proportional to the mass of material must also be paid. In addition, the cooling time is also reduced by a considerable margin,

Table 21 Opportunities and risks involved in making a toothed wheel out of plastic compared with a toothed wheel made of metal

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Minimal sliding friction (dry run) – Resistant to water and many mediums – Wear-resistant – High level of viscosity – In many cases sufficient thermal form stability – In many cases sufficient strength – Damping capacity (running smoothness) – Low forces of gravity	– Strength sometimes insufficient – Not heat resistant in some cases – Product life too short under maximum loads (combination of steel or aluminum with plastics as an alternative) – Lower stress load reserves
Economic	– Low-cost production, even in large series and with complex geometries – Integration of function e.g., sensory function	– High repair costs if gear fails due to tooth breakage
Environmental	– Lightweight constructions save energy in mobile applications	– Not as readily recyclable as the metal variant; overall environmental impact must be analyzed for the specific application – False material selection (plastic) results in follow-up damage and shorter product life
Social	– Plastic toothed wheels are high-tech products, i.e., they embody an on-site advantage in terms of know-how	– Production transfers to other countries if no innovations are forthcoming

since it is proportional to the square of the wall thickness. In technical articles such as cell phones and laptops, the factors mass reduction and increasing miniaturization are even more important than cost savings. Reduction of wall thickness makes it possible to reduce device size or make more room for better electronic components.

4.4.2 What is Thin-Wall Technology?

Generally speaking, thin-walled parts can be characterized by the ratio between the flow path and wall thickness and the mean wall thickness. Thin-walled parts begin at a flow path:wall thickness ratio of >100 and at a wall thickness of <1 mm.

The production of thin-walled moldings is nothing new. Cups made of PS or PP with wall thicknesses of 0.5–0.6 mm were being injection-molded over

20 years ago. The materials used were relatively free-flowing, with injection rates of approx. 300 mm/s. In areas other than cup production, present-day thin-wall injection moldings are not made of free-flowing PS and PP, but rather mainly of ABS, ABS-PC blends, PC, and LCP (liquid crystalline polymers). With the exception of LCP, the viscosity of these materials is much higher than in the "cup types." Nonetheless, wall thicknesses of 0.6 mm or even less are achieved under certain conditions regarding the form (flat-ribbed), the material (low viscosity, thermal stability), the process (thermally homogeneous, high injection rate), and the mold (rigidity, sprue, cooling system). In thin-walled injection molding as well, the injection filling process is governed solely by the physical laws of rheology. The essential parameters are distribution of pressure, temperature, viscosity, and rate of flow. Therefore, successful production is based mainly on consistent application of simulation techniques as well as on quality material and process engineering.

4.4.3 Materials

Nearly all raw material producers offer, in addition to the standard injection molding types, molding compounds with a very low viscosity due to their molar mass. It must be remembered, however, that these injection molding types also, in addition to their good flow properties, meet mechanical criteria such as rigidity, impact strength, extensibility as well chemical, thermal, and electrical specifications. Testing was done in the past on reduction of viscosity due to microwave and shear heating at various research institutions. The results have been reflected mainly in the success of duroplastic and elastomer processing. The introduction of overcritical fluids also reduces the viscosity of the molding compound, albeit with the drawback of a noncompact molding.

4.4.4 Process Engineering

The flow paths must not be excessively long and the required injection rates are 1,000 mm/s and more. Since the parts involved are very thin, and therefore very light, the injection stroke and time in thin-wall injection molding are very low accordingly. Typical injection times are less than $t_E = 0.1$ s, whereby it is observed that the pressure requirement increases disproportionately with decreasing wall thickness. Because of the intrinsically viscous behavior of plastic melts, increasing the injection rates results in a subproportionate increase in the pressure requirement. Making the process more difficult, and thereby increasing the pressure, is the fact that the effective wall thickness for melt flow, and the derivative flow cross-section, are drastically reduced due to the rapidly transforming boundary layer. No wonder that in some cases injection pressure levels of $p_E = 3{,}000$ bar are required to produce some thin-walled articles, with these levels being reached a few hundredths of a second after the injection stroke begins.

4.4.5 Machine Technology

To master the problems described above, machine manufacturers developed new design concepts accordingly. Production of thin-walled articles makes considerable demands with exacting specifications on the entire injection molding machine. Injection molding machinery for this product type must be highly robust, suitable for fast cycle times and high injection parameters and guarantee optimized part quality. The required measures are reflected in the entire machine, beginning with plastification and including the drive, clamping unit, and mechanical design. Highly satisfactory plastification results are obtained with screws designed for processing of materials that are sensitive to shear stress such as blends based on PC+ABS. The clamping unit plates must also be stable enough to withstand the high injection pressures of up to $p_{\mathrm{E}} = 3{,}000$ bar as required for filling.

4.4.6 Mold Technology

In addition to the rheological design of the mold, including optimized sprue technology (e.g., also cascade technology), the high injection pressures make it necessary to pay particular attention to the strength of the mold. Careful control of mold tempering and cooling is also necessary, for which reason thin-walled and microstructure injection molding in particular require innovative technologies such as contoured cooling channels, variothermal tempering, and impulse cooling. The ejection system is also more critical for thin-walled parts. Because of the ribbing, usually employed to render structures more rigid, such parts are more difficult to demold or show deformities due to their thin walls. Space restrictions often afford room for thin ejector pins only, whereby molding adhesion is relatively pronounced due to the high injection and postmolding pressure levels.

4.4.7 Special Processes

Currently, multiple-component, internal gas-assisted and decorative processes are being used more and more frequently in combination with thin-wall techniques. A good example of this is the trend to highly individualized cell phone designs. Decorative processes such as inmold decoration or insertion of preformed, printed foils makes variable coloration of even small run volumes possible. The internal gas-assisted method is used for example to reduce the mass of thick-walled parts and to avoid sink marks; minimization of warpage is thus a primary requirement for thin-walled parts. A wide variety of functions can be realized by means of the multiple-component technique, including seals, napped surfaces, improved antislip properties and functional elements, some of which are now still being mounted in complex and expensive additional steps.

Table 22 Opportunities and risks (advantages and disadvantages) of thin-wall injection molding techniques compared with conventional injection molding

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Reduced mass for smaller, more convenient products – New thin-walled or microscaled applications, e.g., in medical engineering – Shorter cycle times	– Simpler and safer molding and mold design – Wider process window for more stable process
Economic	– Cost savings resulting from use of less material – Greater productivity resulting from shorter cycle times	– Standard injection molding machines can be used with standard equipment – Smaller injection molding machines and smaller mold dimensions – Potential for smaller molds (without hot runner, simple cooling)
Environmental	– Lower material volumes for improved environmental compatibility – Smaller transport volumes and weights	– Depending on lot size, energy savings with smaller machines and molds
Social	– Specialist know-how for competitive advantages	– Conventional injection molding is widely practiced in low-wage countries (e.g., China)

4.4.8 Summary

Thin-wall technology makes very heavy demands on moldmakers, machine manufacturers, and plastics processors. In terms of product development, the trend to thinner walls will continue and the number of parts produced using multiple-component techniques will increase many times over in the coming years. Continued developments in material, machine and mold engineering will lead to even thinner walls. The Fraunhofer ICT has been doing research since October of 2002 within the framework of a multiindustry project sponsored by the state of Baden-Württemberg in the field of extremely thin-walled injection moldings for use in medical engineering applications.

Table 22 compares the opportunities and risks of thin-wall injection molding techniques with conventional injection molding.

4.5 Inmold Lamination (Back Injection) Vs. Lamination/Coating

In the automobile branch in particular, the design and finish of both interior and exterior components are subject to spiraling qualitative demands. The term “premium class,” coined by the automotive industry, is no longer the sole preserve of

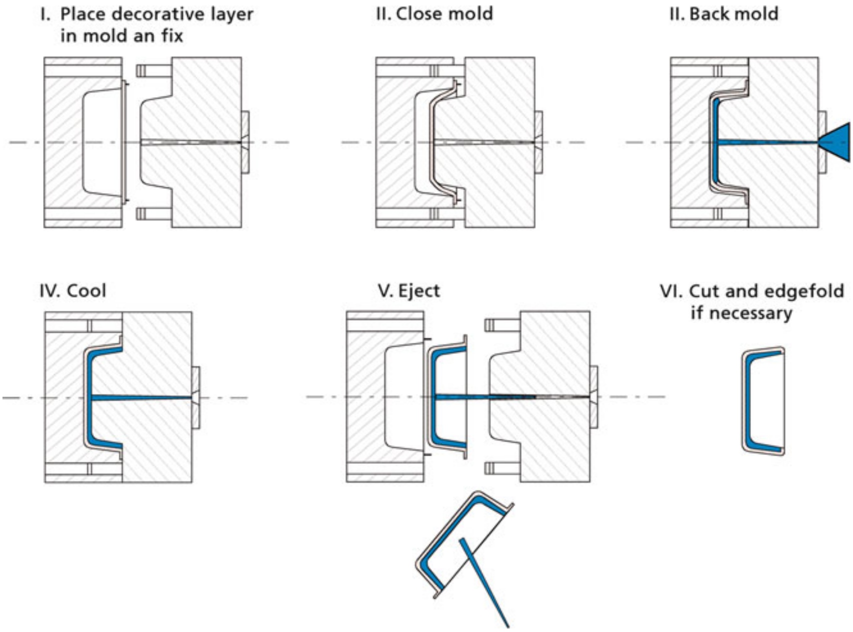


Fig. 27 The back injection process

upper class vehicles. Compact and small cars are now also expected to combine optical finesse with high-quality surfaces.

The challenge to the system supplier can be formulated as follows: Production of high-quality parts in high-volume runs within narrow price limits.

To meet these requirements, inmold lamination and back injection techniques have become standard tools of suppliers to the automotive industry (see Fig. 27).

In contrast to the lamination method by means of which surfaces are provided with decorative coverings in a separate follow-up step, back injection technology affords production of a fully decorated part in a single production step. The lamination press and application of contact or hot melt adhesives are no longer required. The environment is also spared the additional solvent-bearing vapors arising from these methods.

The range of back-injected décor materials is quite broad:

Textiles and artificial leather for vehicle interiors, carbon look and imitation wood foils for the dashboard, paint foils in the car color for radiator masks, décor strips, and door sills. The remaining difficulties include the class A surface quality demanded by carmakers as well as so-called color-matching (same optical impression of sheen and color adjacent to conventionally painted parts). In these fields, the back injection process competes more directly with painting processes than with laminating processes. Here as well, this technology offers excellent opportunities for greater cost efficiency in future production processes (Figs. 28 and 29).

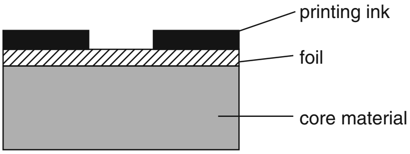
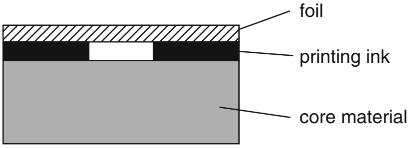
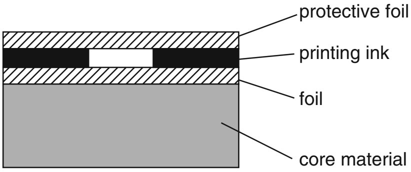
Layer structure of decorative layers	Remarks
	Monolayer foils • printing ink not protected against wear • no protection against environmental influences
	• shearing forces and high melt temperatures operate directly on the printing ink → thermal damage, smearing
	Multilayer foils • decorative layer between two foils → ink layer protected against outside influences

Fig. 28 Schematic layer structure of BIT foils

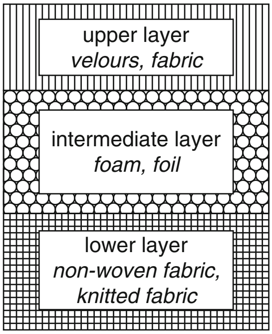
Layer	Normal wall thickness	Material	Function
	1 to 4 mm	PET, PA, PP	Optics, surface feel
	1 to 3 mm	PUR, PVC, PP	soft-touch, damping, thermal insulation, barrier against melt
	0.5 to 1 mm	PET, PP	thermal insulation, adhesion, stabilization of the upper layer to prevent displacment

Fig. 29 Typical structure of textile décor materials

Progress has also been made in lamination techniques in recent years. The current state of the art is represented by solvent-free hot melt adhesives applied directly to the back of the décor elements. The hot melt adhesives are activated by means of hot-air blowers or infrared heat lamps, whereupon the décor element is pressed onto the substrate part. The long process cycle times involved remain problematic, so that this method is only practicable in smaller series.

The opportunities and risks are summarized in Table 23.

Table 23 Opportunities and risks of the back injection technique

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Rapid individualized décor changes	– Deep-drawing ratio limited with décor inserts that are not preformed
	– Individual designs (airbrush), even in large series	– Décor materials must be resistant to pressure and temperature
	– Good adhesion between suitable material combinations	– Décor and substrate materials must be compatible
	– Scratchproof surface, e.g., with PMMA foils	– Risk of warpage due to nonuniform cooling conditions on décor side and pack of part
	– "Functional integration" e.g., in backlit operating elements (ventilation/air-conditioning in vehicle, covers)	– Risk of warpage due to relaxation of inserted décor foils
	– Covering small injection molding errors – as opposed to paint-over job	– Wrinkling due to shear forces in melt
		– Overstretching of decor
		– Décor image distorted due to different coefficients of expansion
		– Requirements for dust-free environment and high mold surface quality
		– Exact positioning of decor materials in mold
		– Less amenable to repairs than painted surfaces
		– Color-matching between foil back-injected and painted parts difficult
Economic	– Reduction of number of steps required: primary forming, secondary forming and decoration in a single step	– High level of value added concentrated in a single step
	– Low-cost production	– Trained personnel must be available
	– Rapid reaction to new design trends	– Dependence on décor supplier
Environmental	– Monocomposites are readily recyclable	– More difficult to separate pure types from heterogeneous material composites
	– Environmentally compatible application process (no adhesives or solvents)	
Social	– Competitive advantage with low-cost production, hence production site security	– Insufficient numbers of trained specialists available

4.6 Explosive Embossed Mold Surface

Plastic parts often need a structured surface for decoration or for lamination.

4.6.1 State of the Art in Surface Structuring

Natural surface structures, such as leather and wood textures, markings for veneers and technical surface structures, are currently introduced into injection molds almost exclusively by means of photoetching processes. To ensure that these conventionally produced structures (especially in the case of natural surface structures) do not have a regular appearance and therefore look artificial, a great deal of time, effort and therefore financial resources must be invested in product design and production. For this reason, new, economical and environmentally compatible methods of producing true-to-life surface structures are a current focus of interest. There are also several surface structuring techniques that are currently generating a somewhat lower level of interest, for example spark erosion, (micro)milling, laser beam structuring, etc.

4.6.2 Explosive Embossing of Mold Surfaces for Structure Transfer

Explosive embossing is an intriguing process which allows the imprinting of even relatively soft materials, with almost any structure, into metals. The structural template, for example a wood veneer or a holographic structural template, is placed on the mold surface and then transferred into the metal by a strong impulse from an explosive (Figs. 30 and 31).

The structural template can only be used for one stamping process as it is destroyed in the process. This means that the process cannot be copied even where an identical structural template is used, as a “complex” process such as embossing with detonation cannot be reproduced in detail. Clever selection and the appropriate positioning of a number of structured templates make it possible to stamp two or

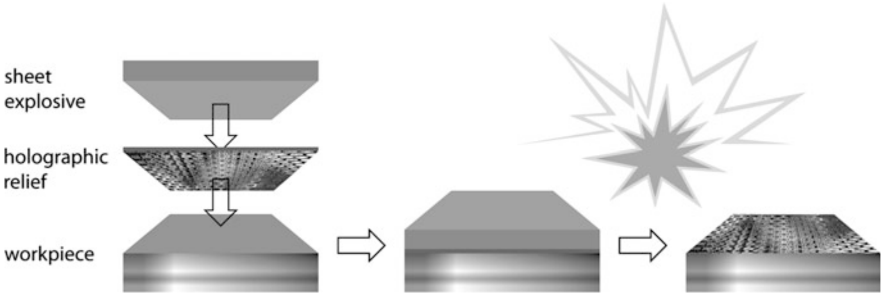


Fig. 30 Explosive embossing – process diagram

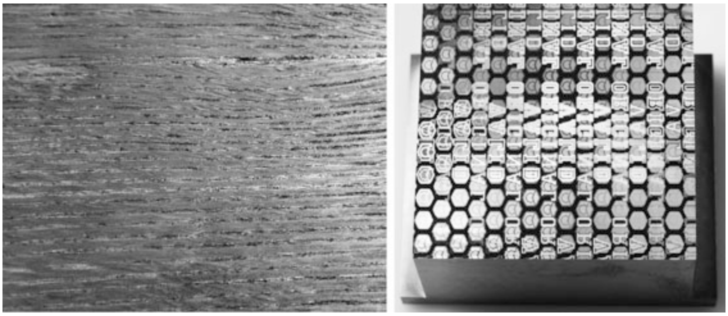


Fig. 31 Mold plate with wood veneer embossing (*left*) and explosively embossed steel mold insert with holographic surface structures (*right*)

even more patterns, one on top of the other, into an object. The detonation also hardens the embossed material. Significantly higher residence times of the molds can be achieved in injection molding.

In addition to the method of explosive embossing described above, a further method is also possible. For example, if the structural template is not available as a thin sheet or if the template must remain intact, a cast is made of the required structure of the template using an explosive mass of curing polyurethane, thus producing a structured sheet explosive. The sheet explosive is then detonated directly on the metal surface and the texture is transferred directly from the explosive to the metal.

Potential fields of application with increasing requirements for explosive embossing:

- Art and design (embossed templates for engravers, sculptures – detonography – jewels, explosively embossed portraits, etc.)
- Packaging and consumer goods (e.g., also for upscale goods such as high-quality perfumes, housing and furniture parts, toys, etc.)
- Automotive (interior and exterior)
- Safety and security (printing plates, anticounterfeit marking of products to avoid "reverse engineering," optical elements, light guidance, etc.) (Table 24).

4.7 Computer-Aided Engineering (CAE) in Plastics Processing

4.7.1 Introduction

Electronic data processing has seen increased use in all industrial fields in recent years. In the plastics industry in particular, quality demands are being raised continuously, while the product cycle and supply times grow shorter and shorter. The required level of flexibility in terms of market demands should be reached by introduction of suitable computer-aided engineering (CAE) concepts. Efficient

Table 24 Opportunities and risks of explosive embossing vs. the established photoetching process

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages, open points)
Technical	– Anticounterfeiting identification of branded products (protection against plagiarism) – Superposed embossed structures (decoration/protection against plagiarism) – The transfer of micro- and nanostructures is possible – Reproduction of irregular structures and unique objects – Detailed embossing of the structural pattern into the mold material – A combined process with etching is possible – Mold steels that are difficult or impossible to etch can be structured – Increased mold durability due to higher surface hardness – Texturizing of embossing and print rollers as well as erosion electrodes	– Freely formed 3D surfaces are not structurable at present – The reproduction of the structures in the mold surface is well below 100% of template size – Particularly suitable for small surfaces (up to 0.25 m^2) – The structured mold plate must be "caught" to prevent damage subsequent to embossing – The complete mold may be deformed by the explosive load – further process optimization required
Economic	– Rapid structuring of metal surfaces – More cost-effective structuring – Explosively embossed templates make useful 3D templates for engravers	– Requirements for explosion bunker and trained staff limits group of potential technology users
Environmental	– Replacement of conventional galvanic or etching baths	– Lower emissions compared to etching chemicals
Social	– Process development creates new jobs	– Residual hazard potential

hardware and software modules, suitable interfaces and trained employees are the main prerequisites for success of a CAE concept.

Injection molding is one of the most rationalized processing methods for production of plastic parts. On the other hand, injection molds are relatively expensive, opening up a field in which the potential for CAE system support is considerable. Instead of wasting development time and costs on construction of various different prototype molds for product fine-tuning, numeric simulation facilitates product optimization in accordance with the material and load situation as well as early recognition of production problems. Realization of a high-investment CAE concept is a profitable choice in an operation in which frequent product changes, a variety of different modules and variants, custom orders and production-on-order are commonplace. Use of individual CAD and CAM modules has been generally accepted for years now, in contrast to the more controversial applicability of the CAE calculation modules. The method of numeric part design, especially with computer-aided optimization (CAO) modules, functions on a completely new design basis and has considerable advantages over the classic design methods: Lighter constructions for material savings, coupled with longer part life. The simulation of part production, in injection molding specifically mold filling simulation, affords a very high level of flexibility with determination of the effects of different sprue locations and types, geometric elements (breaches, ribs), and of altered process parameters, on injection moldability and molding quality. Although the CAE tools, often combined with rapid prototyping, do reduce development times appreciably, they are not the solution to everything. Every simulation method has certain limits and every idealization of a practical problem demands a certain level of expertise before it can lead to reasonable practical results and useful interpretations.

4.7.2 Molding Design

Functional injection-molded parts often feature a complex spatial structure or free-form surfaces. Use of 3D CAD systems can be recommended with a view to subsequent process steps such as simulation and rapid prototyping. In various sectors of the model, aircraft and automobile production industries (e.g., body parts), so-called free-form surfaces must be imageable. Free-form surfaces are surfaces curved in space that cannot be analytically described in a direct manner. However, various methods are in use to approximate free-form surfaces depending on the application in question. These surfaces are divided into any number of patches, then imaged as matrices. Ideally, a hybrid CAD module used in plastic processing should be able to realize design constructions with both surfaces and volume. Further special functions especially for plastics engineering such as macros for functional elements (ribs, foil hinges, snap elements, etc.) and afterprocessing form control modules have not succeeded in establishing a market for themselves.

4.7.3 Part Dimensioning

Now that high-performance computing power is available to do the job, numeric calculation methods are seeing increasing use in dimensioning of plastic parts, for instance the finite element method (FEM).

FEM has the following advantages over analytical methods:

- Any and every part geometry can be modeled, no matter how complex
- Tension, expansion, temperatures, etc. are calculated over the entire cross-sectional area
- The real-time process can be simulated
- Anisotropes and nonlinear material behavior, as well as couplings (e.g., thermo-mechanical) are taken into account
- Special elements, e.g., contact and frictional elements, are available

Potential applications for FEM in plastics processing have multiplied in recent years due to development and implementation of additional substance-related laws and calculatory methods.

Examples include:

- Thermoplastic, elastoplastic and creep laws
- Plastic stress–strain relations (NeoHooke, Mooney–Rivlin, Kilian)
- Approaches applying to porous and foam materials
- Laws applying to viscoelastic–viscoplastic materials
- Composites (multilayer, anisotropic)
- Dynamic, crash behavior

The calculated results can only be accurate when substance laws applied describe the relevant material behavior with sufficient accuracy. Also, the required material parameters, for example modulus of elasticity E, shear modulus G, transversal contraction number must be available plotted against elongation, time, rate, temperature, as well as the effects of mediums or radiation as applicable. Most commercially available databases are still deficient in this respect.

4.7.4 Mold-Filling Process Simulation

The mold-filling process is simulated in order to determine whether they can be produced with the selected molding compound. The relevant parameters include the injection type and position, flow lines, the injection molding pressure and temperature, and the expected cycle times.

A simplified model based on the following assumptions can be constructed with the differential equation for conservation of mass, impulse, and energy as well as a law uniting the viscosity, density, and thermal properties of a substance:

- Marginal influences will be ignored, wall-slippage, etc.
- Incompressible, isotropic fluid, laminar flow
- Forces of gravity and inertia will be ignored
- Capillary forces will be ignored
- Direct stress effects will be ignored
- Parallel laminar flow through the middle plane
- Division of structure into shell elements with “n” lamina parallel to the walls.

The basis for the rheological calculation is the description of the viscosity function of the plastic used with the help of the Carreau model, which describes the viscosity in its dependence on shear rate in the three regions:

- Newtonian region
- Transitional region
- Intrinsically viscous region.

The temperature-dependence of the viscosity function is described according to the Williams, Landel and Ferry law (WLF). When calculating the flow processes, the flow volume distribution in different flow paths and changes in the free cross-section up transition of the boundary layers.

4.7.5 Calculation of the Holding Pressure Phase, Shrinkage, and Internal Stresses

The purpose of the holding pressure phase, which follows the filling phase, is to compensate the volumetric changes in the plastic material. This is only possible if liquefied plastic melt can continue to flow into shrinkage areas. On the basis of the material's *p–v–T* behavior, the cross-section of the passing flow and the volume of refilled material can be calculated. Following transition of the gate (sealing point), the volume shrinkage and the internal stress distribution are calculated. Conclusions concerning linear shrinkage dimensions, and thus cavity dimensions, based on the volume shrinkage are currently only feasible for simple geometries. Further, only thermally induced internal stresses are calculated. Internal stresses due to different orientations or degrees of crystallinity cannot be determined.

4.7.6 Mold Construction Design

Injection molds comprise the contour-forming elements and the accessory mold structures. For reasons of rationalization, moldmakers have decided to specialize on the contour-forming elements and purchase standardized accessory structures such as plates, bolts, guides, pins, ejectors, etc. from special manufacturers who make and sell them acc. to DIN or factory standards in series and list them in catalogs.

For a number of years now, libraries of standards have been available in connection with CAD programs. Both individual standard items and complete mold accessory sets can be called up. Individual parts of the mold accessory sets can be taken out and altered, whereby such changes are then also included in the 2D production drawings and parts lists.

4.7.7 Thermal Mold Design

In a thermal design, a heat energy balance of the mold is performed to determine the heat flow from the plastic molding to the mold, the heat flow from the mold to the environment, and what heat flow must be taken up by the tempering medium.

Assuming framework conditions such as:

- Maximum temperature difference of medium
- Turbulent flow
- Maximum pressure loss in tempering system

as well as the criterion of homogeneous cooling, the following can then be iteratively calculated:

- Position of the temperature canals
- Diameter of the canals
- Distance between the canals
- Distance between canals and plate surface

4.7.8 Mechanical Tool Design

The objective of mechanical tool design is to find a compromise between mass and stiffness. The required calculations can also be carried out with the help of the FEM. Another possibility is to use a simplified calculation module built up on a simple plate-spring model. The time and expense spent on idealization and calculating time are therefore much lower.

4.7.9 NC Production

To generate an NC program, the molding geometry is transferred from the CAD into the processing module. Once the material, mold specification, and other process data have been entered, the milling paths for the cavity or electrode are calculated automatically. Further data such as rpm and feeds are selected from mold and material libraries on the basis of the input data. The NC program thus created can then be interactively simulated on the monitor, completely or step-by-step, and altered as necessary.

Table 25 presents the opportunities and risks of a part/and mold design based on a numeric simulation, compared to analytical/empirical dimensioning.

4.8 Tailored Polymer Testing for Improved Simulations

Simulation is currently used as an established tool in part design. In the early design stages in particular, simulation methods help rule out possible versions of a part without having to make real prototypes. It is in this stage that the fundamental design work, with its major influences on all features of the final part, is done. Errors made in this phase of the design work can be very costly in terms of money and resources, so the virtual process saves time, energy, and money.

In the field of polymers, the potential of simulation software has not yet been fully exploited. The standard numeric models for polymers are nowadays far from precise and the corresponding determination of material parameters is not well defined. It can be assumed that tailored testing in combination with better simulation tools would improve the early phase of the design process enormously.

Table 25 Opportunities (advantages) and risks (disadvantages) of a part and mold design based on a numeric simulation, compared with analytical/empirical dimensioning

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– FEA is difficult, only experts can use it properly	– Years of experience required
	– Complex and time-consuming model generation, in particular for several alteration stages, since there is usually no association between geometry and FE network	– Decision-making frequently not simple and linear
	– Models and material data not always available	
Economic	– Simulation experts must be kept on staff	– Repetitive work for overdimensioning, prototypes, and rejects
	– Software very expensive	– Longer development times
	– Hardware also expensive, depending on application	
Environmental	– FEA is environmentally beneficial	– Overdimensioning, rejects, and prototypes are environmentally harmful
Social	– Computer operator is often a boring and thankless job, so it is not very popular	– Knowledge is lost when experts leave

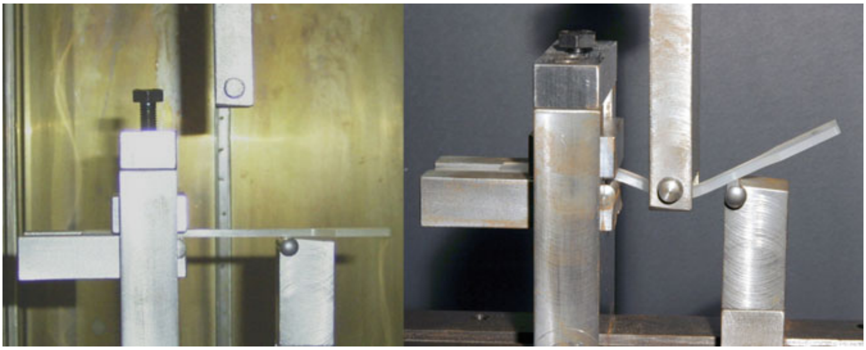


Fig. 32 Differences in failure behavior of isotactic polypropylene at the speed of 1 mm/s (*top*) and 3 mm/s (*bottom*), at room temperature (Photo: IKP, Universität Stuttgart)

As an example, polymer behavior is sensitive to speed (see Fig. 32).

To obtain a correct and useful prediction of the crash behavior of a part in a simulation, one has to test the material at speeds slower than 1 mm/s, in addition to the standard speeds. By contrast, high-speed tests up to 10 m/s (faster by a factor of 10,000) are appropriate for generating material strain levels similar to what is

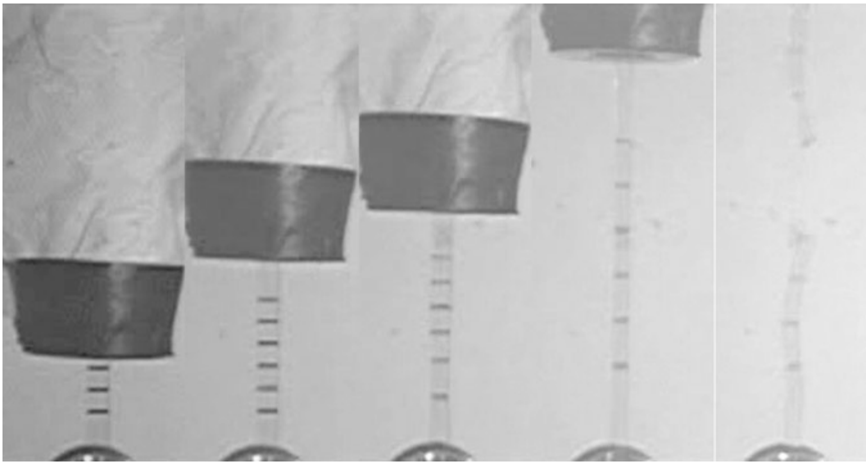


Fig. 33 High-speed testing sequence with polycarbonate material (Photo: IKP, Universität Stuttgart)

Table 26 Opportunities and risks of tailored polymer testing for improved simulations

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Higher design precision for polymer modules – Facilitates error analysis in complex simulations – Easier determination of standard deviation and aging of materials	– Inaccuracies due to a lack of valid standards – Tailored testing also requires high levels of testing precision
Economic	– Fewer expensive product tests means cost reductions	– All materials have to be retested and recharacterized due to the inadequacy of standard database material, e.g., CAMPUS
Environmental	– Complex and resource-consuming prototyping can be diminished – New technical developments are applied to current products more quickly due to shorter development cycles	– Since simulation is a virtual process, it requires no resources except energy, so there are no noteworthy risks
Social	– Safety issues are more closely integrated in products – only possible with improved simulations – Simulations are also useful in low-cost student training	– Training of FEM users is becoming more and more complex – Engineers no longer challenge results of simulation

involved in a real crash. Figure 33 shows a high-speed testing sequence with a polycarbonate.

Table 26 summarizes the opportunities and risks of tailored polymer testing for improved simulations.

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Opportunities and (in Particular) Risks of Use (Utilization Phase) of Plastic Structural Components

Peter Eyerer, Fabian Beilharz, Christof Hübner, Thilo Kupfer, and Christian Ulrich

Abstract The previous chapters have described the opportunities and risks of plastics as materials, whereas in this chapter and the chapters, “Opportunities and Risks Involved in Designing Structural Components Made of Polymers,” “Plastics and Structural Components – The Environment and Recycling,” they will be discussed in terms of the structural components made of plastics. The opportunities often predominate due to the advantages of plastics over other materials, for example metals, ceramics, and wood. To avoid repetition, this chapter will deal primarily with the risks of the utilization phase of plastic products. The specific applications used to illustrate this are listed in the keywords.

Keywords Automotive interiors, Biodegradable plastics, Condoms, Designing structural components, Door handles, Fiber composites, Interior paneling elements, Joint endoprostheses, Kneading clay, Mats for office chairs (carpet protection), Packaging material, Parts in cars, Polycarbonate glasses, Pressboard, Rubber plates, Tires, Toys made of soft PVC, Utilization phase

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P. Eyerer (ed.), *Polymers – Opportunities and Risks I: General and Environmental Aspects,* Hdb Env Chem (2010) 11,
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1 Introduction

The previous chapters have described the opportunities and risks of plastics as materials, whereas in this chapter and the chapters, "Opportunities and Risks Involved in Designing Structural Components Made of Polymers," "Plastics and Structural Components – The Environment and Recycling," they will be discussed in terms of the structural components made of plastics. The opportunities often predominate due to the advantages of plastics over other materials, for example metals, ceramics, and wood.

To avoid repetition, this chapter will deal primarily with the risks of the utilization phase of plastic products. Before these risks are illustrated by specific applications in the following sections in the categories thermoplastics, duroplastics, and elastomers, below is a review of some of the general risks.

Plastics involve risks of entrainment of low molecular components into the polymer during the synthesizing process and splitting off of these components during utilization, see Sects. 2 and 3 in chapter, "Synthesis (Manufacture, Production) of Plastics", Sect. 4 in chapter "Properties of Plastics in Structural Components", Sect. 5 in chapter "Processing (Primary Forming) of Plastics Into Structural Components" and chapter "Opportunities and Risks Involved in Designing Structural Components Made of Polymers."

A highly sensitive issue in this context is the residual content of vinyl chloride (VC) in PVC with it carcinogenic effects. Under global competitive pressure, cheap products that do not comply with the stringent regulations issued by the industrialized countries are often thrown onto the market by the economies of emerging countries.

Other examples of this phenomenon include residual crosslinking agents from partially cured duroplastics, formaldehyde from phenolic resin, amines in epoxy resins, and benzoyl peroxide from unsaturated polyesters. Section 5.3 in chapter "Processing (Primary Forming) of Plastics into Structural Components" addresses the nitrosamine in elastomers.

Opportunities inherent in use of parts made of thermoplastics and thermoplastic elastomers (TPE):

- Light construction potential (energy savings)
- Insulating effect (electrical, thermal, acoustic) (energy savings)
- Low costs
- Accident prevention or alleviating effect (damping, viscosity)
- System compatibility (integrated functions)
- Resistance to chemical corrosion if material selection correct
- The extended life of foods and other goods (packages)
- Protective effect against weathering influences (textiles)

As with every material, there are also a number of *risks*.

- Our knowledge concerning plastic applications is not nearly as extensive as with metals (5,000 years of experience with metals, 100 years with polymers)
- This results in many mistakes in material selection, processing, design, and surfacing, resulting in risky part failures.
- In children's toys in particular, the frequency of damage resulting in breakage represents irreparable damage to the image of the material plastic: disappointment in and mistrust of this group of materials often remain with people for decades.
- The main health risks arise from use of residual crosslinking agents for partial hardening of duroplastics – formaldehyde in phenolic resin, amines in epoxide resins, and benzoyl peroxide in unsaturated polyesters are exemplary. The nitrosamine problem in elastomers is discussed in Sect. 5.3 in chapter "Processing (Primary Forming) of Plastics into Structural Components."

These few examples show that all plastics release emissions in the form of more or less critically hazardous volatile organic components (VOCs) during the synthesis, compounding, and subsequent utilization phases (see above all Sect. 4 in chapter "Properties of Plastics in Structural Components").

Inorganic additives can also cause environmental damage, see Sects. 5 and 6 in chapter "Properties of Plastics in Structural Components."

The exemplary specific structural components from the plastic type groups are covered in the following sections.

2 Structural Components Made of Thermoplastics and Thermoplastic Elastomers

The author sees the main risks of thermoplastic plastics in the emission of organic substances in interiors, affecting the persons residing there, in particular children. These considerations define the focus of the following three examples.

2.1 Structural Components in Automobile Interiors

Although the following summary, derived for most part from [1] in [2], focuses on the car, the principles involved apply as well to other interiors such as aircraft, buses, passenger trains, living space, and public buildings.

The extremely dense population of parts of California (Los Angeles, San Francisco) and the resulting rigorous legislation are beginning to force the automotive industry to act in response to the restrictive standards that have become law in this area over the past decades. The state of California is also seeking to reduce all automobile emissions by means of supplementary legislation within the framework of the “Low Emission Vehicle (LEV)” program. “Nonfuel emissions,” also covered by these regulations, are the (evaporative) emissions from structural components.

California law prescribes a limit of 0.5 g/test for the sum of evaporative emissions from a motor vehicle beginning with model year 2004. Compliance with the limits must be confirmed by defined testing methods. In the “3-day diurnal test,” for example, evaporative emissions from the entire vehicle are measured over a 3-day period in a SHED (Sealed Housing for Evaporative Determination) test chamber subjected to a predefined, 24-h temperature stress program (from 18.3 to 40.6 °C). After each 24-h period, the concentration of hydrocarbons (HC in ppm) is measured and converted into HC equivalents (in grams). The highest of the three measured values is then the test result.

Even stiffer regulations apply to so-called Zero Emission Vehicles (ZEV), available to carmakers since 2003 for reduction of their average fleet emissions figures – also regulated by California law. ZEVs have to meet very tough exhaust standards (“SULEV”), in addition to which their HC emission from structural components (“nonfuel emissions”) must not exceed 0.35 g/test. Evaporative emissions from fuel and other liquid supplies (“fuel emissions”) are absolutely prohibited in these vehicles.

On the basis of these regulations, the most stringent demands are made, for example, on air-conditioner system seals (refrigerant lines) and vehicle fuel systems [1].

Nearly all structural components in the interior of a car, for example, dashboard, seats, carpeting, interior paneling, rubber-based seals, floormats emit low molecular substances (cheap products installed after purchase more than series equipment).

In response to these insights and practices, the Federal German Education and Research Ministry (BMBF) and the Association of the German Automotive Industry (VDA) in its *Forschungsvereinigung Automobiltechnik e. V.* (Automotive Technology Research Group) carried out a research project from 1990 to 1996 at TÜV (Technical Inspectorate) North Germany and the Institute for Polymer Testing and Polymer Science (IKP) at the University of Stuttgart with the theme of “Development and Testing of Standard Measurement Methods for Evaluation of the Contributions of Motor Vehicles to Air Contamination in Passenger Compartments of Passenger Cars” [3].

As a result of these studies, emissions limits were established by some carmakers for certain structural components, contaminants, and contaminant groups. DIN 75201 “Determination of Fogging Behavior” and “Determination of Odor Behavior of Materials in Car Interiors” (VDA 270) are among the other relevant test methods for structural components.

There are also a number of analogous test methods for emissions from materials and structural components in residential interiors. The know-how and level of awareness of both technical professionals and consumers have increased encouragingly in the past decades. New legislation has not, however, put a stop to the egregious practices of some profiteers. Some examples are related below.

2.2 Braiding Materials Made of Soft PVC for Children and Youths; Mats for Roller-Mounted Office Chairs (Carpet Protection)

Colorful soft PVC bands have recently become a favorite game among children and youths. They braid a number of bands together to make key chain holders or arm bands.

The strong chemical odor the new PVC material gives off hangs in their rooms for weeks. The label on the package says: Made in China.

A chemical analysis of these PVC bands produces the following result:

Diisoactyl phthalate (DOP) (or the synonymous designation: Phthalic acid (2-ethylhexyl ester) or di-(2-ethylhexyl)-phthalate) in considerable amounts.

DOP is the standard plasticizer for PVC. To save money, the so-called external plasticization is carried out. DOP is technically, and therefore economically, easy to mix in. It permeates back out again as a function of time and temperature.

In a Safety Data Sheet issued by Merck, three potential hazards are listed for this substance:

“May cause reproductive sterility. May cause fetal damage. For professional users only” (Excerpt) [4].

If these bands are allowed to air out for a few weeks outdoors, the analysis shows a good deal less of this plasticizer. These are very cheap products, i.e., externally plasticized PVC, the plasticizer of which is known to permeate back out of the product over a period of time, dependent on temperature.

Since this braiding material is produced in a foreign country, German emissions laws do not apply to its production. What has not been investigated as yet, and is therefore still unknown, the proportion of monomeric, carcinogenic VC. In Germany, the monomeric VC content in PVC must be less than 10 g VCM per ton of PVC in mass PVC and under 1,500 g VCM per ton PVC in emulsion PVC. The material is then demonomerized with large air volumes [5]. Imports are not tested for this.

Many German consumers would pay considerably more for these products for their children in order to obtain safe materials. Unfortunately, it does not occur to hardly any German companies to produce such safe, risk-free bands and to advertise on the market with these health-related arguments. Consumer protection should give this theme dense coverage.

Flip-flops and beach toys are normally also made of externally plasticized PVC in low-wage countries and show an analogous behavior. In 25 of the flip-flops tested by “Öko-Test,” 17 showed excessive DOP or similar phthalates; the same was true of 14 out of 18 tested inflatable beach toys.

This also applies, for example, to the soft PVC mats made for roller-mounted office chairs. These thick foil mats, about 1 m in size, emit plasticizers into the breathing air of the desk worker over a period of months. Since very few low-emission or emission-free products are available, the only piece of advice worth following is to unpack the carpet protection mats and leave them exposed to the sun on the balcony for three months before using them.

2.3 Joint Endoprostheses Made of Ultrahigh Molecular Weight Polyethylene

For decades now, hip acetabula, knee plateaus, shoulder joint capsules, and other implant components have been made of, for example, ultrahigh molecular weight polyethylene (UHMW PE). The material used is so-called medical UHMW PE, which is not age-stabilized.

Physicians fear pathological reactions to chemical stabilizers. Accurate research and analyses [6] have revealed that medical UHMW PE, just like technically stabilized UHMW PE, is enriched with calcium stearate as corrosion protection for the compression molds. It was also determined that UHMW PE still contains 10 mg of residual traces of precipitant (diesel oil) from the synthetic process prior to implantation, which after 9 years of in vivo implantation is reduced to 1 mg [6] and has therefore permeated into the body.

The scientific controversy over use of calcium stearate continued for a number of years. Although the UHMW PE powders now offered by manufacturers contain smaller amounts of calcium stearate, the matter of diesel oil contamination has not received due attention. Ten microgram of diesel oil in the body over a period of 9 years is apparently too small an amount to be worthy of notice.

Another considerable risk involved in use of joint endoprostheses components made of standard UHMW PE is the abraded PE particles. These particles remain in tissues surrounding the joint, where they cause inflammatory reactions (osteolysis), which in turn lead to a loosening of the artificial joint, potentially shortening its useful life. Individual physiological rejection reactions, the assumption goes, may accelerate the degradation processes in the material UHMW PE.

This is an example of how suitable aging stabilizers may entail medical risks, but also opportunities to lengthen their useful lives by taking the right measures.

Table 1 Opportunities and risks of a standard UHMW PE inlay compared to a steel (CoCrMo) acetabulum

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Better damping qualities – Can be crosslinked (resulting in high level of abrasion and aging resistance)	– High level of wear – Abrasion can lead to loosening – Ages in the body, raising levels of abrasion and wear – Brittle rupture at advanced product age
Economic	– Lower cost	
Environmental, in the body	– Implant mass is an important factor	
Social	– Physiologically compatible, no allergies	– High rate of loosening shortens life of implant, reducing the quality of life of patient due to surgical revisions – Traces (mg) of diesel oil enter the body – Calcium stearate as an anti-corrosion agent

The use of such aging stabilizers in medical UHMW PE is practically a forbidden subject, but it should be addressed in a clear manner for the good of the patients.

Table 1 lists the qualitative opportunities and risks of UHMW PE inlays in a hip endoprosthesis as compared to a steel (CrCoMo) acetabulum.

More recent developments in UHMW PE have to do with the crosslinking of the linear polyethylene molecules to form a close-knit spatial network using high-energy radiation followed by tempering to eliminate free radicals. The resulting high crosslinked UHMW PE shows lower wear by a factor of 10 and much greater aging resistance in laboratory tests. However, it will take a further 10 years before we can obtain useful, statistically reliable in vivo data on hip joints. The material is not yet used in the knee area because of potential risks.

2.4 Biodegradable Plastics for Packaging Materials

After about two decades in a quiet corner of the market, biodegradable materials (BDM) are now moving forward to grab a larger share [7] (see also Sect. 4 in chapter “Processing (Primary Forming) of Plastics into Structural Components”). Biodegradability is, however, almost always environmentally harmful. The use of renewable raw materials for plastics entails as many risks as opportunities and these risks must be managed on a case-by-case basis (see chapter, “Synthesis (Manufacture, Production) of Plastics”).

Figure 1 [7] lists the main materials and their subgroups.

These products, mostly manufactured from substances obtained from farming production, are still in an early marketing stage.

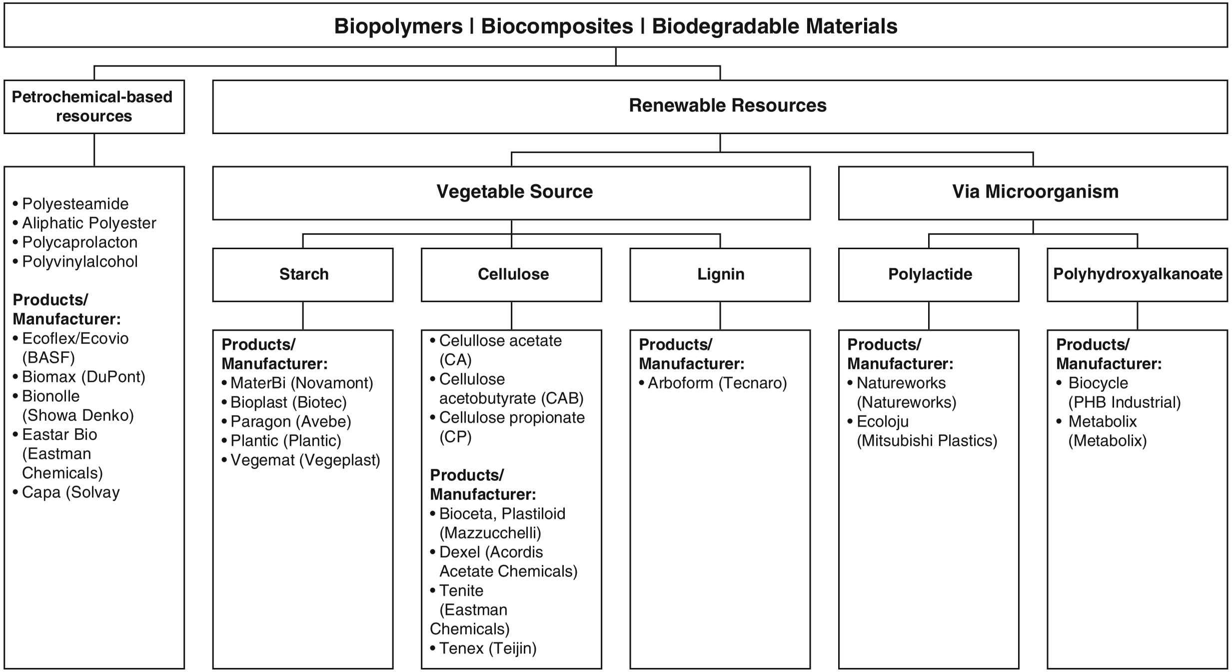

Fig. 1 Categories of biodegradable materials (BDM) with listings of products and manufacturers [7]

In concrete terms, the products are:

- Biodegradable agricultural foils
- Compostable biological waste sacks
- BDM packaging

Table 2 shows more details of the current market situation.

The Interest Group for Biodegradable Materials (BDM), Berlin [8] estimates that the market for BDM in Western Europe in 2003 was about 40,000 ton (compared to 25,000 ton in 2001). Estimates for 2002 in Japan and the US are around 10,000 ton each.

Compostable waste sacks and loose fill are now well-established, but still have significant potential. Consumers are likely to show even more acceptance for the concept: "First it's a carrying bag, then it's a trash bag." This concept is already widespread in Italy and is just starting up in Germany.

Biodegradable packaging for foods is already quite prevalent in supermarkets and chain stores in Belgium (Carrefour, Covee), the UK (Tesco, Sainsbury), Italy (Iper, Esselunga), the Netherlands (Albert Heijn), Switzerland (Migros, Coop), and Scandinavia.

A wide-ranging market introduction of biodegradable packaging materials is still being held up by the higher cost factor and the limited technical application profile of these materials in the packaging sector. The situation is different for BDM mulching foils. In Spain, France, Belgium, and the Netherlands total use of this foil has probably exceeded 5,000 ha (2003), with a continuously rising tendency.

A study published by Toyota in March of 2004 [8] estimates total company sales of biodegradable plastics at USD 38 billion for the year 2020.

Until that time, the political and legal basis for such development must be improved or created in Germany above all, and in Europe as well, since the current situation presents a number of hindrances. In contrast to the related themes of "energy from biomass" and "biogenic fuels," exploitation of renewable raw materials to produce material products is not yet receiving encouragement in the form of fiscal instruments and legislation ("renewable energies").

2.5 Transparent Polycarbonates in Competition with Glass

Transparent plastics have already occupied niches previously held by glass in many applications. The advantages of the plastic material over glass include its lower density, reduced tendency to splinter when it breaks, and the relatively low levels of energy required to manufacture and process the material.

These advantages must be set alongside a number of weaknesses of plastic compared to glass, due in most cases to its lower levels of stiffness and hardness, so that the surface is more easily scratched.

A common method of improving the properties of materials is to combine them in suitable mixtures. The weakness of glass and plastic materials are often compensated by such means. An example of this is laminated sheet (safety) glass, in which two

Table 2 Current market situation – biodegradable materials BDM

BDM	Manufacturer (H)/ Processor (V) Location	Capacity tons/a € per kg	Market/trade name Products
Polylactic acid (PLA) made from grain	Cargill-Dow, Blair, Nebraska, USA (H)	140,000	Nature Works bags, sacks, service packages, for instance
	Hycail, NL (H) Toyota, J (H)	Smaller production capacity	dishes, cups, tableware; fast food packaging First car parts in "spatial" model
– Higher melting. C-PLA – PLA blends	Mitsubishi + Sony (V) Sanyo, Japan (V) Treofan + Avery Bennison (V) Nokia, Finland (V)		Walkman housings CD, PC monitor, notebook housing, Biophan, overhead transparencies, envelope windows, cell phone covers
Starch-based materials – Thermoplastic Plant starch with synth. degradable polyester – Vegetable oil-based polymers	Novamont (H) Novara, Italy Goodyear	35,000 1–3	MaterBi foam foils, packaging nets, black mulching foils, nap foils; tire additive Glass-clear, water-soluble packaging trays
	Plantic Technology Australia (H) + (V)	?	Foil products
	Polargruppen, Norway (V) Loick AG, Germany (H+V)	?	Play corn, toys
Aliphatic, bio-based polyester: polyhydroxyalcanoates (PHA)	Procter & Gamble Chemicals	?	Nodax (market introduction upcoming) packaging of hygiene articles
Aliphatic copolyester	BASF, Ludwigshafen, D	? 3–5	Ecoflex food packaging
	Eastman Chemicals, The Hague, NL	?	EastarBio food packaging
	SK Chemicals, Seoul, Korea	?	Skygreen food packaging
Lignin and wood fiber dominated compounds – Lignin and natural fibers (from paper production)	Tecnaro, Eisenach, D	300 6–10	Arboform (Sect. 1.2 in chapter, "Opportunities and Risks Involved in Designing Structural Components Made of Polymers") Acoustic bodies, loudspeakers, automobile interior parts, toy figures, golf tees
– Wood fibers and protein (from leather processing)	IFA, Tullen, AU	0.5–1 ∼2.50	Fasale profiles, Fasal-Prosin (injection molding type)
Grain meal	Inst. f. plastictechn., Paderborn, D	? 0.1–0.15	
1,3-propandiol	DuPont & Genencor, USA	(Fermentative production) ?	Monomeric building block for many polymers

panes of glass are glued together with a tough plastic film that prevents glass splinters from flying about in case of breakage. To increase the scratch resistance of plastic, transparent hard layers or thin glass foils are laminated to the surface of the plastic.

Besides combinations of the two competing materials transparent plastic and glass, there are a number of other methods of giving the panes special properties that go far beyond their own. Combinations of glass or plastic with other materials can create a number of additional functionalities, such as

- Antireflection coatings
- Antifogging coatings
- Surface conductivity
- Light penetration control

All of the measures taken to improve the properties of the materials that involve use of an additive material automatically worsen the recycling profile of the resulting material composite.

Automotive applications are currently a major field for development of plastic panes. Glass panes (or laminated sheet glass) are now still used exclusively in cars. With annual production volumes in Germany (2001) of approximately 8.2 Mio. m^2 of single-pane laminated glass and approximately 4.7 Mio. m^2 (2003) of safety glass in motor vehicles, replacement of glass with plastic in this sector would have significant economical and ecological effects.

Transparent roof modules are now the state of the art.

Small lateral panes made of PC have been installed in large series production in Germany for many years now. Large lateral panes have now been introduced for the car SMART [9] 2004 or will soon be released for series production by other vehicle manufacturers, along with transparent sliding roofs [10, 11]. Available processing technologies include injection molding, e.g., Battenfeld, Bielefeld, injection compression molding, and sheet molding.

The surface hardnesses achieved for front windshields are not yet sufficient. Extensive material recycling experiments with maximum foreign substance input (e.g., silicatized surface coating) have been carried out. Transfer of the knowledge gained to series production has yet to take place. It is also still open whether recycled materials can be used in original equipment applications.

Should the panes first be removed from recycled vehicles or can they be included in the light shredder fraction?

A detailed balance of how much sense this recycling procedure makes must be carried out on a holistic basis (technical, economic, environmental, social) [9]. Table 3 compares qualitatively the opportunities and risks of PC car panes.

2.6 Kneading Clay that Bounces as a Toy for Children

The mixtures of kneading clay and “rubber” known as “bouncing clay” should not be given to children! The Federal German Institute for Risk Assessment issued a

Table 3 Opportunities and risks of polycarbonate car panes compared with automotive safety glass

Evaluation Segment	Opportunities (advantages)	Risks (disadvantages)
Technical	– Weight savings in upper part of vehicle – Freedom of design – Functional integration with thermoplastic processing, (e.g., lamp unit integration) – High impact strength – Double-sided plates in material/process technology	– Scratch resistance not yet sufficient (e.g., rear pane with wiper) – Allows IR radiation to pass (IR absorber required) – Low level of heat conductivity and softening problematic with pane heating systems – Improvement in injection molding: opt. quality and product size – Improve: UV protection, heatability, IR reflection
Economic	– System cost potential – Lower cost than large-surface safety glass[a]	– Glass producers are also innovative! Competing solutions?
Environmental	– Lower levels of primary energy consumption possible by means of mass reduction: life cycle of PC 1,800 MJ, glass 3,600 MJ – Material recycling PCwithout coating – Experiential data from PC CD recycling	– Material recycling PC with coating? – Petroleum-based (shortage?) – Glass is currently not recycled (ends up in light waste shredder fraction) – Pay attention to end-of-life vehicle ordinance
Social	– High innovative potential at location – Head injuries will presumably be reduced	– Lack of years of experience with new product

[a] Production reduction of safety glass in Germany 2001 to 2003 from 9.5 to 4.7 Mio m$^{2!}$

warning in April 2005 to the effect that these deformable masses, which bounce as projectiles, emit boric acid, which then migrates though the skin or, if ingested, through the digestive system, into the body. The legal threshold values (0.1 mg/kg mass) can be exceeded by the standard 17 g packages.

In tests of excessive amounts of boric acid in animals, this substance is seen to cause fetal and developmental damage. It is added to the “bouncing clays” for its flame-retardant and preservative properties. The boric acid content of toys must be greatly reduced – or the substance should not be used in them at all.

3 Duroplastics

The *opportunities* afforded by duroplastics can be ascribed to their excellent mechanical, thermal, electrical and chemical properties.

Potential *risks* of these substances include low molecular cleavage products from the crosslinking reaction, longer cycle times and recycling. Following comminution, these materials can only be used as such and only as added filler material in the

Table 4 Duroplastics, processing, application [3]

Duroplastics	Process	Applications
Phenolic resins (PF)	Pressing, drawing, laminating, impregnation	Pressboard and plywood,electroengineering, insulating materials, molding compounds, papers, fire protection
Melamine resins (MF)	Injection molding, pressing, casting, winding, RTM, SRIM, foaming	Décor papers, wood materials, molding compounds, electroengineering, noise and fire protection
Epoxide resins (EP)	Impregnation, lamination, drawing, pressing	Aeronautics, medicine, electroengineering, foundations, civil engineering, sporting equipment, adhesives
Silicone resins (SI)	SMC, BMC, ZMC, winding, lamination, drawing, casting	Electroengineering, seals, construction
Unsaturated polyesters (UP)	Pressing, impregnation	Vehicles (body, engine), containers, housings, polymer concrete
Triazine resins	Dripping, lamination, casting, foaming, pressing, injection molding	Medicine, electronics, bearings, aircraft engines
Polyimide (PI)	Injection molding, casting, impregnation, pressing	Electroengineering, electronics
Methacrylate	Injection molding, casting, impregnation, pressing	Polymer concrete, electroengineering, sanitary installations
Polyurethane (PUR)	Casting, foaming, reaction injection molding (RIM, RRIM, SRIM)	Vehicles, construction (insulating materials), housings, machine elements, electroengineering

production of new material. The price of material recycling of duroplastics will remain prohibitive barring a considerable increase in the price of new material.

The disadvantage of incineration is that the often high proportions of inorganic fillers and reinforcing agents leave behind large volumes of incineration slag. Landfill waste disposal is in most cases acceptable from a chemical point of view, but it does require a good deal of space. Table 4 provides a summary list of the most important duroplastics, their processing technologies, and main applications.

3.1 Pressboard

Pressboard has been used for over 50 years on a broad basis in production of furniture, add-on constructions to living space, and in wood constructions. This material unites a number of essential advantages such as large surfaces, form stability, absence of grain, and exact thickness with ready processability and favorable strength properties in relation to its bulk density.

These boards are pressed out of wood chips with binding agents added. In Europe, mainly conifer chips from forestry cuttings, and some recycled wood, are used as the raw materials. The binding agents used are mainly urea formaldehyde resins, sometimes in combination with melamine formaldehyde resins, phenolic formaldehyde resins, and isocyanates. Pressboard contains about 12 % binding agent OSB (oriented strand board) only 4–6 %.

Because of increasing environmental awareness, pressboards and plywood fell into disrepute, particularly due to emissions of formaldehyde, which is classified as carcinogenic,[1] from the binding agents. To prevent excessive levels, the Federal German Health Office recommends an indoor air guideline limit for formaldehyde of 0.1 ppm. The main problem was with boards containing the binding agent urea formaldehyde resin, which are suitable for use in dry indoor structures. The limit value can, however, be complied with by altering the formula to minimize excess formaldehyde.

Boards with isocyanate-based binding agent are nearly free of formaldehyde, since only the covering layers are often glued with binding agents containing formaldehyde, since isocyanates also adhere well to metal, which would otherwise lead to pressing problems.

These are mainly the OSB (oriented strand boards) from the US with higher strength levels and a surface that is structured accordingly. They are used mainly in construction or for decorative purposes and do not emit any isocyanates, even when they are sawn.

Pressboards bind over 900 kg (CO_2-equiv.)/m (CO_2 sink). On the basis of the calorific value, other fossil energy carriers with CO_2 emissions of 700–800 kg can be saved per m of pressboard.

Table 5 compares the opportunities and risks of pressboard and massive wood.

For further reading see the end of this chapter.

3.2 Use of Composite Material Parts in Motor Vehicles

In motor vehicles, long glass fiber-reinforced parts with a matrix consisting of unsaturated polyester resin (SMC/sheet molding compounds) are used for example in front-ends, radiator grills, or bumper (frames). After utilization, they are discarded as waste by workshops or as part of the plastic and composite material share in used vehicles.

An analysis of the plastic wastes from automotive workshops reveals that a good 50 % of the entire plastic mass comes from bumpers. Estimates are based on replacement of about one pair of bumpers in every passenger vehicle. In principle, this material potential would be available from the workshops.

Figure 2 shows examples of fiber-reinforced waste materials in Western Europe from the automotive sector.

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[1] Classification in category 4 for cancerogenic materials TLV List, DFG, 2000.

Table 5 Opportunities and risks of pressboard compared with massive wood

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Form stability – Large surface area – Ready processability – Lack of grain – Consistent thickness – Good strength levels, especially OSB	– Low quality of thin edges in furniture – Edges cannot be bolted or nailed – Low level of moisture resistance
Economic	– Low price – Ready processability – No warpage, resulting in simplified construction of large-surfaced elements	– Raw material competitor of paper industry and energy production from biomass
Environmental	– Use of renewable raw materials – Waste volume reduction due to use of residual and waste wood – Material or thermal recycling after utilization phase – CO_2-neutral	– Formaldehyde emissions (D: regulated since 1986) – Emissions of wood preservative agents possible if used wood is integrated in material
Social	– Renewable and natural structural materials are available on a broad basis	– Production is shifted from skilled labor to industry

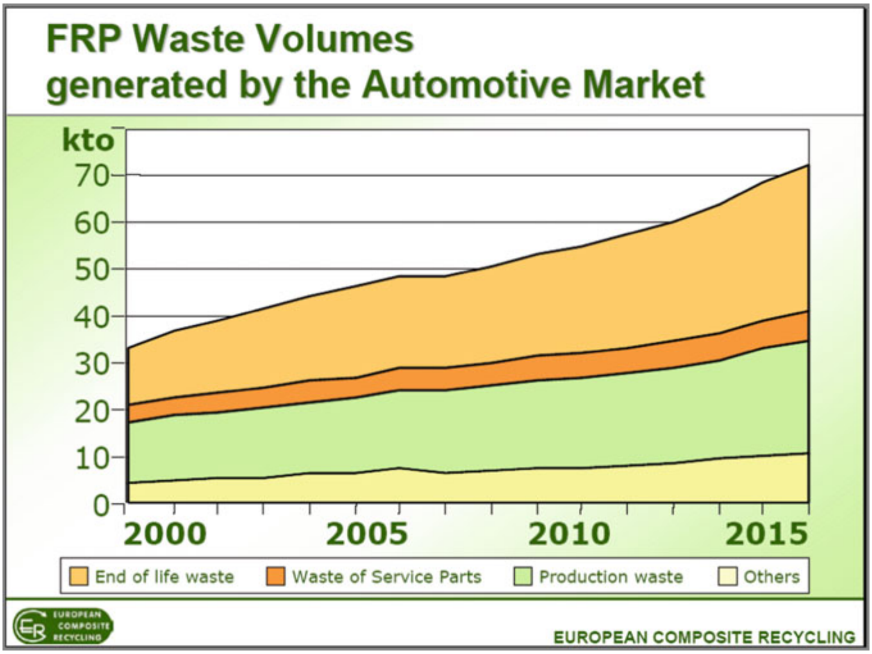

Fig. 2 Fiber-reinforced plastic waste generation in western Europe from automotive applications [12]

Such materials can also be expected from scrapped cars. The European Union, with its Directive 2000/53/EC dated 18.09.2000, established quotas as of 1.1.2006 for reuse and recycling of 85 % of scrapped vehicle weight (with a maximum of 5 % energy recycling) and beginning on 1.1.2015 95 % (with a maximum of 10 % energy recycling). Whereas the metal portions of the scrapped vehicle can be recovered efficiently in the shredder process, plastic and composite material recovery is still in the developmental stages. The quotas designated by the EU can be reached either by dismantling the used cars or by means of so-called "postshredder technologies" that make useful products out of the shredded material. Some postshredder technologies have been implemented in Belgium and Austria, and additional plants are planned in the near future.

Whereas gasification (production of synthetic gas) of the automotive shredder residues proved merely technically, but not economically viable, "postshredder" mechanical processing, for example in the "VW-SiCon" process that produces three fractions (lint as a dewatering agent, a high-calorific granulate and a mineral-rich fine fraction) was implemented in pilot and large scale. As things now stand, however, such methods are not yet capable of recycling the products in material form. On the other hand, these methods can be applied to all shredder wastes from passenger cars, i.e., for all plastic and composite material parts. Dismantling of used parts with the aim of material recycling often turns out to be so expensive compared to earnings from sale of the material or savings of disposal costs that it is often not done for economic reasons. Calculations showed that cost for recovered thermoplastic polymers from end of life vehicles might be up to five times higher than those of virgin materials.

However, if it does prove possible to separate the SMC parts from dismantling or from workshops, material recycling is readily feasible from a technical point of view: The material is comminuted and sieved in several stages to make fiber-matrix mixtures with fiber lengths up to about 20 mm. Technical applications for the fine fraction include integration as a filler in SMC production with about 8% less density than the standard calcium carbonate filler due to its composition. The fiber fractions up to 3 mm can be readily integrated as short fibers in thermoplastic matrices. The longer fiber fractions can, in principle, be used as fillers in concrete or sealing masses [13]. There was one pilot plant each in North America and Germany for mechanical processing of SMC, but they are no longer in operation for economic reasons (see Table 6).

More economical solutions are currently being sought in Europe, integrating organizational changes to redefine product responsibility by the "European Composite Association" (GPRMC) in the technical field, for instance by integrating other material flows, for example in incineration for energy production purposes or for pyrolysis [14], the aim being to comply with the EU requirements and reuse the material at a later time. The more stringent EU requirements regarding landfill wastes, resulting in higher landfill deposit prices, may tip the economic scale in favor of recycling solutions in the future. For example, landfill deposition fees are expected to rise in Germany due to the more stringent dumping conditions by more than 300 %.

Table 6 SMC – Material recycling

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technology	– Recycled filler material decreases SMC part weights up to 2.5 %	– Maximum recycled content in SMC parts limited to 40 %
Ecology	– Waste avoidance – Saving of landfill space – Saving of resources – Saving fuel due to weight savings from recycled content in car parts	– Additional transport emissions
Economy	– Lower disposal cost for shredder residues as their mass is decreased by dismantling of parts – Savings on fuel due to weight savings from recycled content in car parts	– High dismantling costs – Mechanical recycling is not economically viable as of today – Additional logistic costs
Social	– Job creation	– Lacking recycling options may lead to a political ban of the material

3.3 Interior Paneling Elements in Intercity Express (ICE) Trains

Paneling elements in ICE train interiors, as well as in some exterior parts (front paneling of ICE locomotives) and in the automotive, utility vehicle, construction and electrical industries in general – for example in bumpers, spoilers, windscreens, guest compartments, truck underclearance protectors, oil pans, switching cabinets, mobile radio antenna systems, trunk lids or hardtops (removable) – have been made for decades out of long fiber-reinforced duroplastics (unsaturated polyesters) in the form of sheet molding compounds (SMC) (see also Sect. 6.3 in chapter "Processing (Primary Forming) of Plastics into Structural Components"), and/or bulk molding compounds (BMC).

The semifinished goods used for this purpose are resin materials in the form of doughy, weakly crosslinked masses, mixed from the required components (UP resins, thermoplastic additives, styrene, fillers, E-glass, hardeners, initiators, dyestuffs, catalytic agents, separators, stabilizers, thickeners, and dispersants) before they are pressed or injection molded.

During processing into a finished part – for interior paneling in ICE trains by pressing at approximately 180 °C and for approximately 1 min reaction time per mm of part wall thickness – the chemical crosslinking reaction takes place (curing). In the process, radical formers, in most cases peroxides, open the double bonds of the linear unsaturated polyester. Linear polyester molecules are produced that form a spatial molecular network interconnected by monostyrene. Optimum mechanical properties are obtained when the linear polyester chains are connected statistically by two styrene molecules. Insufficient crosslinkage during processing results in styrene emissions from the interior paneling material. However, this problem can be solved by optimized processing conditions, so that today practically emission-free

Table 7 Opportunities and risks of SMC interior paneling elements in ICE trains compared with sheetmetal paneling

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Lighter – Other functions can be integrated at lower cost – Better noise dampening – Surface structuring – Inmold painting (IMP) possible	– Quality variations due to semifinished goods – Flammable with smoke gas formation – Splinters/tears open in accidents – Less absorption of energy
Economic	– Part costs lower if functions are integrated – With IMP costs lower than with sheetmetal painting	– Petroleum price – Material recycling complex and expensive
Environmental	– Weight savings lead to energy savings in utilization phase – With IMP emissions lower than with sheetmetal painting	– Styrene emissions if crosslinkage poor – Flammable with smoke gas formation – Recycling technically feasible, but limited in economic terms (see Sect. 2.3 in chapter, “Plastics and Structural Components – the Environment and Recycling”)
Social	– Jobs tend to stay in the country, since compared with steel specific know-how is required and production investment is lower – Use of natural fibers possible – Can preserve/create jobs in third-party countries	– Lower investment level may accelerate migration of technology to low-wage countries

SMC elements can be installed at no risk. The opportunities of excellent product properties over the entire life of the ICE interior paneling, and in all the other applications, outweigh the risks by far.

There are, however, clear disadvantages when it comes to maximum surface quality requirements (paint work) on upper class car bodies. High afterprocessing quotas have such a negative effect on the part costs that current improvements in the processing technique (direct processing without semifinished goods) are urgently awaited. If this does not work out, this application sector would have to be removed from the potential applications of “SMC.”

Table 7 shows the opportunities and risks of interior paneling elements made of unsaturated polyester in the SMC process, compared in terms of quality to paneling made of sheetmetal and painted.

4 Structural Components and Products Made of Elastomers

Section 3 in chapter “Synthesis (Manufacture, Production) of Plastics” lists a number of risks presented by the range of raw materials used in the rubber industry [1]. Section 5.3 in chapter, “Processing (Primary Forming) of Plastics into

Structural Components" and the further reading contain informations and references to waste gases and other wastes resulting from elastomer production.

Residual amounts of some of these problematical substances remain in the product (low molecular components) and permeate to the outside during the utilization phase. Other processes (aging, degradation) continue throughout the lifecycle of the product beginning with new status. The aging rate, for example hydrolysis, depends on environmental conditions such as temperature, pressure, mediums, and time.

4.1 Particles and Emissions in Automobile Tires

In view of the large amounts of material abraded from automobile tires (estimated abraded mass in Germany in the year 2000: 65,000 tons [15, 16], a summary is included here of the more detailed treatment of the subject provided by Schober, Stark and Strothenk [1] in [2]. Focusing on potential soil contamination, they report annual environmental contamination totaling 6–6.5 tons of polyaromatic hydrocarbons (PAH) – bound in the rubber matrix of the abraded tire material. PAH concentrations in the soil adjacent to highways drop off markedly beginning a few yards from the edge of the road. PAH enrichment is not observed in these roadside soils, since a balanced concentration of abraded tire material is established (16 g/m) at the depth of penetration of all 0.1 m of soil. The rate of contamination and constant chemical and biological degradation (0.7 % per day) has to be equal.

Although organic contaminants from the abraded tire material are apparently not enriched in the soil, some manufacturers are switching to alternative plasticizer oils with low PAH contamination levels [17, 18].

The *inorganic tread components* contained in the abraded material, *zinc* in particular, are not degraded, but rather remain in the soil where they are potentially enriched. In a *"worst-case scenario" with a zinc content of approximately 1.2 % in the abraded tire material*, soils adjacent to regional thoroughfares are contaminated with *approximately 1.2 g zinc per meter of road in both directions in Germany every year*. The *zinc oxide* contained in the tire tread *shows natural levels of contamination with cadmium oxide and lead(II)oxide, so that each year 0.0003 g cadmium and 0.0015 g lead are also deposited in Germany per meter of roadway in both directions along regional roads* (see Table 8).

Parallel to the process of chemical and biological degradation, components of the abraded material may also be washed out by precipitation water. *The elutive behavior of tires* and abraded tire material has already been investigated in a number of studies, in particular the possibility of contamination of the environment with components of rubber during utilization [19] and as the result of waste deposition [20]. These studies concluded that the environment can, in principle, be contaminated due to elution of antioxidants, vulcanization accelerators and the conversion products resulting from vulcanization [1].

Table 8 Annual emissions from abraded tire material in Germany for the year 2000 [1]

	Percentage by weight (%)	Total mass in Germany (t)	Total mass along 228,000 km of regional thoroughfares (t)	Mass per meter in both directions, regional thoroughfares (g)
Abraded tire material	100	65,000	46,000	100
PAH	0.01	6.5	4.6	0.01
Zinc oxide	1.5	975	690	1.5
Zinc	1.2	780	552	1.2
Cadmium	0.0003	0.195	0.138	0.0003
Lead	0.0015	0.975	0.690	0.0015

We users are certainly not aware of the risks involved in the product tire, the dominant elastomer product in terms of volume, in such detail. On the other hand, the opportunities afforded by our practically unrestricted mobility, with all of its consequences, leave us no alternative for the foreseeable future. Without rubber we would still be riding on leather-shod metal or wooden wheels.

As in most cases, the opportunities have to be weighed against the risks. Most users have opted in favor of rubber tires.

4.2 Rubber Plate for Children's Microscope

Similarly to the braiding material made of soft PVC (Sect. 1.2), cheap microscopes for children come from Taiwan, PR China, and other low-wage countries. The handling of the relevant plastic product risks is correspondingly irresponsible, whereby low prices are considered more important than the health of the consumer and the environment.

For example, the rubber base plates of such microscopes, and many other analogous products such as toy figures, emit hazardous substances such as amines, phenols, and many other formula components for months. Children peer through the microscopes with their noses only a few cm away from the material and these substances also accumulate in their rooms.

Here as well, the proper thing to do is to store such stinking plastic products for 6 months out of doors or to discard them immediately. In the case of toy figures, there are serious German manufacturers supplying emission-free products, and of course the price is much higher. But better no toys at all than harmful toys!

4.3 Condoms with High Carcinogenic Nitrosamine Levels

In the summer of 2004, [21] reported on a study by the Chemical and Veterinary Analysis Office, Stuttgart, according to which 29 of 32 condoms investigated contained considerable amounts of N-nitrosamines. In one condom with a chocolate flavor, the scientists from Stuttgart measured a nitrosamine concentration that was 60-times higher than the permitted threshold level in baby pacifiers. Although there is no such limit for condoms, the scientists state that the female body would absorb an amount of nitrosamine through the mucosa from use of one such condom per day that would be two to three times what the body takes in every day in foods (pickled meats, smoked bacon with added nitrite pickling salts, and tobacco smoke).

The German Cancer Research Center in Heidelberg recommended the limit value as applies to baby pacifiers according to [21]) as early as 1998 in a position paper sent to the Federal Institute for Drugs and Medical Products (BfArM) in Bonn. At the time, the Heidelberg experts were reacting to evidence of a connection between long-term use of condoms and breast cancer in women.

Explanatory note [21]:

In the rubber industry, chemicals containing amines are used as vulcanization accelerating agents, which may be transformed during the production process (vulcanization) into nitrosamines. Such substances are added to condoms to give the rubber the needed degree of elasticity.

5 Fiber Composite Materials

Plastics (thermoplastics, duroplastics, elastomers) have been reinforced for decades to enhance mainly mechanical properties with fibers (glass, carbon, aramide, metal, ceramic, natural).

E-short glass fibers are added to thermoplastics (0.1–0.5 mm long) in the injection molding process. Glass mat-reinforcements (GMT) feature fiber lengths in the cm range, pressed in semifinished elements. More recently, long-fiber applications in the direct pressing method (LFT-D) or inmold compounding (IMC) (injection molding) have come to the fore (see Sect. 1.1 in chapter, “Opportunities and Risks Involved in Designing Structural Components Made of Polymers”). Reinforcement with natural fibers (sisal, flax, hemp, Chinese reeds, etc.) are also attracting attention (see Sect. 1.2 in chapter, “Opportunities and Risks Involved in Designing Structural Components Made of Polymers”).

Duroplastics are rendered useful by addition of fillers or reinforcement fibers. For about 60 years now, the aerospace industry has been using mainly epoxide resin fiber-reinforced products. In addition to glass and aramide fibers, the main materials used in this field are carbon fibers. The predominant processing technologies are winding, drawing (pultrusion), or laying of saturated fiber bundles followed by pressing. In large-series automobile production, such applications have to date been found only in a few niche types (cardan shaft, steering column, etc.). In car racing, these high-performance fiber composites are the materials of choice. The best-known and most commonly used example of fiber-reinforced elastomers is found in tires (carcasses). Rubberized textiles are another large market.

The opportunities and risks of fiber composite materials are exemplified in brief by the following applications.

Table 9 Opportunities and risks of car door handles made of polypropylene GF 30 compared with a chromed metal handle

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Lighter – Cold haptics – Functions can be integrated, i.e., surface, sensory aspects – Lower coefficient of expansion (α) than nonreinforced PP – Galvanizing after intermediate layer also possible	– May break in case of accident or application of force – Glass fibers become shiny at surface after long use (aging) – α still too high – Sensitive to stress cracking when exposed to certain mediums – Long-term adhesion of galvanized layer uncertain
Economic	– Lower cost in overall system – Easy to install	– Petroleum price
Environmental	– Light construction saves energy in utilization phase; can lead to environmental advantage in overall view (see chapter, “Sustainability Assessment”)	– Poor recyclability of (aged) PP compared with metal solution; usually only as energy-producing fuel – Light waste fraction with shredder technique – Glass slag residue after incineration – Chrome plating is a critical process
Social	– Opportunities for innovation, since plastic applications are not exhausted	– Suppliers are subject to global competition: migration, shutdowns, risk of job loss

5.1 GFP-PP Car Door Handle

Pump casings for washing machines (PP-GF25), hand drill housings (PA-GF35), bumpers (EPDM-GF20), ventilator vanes (PP- or PA-GF30), and car door handles (PP-GF30) are just a few examples of the large number of applications for short glass fiber-reinforced thermoplastics.

With 10–40 % by weight short glass fibers (length 0.01–0.5 mm; mean length of glass fibers approximately 0.2 mm) mixed into, for example, polypropylene, the mechanical and thermal properties of the material can be improved to such an extent the applications listed above, often in housings and casings, can be realized.

Table 9 summarizes the opportunities and risks of this material group compared with metallic competitive products.

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Plastics and Structural Components: The Environment and Recycling

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Abstract Assuming the goal is sustainable development, it is important, when making ecological decisions, not to ignore economic aspects such as value added and profit use, whereby the profit earned could be put to either technical, social, or economic use. A holistic lifecycle approach therefore aims to support or find solutions that are technical feasible, ecologically, and socially defensible and economically rational. A definition of the overall optimum must always take into account the interactions between ecology, economy, and technology. Ecological optimization must not, for instance, be purchased at the cost of failing to satisfy minimum technical specifications or designing a project that cannot be financed as a whole.

Keywords Clean air, Databased balance, Degradable plastics, Environmental policies and protection regulations, Evaluation and interpretation, Food packaging, Framework, Holistic balancing, Impact assessment, Landfills, Lifecycle approach, Lifecycle engineering, Medicine, Ozone layer and greenhouse effect, Product lifecycles and recycling, Recycling of vulcanized elastomer wastes, Renewable raw materials, Toys, Waste products, Wastewater

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P. Eyerer (ed.), *Polymers – Opportunities and Risks I: General and Environmental Aspects,*
Hdb Env Chem (2010) 11,
DOI 10.1007/978-3-540-88417-0_8,

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1 Environmental Policies and Environmental Management (EM)

According to EEC Directive 1836/1893 of 29 June 1993, environmental policy-making covers “Measures directed toward lasting and environmentally compatible development, … in particular prevention, reduction and, as far as possible, elimination of environmental contamination at the source on the basis of the “polluter pays” principle, efficient management of raw materials sources and use of clean and cleaner technologies … Industry is responsible for bearing the environmental consequences of its activities and should therefore develop an active approach in this field. This responsibility demands that companies design and implement … effective environmental management systems …, providing not only for compliance with all relevant environmental regulations but also for the assumption of the obligation to ensure continuous improvement of operational environmental protection accordingly.” Such a “common system of environmental management and environmental operational assessment” encourages establishment of locally relevant environmental policy programs and management systems within the company that can be assessed and evaluated on a regular, systematic and objective basis, both by executive management and by licensed external experts. The public (and local neighbors of an operation in particular) should be drawn into an open dialog. An “environmental declaration” issued at regular intervals should, in addition to the above-mentioned objectives, include figures and data on contaminant emissions, waste for humans, consumption of raw materials, energy and water, noise emissions, visual effects, soil contamination and other environmentally relevant aspects as well as any operational emergencies or relevant changes made since the last environmental declaration was issued. On the basis of this European directive, the Draft DIN ISO 14001 of October, 1995 provides a structured plan for implementing such EM systems. Both the EU Directive and DIN ISO 14001 intentionally draw many parallels to quality management (QM) according to DIN EN ISO 9001. The control of the documents, the instructions for processes, testing and procedures, will have to be in accordance with QM principles if they are to function reliably. Although not mandatory, a EM Manual makes just as much sense as the QM Manual. EM can handle complaints from customers, the public at large and the authorities. Because of the safety regulations and technical standards involved, this of course also applies to QM in the private economy. If QM and EM are organized along similar lines and interrelated, as long as there are no conflicts of interest, this will make for a broader point of view and raise the level of awareness within the company.

In a corporate entity that is to be run on the basis of the principle of sustainability, environmental policymaking, environmental management and, and thus environmental protection as a whole, cannot be considered in isolation. Industrial safety, chemical safety, safety in general and the image of the company and its products in the eyes of employees and customers, are closely bound up with environmental policy.

In the polymer industry, for example, chemicals are used such as monomers, catalysts, accelerators, solvents, etc. involving hazards the employees must be informed about, and health risks they must be protected from. Waste air must be extracted, at specified locations and at frequent intervals. The degree of purification or cleaning, and thus of environmental contamination, can do good or harm to the surrounding area outside the company grounds.

A holistic point of view, i.e., preemptive planning and procedures based on long-term consequences, inside the company and out, will serve corporate success in the long run.

1.1 Environmental Protection Regulations

Maximum limits apply to the additives and residual monomers in plastics used in conjunction with foodstuffs. The immission limits (polluter-caused air contamination) are regulated by the *TA Luft* (Technical Clean Air Regulations) in Germany. Technical regulations have also been issued for solid wastes and wastewater.

Immission is the term for the air contamination affecting humans, animals or property. The maximum allowable workplace concentration, or TLV (threshold limit value) defines still-harmless levels of substances inherently dangerous to health under exposure for 8 h/d and 45 h/week.

The general principle applying to maximum allowable concentrations: Emission > TLV > immission. The immission limits for residential areas are the most stringent, applying as they do to uninterrupted day-and-night exposure.

The TLV values are relevant in curing of the following duroplastics: formaldehyde in PF, MF, UF; isocyanate in PUR, amines especially in cold-curing EP; styrene in UP. Emission values apply to these substances accordingly.

The assessment of health-related effects is based, for example, on the following contaminant effects:

Toxicity: Health-damaging effects, sometimes used as a general term for all of these effects, and sometimes also in a special sense for the triggering of acute or chronic illnesses other than cancer.

Carcinogenicity: Cancer-inducing effect (whereby the carcinogen has in most cases acted over a longer period). Carcinogenic monomers include in particular vinyl chloride and acrylonitrile. The permissible residual monomer content levels in plastics are very low.

Mutagenicity: Spontaneous or artificial changes in the genetic material (caused in particular by high-energy radiation or chemical substances).

Teratogenicity: Effects resulting in deformities (in an embryo via the mother, for example Contergan).

1.2 Food Packaging, Toys, Medicine

In Germany, the types and amounts of additives and residual monomers in plastics that come into contact with food products or are used in children's toys or in medical products are subject to restrictions according to the recommendations of the Federal Office of Health and Consumer Protection (formerly the Federal Health Office/*BGA*). Most pure polymers are physiologically harmless (exceptions e.g., PF, UF).

Here is a list of the advantages of plastic packaging: hygienic, clean, lightweight, unbreakable, hermetic sealing, and low-energy production. Developments serving waste avoidance: a refillable bottle for beverages containing CO_2 made of the composite PC-PA-(amorphous) PC that could be reused an average of 40 times and a maximum of 200 times (Manufacturer: (USA) GE-Plastics). A bottle made of the coextrudate PET-PVAL-PET can also be recycled (Manufacturer: (NL) Akzo). The middle layer in these designs serves as a barrier against CO_2 loss. A system of lightweight refill packages is helping reduce waste volumes in the nonfood sector. Then there are foil packages inside foldable cartons; these two components are readily separable for recycling and do not result in undue waste volumes.

1.3 Keeping the Air Clean

Clean air regulations for carcinogenic substances are particularly stringent, see vinyl chloride. Just as with vinyl chloride, emission reductions are also bound up with the recovery (recycling) of the volatile material (often an environmental contaminant) when it comes to solvents in paint processing or organic blowing agents used in PUR foam production. The solvents or blowing agents from the exhaust air are adsorbed to activated charcoal, then desorbed with water vapor, condensed and separated from the water in the phase separator. The yield from recovery can balance, or even exceed, the costs of emissions reduction.

Activated charcoal impregnated with catalyst can, for example, oxidize formaldehyde into harmless carbon dioxide or convert the highly toxic neural toxin hydrogen sulfide into elemental sulfur. For minor emitters, the impregnated activated charcoal powder is applied to open-celled PUR foam, making it easy to handle.

Use of solvents is avoided where possible in paint technology by means of special water-dispersible paint formulations. This is also the method now used in most cases to meet the high standards set in motor vehicle production. With two-component paints based on PUR-PMMA, low viscosity is achieved with low emission levels. Isocyanate crosslinking agents can be encapsulated in microspheres that prevent reaction with the bonding agent during storage and processing (manufacturer: (D) Bayer). The microspheres do not melt until they are heated to about 80 °C (in the curing oven), whereupon they release the isocyanate and chemical crosslinking cures the coating.

In the rubber industry, vulcanization accelerators based on secondary amines may form carcinogenic nitrosamines. This risk can be avoided by basing production on primary or tertiary amines or using zinc dialkyl phosphates (manufacturer: (D) Rhein-Chemie).

In rubber processing, exhaust air is produced in the following process steps [1]:

- Mixing
- Preform processing
- Vulcanization
- Aftervulcanization
- Cleaning of metals with organic solvents
- Application of adhesion promoter in conjunction with use of organic solvents.

In thermal treatment of the rubber mixture during vulcanization into rubber, components of the rubber mixture evaporate and so get into the air. Table 1 shows the expected resulting emissions for a given mixture based on laboratory tests. This may be a mixture with a high level of relevance in terms of the emission. The loss of oil and rubber may reach up to 4–5 % depending on the processing temperature.

The released substances must be kept away from the workplace and extracted for reasons related to work safety [1].

The German Technical Clean Air Regulations (*TA Luft*) describe the state of the art in terms of emissions limits.

Table 2 [1] summarizes the Germany Technical Clean Air Regulations (1986) in brief form.

The limits are listed for the categories dust, vapor, gaseous and carcinogenic substances, subclassified in three classes respectively:

Class I: highly hazardous substances

Class II: less hazardous substances

Table 1 Loss of mass (in g) from 100 g of mixture and proportional amounts of mixed-in rubber and plasticizer, heated for 20 min [1]

	Temperature (°C)		
	160	180	200
Mixture	1.94	2.08	2.3
Rubber	0.06	0.08	0.08
Plasticizer	0.018	0.021	0.040
Loss of oil and rubber	4 %	4.8 %	5.2 %

Table 2 Emissions limits acc. to German technical clean air regulations (*TA Luft*) [1]

Substances in class	Dusts Total dust Mass flux/emission levels	Vapors or gasses Organic substances Mass flux/emission level	Carcinogenic substances Mass flux/emission level
I	No classification[a]	$\geq$ 0.1 kg/h 20 mg/m^3	$\geq$ 0.5 g/h 0.1 mg/m^3
II		$\geq$ 2.0 kg/h 100 mg/m^3	$\geq$ 5.0 g/h 1.0 mg/m^3
III		$\geq$ 3.0 kg/h 150 mg/m^3	$\geq$ 25.0 g/h 5.0 mg/m^3
	Special inorganic substances Mass flux/emission level	Inorganic substances Mass flux/emission level	
I	$\geq$ 1.0 g/h 0.2 mg/m^3	$\geq$ 10 g/h 1 mg/m^3	
II	$\geq$ 5.0 g/h 1.0 mg/m^3	$\geq$ 50 g/h 5 mg/m^3	
III	$\geq$ 25.0 g/h 5.0 mg/m^3	$\geq$ 0.3 g/h 30 mg/m^3	
IV	– –	$\geq$ 5.0 g/h 500 mg/m^3	

[a] The dust emissions in waste gas must not exceed a mass per unit of volume of 50 mg/m^3 at a mass flux exceeding 0.0.5 kg/h or a mass per unit of volume of 0.0.15 g/m^3 at a mass flux up to and including 0.5 kg/h

Class III: low-hazard substances

"Substances in the form of vapors and gasses are significant for vulcanization plants. As long as there are no hazardous individual components in the waste gas, the state of the art in exhaust air cleaning dictates that a concentration of 150 mg organic substances per m not be exceeded at a contaminant concentration rate exceeding 3 kg organic substances per hour (limit for petty infractions). The total carbon concentration, which is easy to measure, is often used for technical reasons. 150 mg of organic substances are equivalent to approx. 75 mg carbon" [1].

1.4 Damage to the Ozone Layer and Greenhouse Effect

Ozone is a human and plant toxin and is therefore a pollutant in the atmosphere. In the much higher stratosphere, on the other hand, ozone absorbs shortwave UV radiation from the sun and thus protects us from skin cancer.

The foam propellant trichlorofluoromethane (FCHC 11), which is now prohibited, made its way along with other chlorine gasses up to these high air layers, where it is broken down by the high-energy solar radiation, which is unfiltered at these altitudes. The resulting chlorine radicals catalytically destroy ozone, O_3, in the cyclical radical chain reaction. The reaction $O_2 \rightarrow 2O_3$ requires sunlight, so the lost ozone cannot be regenerated in the South Pole winter, resulting in ozone layer depletion. Although ozone depletion is not observed to this extent in other geographic regions, ozone layer damage certainly is. When old refrigerators are disposed of, the FCHCs from the foam and refrigerant circulation systems must be recovered, retained and disposed of in a controlled manner.

The organic blowing agents in use today, for example (cyclo-)pentane, also contribute to the greenhouse effect and must therefore also be recovered: The heat radiating from the earth, especially in summer, is reflected back to earth by these gasses, and this effect can, over the longer term, raise the average temperature of the earth and cause climatic damage. The products of oxidation and degradation of these gasses are also undesirable atmospheric components. Safety precautions must be taken during production and use due to the risk of combustion and explosion. Their mid-level molar mass results in only moderate heat insulating qualities. This is best compensated by improved foam structure and greater foam densities.

Hydrogen fluoroalkanes (HFA), potential new blowing agents, are still in the development and pilot stages. There is no risk of combustion or explosion as long as the fluorine content is high enough. They contain no chlorine and therefore do not destroy ozone. Because of their hydrogen content, these substances are oxidized while still in the atmosphere, then washed out by rain. They still contribute to the greenhouse effect, and the environmental behavior of their oxidation and degradation products should be investigated. Recovery from production and deposition exhaust air is necessary. 1.1.1.4.4.4-Hexafluorobutane (manufacturer: Ⓓ Bayer) is an efficient heat insulator due to its high molar mass and minimum diffusion (half-life >100 years), forms closed microcells and does not initiate stress cracks. Its advantages are particularly in evidence in refrigeration transport vehicles. Liquid carbon dioxide as a blowing agent – for instance in the technology used by Cannon, Ⓓ Mülheim – is environmentally neutral on balance if previously obtained from the atmosphere; the environmental behavior of air or nitrogen as a blowing agent is also ideal, but the heat insulation capacity of these light gasses is limited. Foamless alternative: evacuated double walls.

1.5 Wastewater

Wastewater issues and problems differ widely depending on the particular parties and processes involved: polymer branch, raw material manufacturer, compounder, processor, moldmaker, machine manufacturer, surface processing, finishing, consumer, disposal agent and may include:

- Monomer or emulsifier contamination
- Solvent contamination in wastewater from painting processes and adhesive production
- Dyeing agents in fiber production and processing
- Oil contamination from cleaning of metals
- Acid or lye contamination from phosphatization or galvanization of plastic parts

- Contamination of water with adhesion promoter, for example with rubber–metal compounds
- Heat imbalance
- Etc., etc.

State-of-the-art technology includes a wide variety of solutions to these problems such as recirculation systems, water-based paints, aqueous dispersions, refrigeration plants, purification processes, filtration.

"In the above-mentioned cases it is necessary to determine which substances are contained in the wastewater. Then the contaminant types and concentrations discharged into the wastewater must be determined – especially hazardous substances. If the types and concentrations exceed the threshold levels (Indirect Discharger Ordinance), an official discharger permit must be obtained and a check run on whether the wastewater must be treated. As for exhaust air cleaning (Technical Clean Air Regulations), relevant administrative regulations (appendices to the wastewater administration regulations) list the concentration levels that represent the current state of the art in wastewater treatment. Appendix 40 applies to metals and lists the limits for heavy metals, for example zinc 2 mg/l" [1].

1.6 Waste Products

Waste products are materials resulting from the production process but not contributing to the product per se. A difference is drawn between reusable and disposable waste products and special wastes (usually hazardous wastes).

Some waste products in the rubber industry are discussed here that are exemplary for waste products in other branches as well.

Today, 50–80 % of the waste products from production are reused. Metal wastes, the largest contingent, are sold as scrap. The industry is making considerable efforts to recycle reusable waste products into its own, i.e., internal, processes. Nonreusable waste products are in most cases environmentally neutral and can thus be disposed of by way of deposition. In order to utilize existing waste deposit sites for as long as possible, German industry is attempting to reduce waste product volumes and to increase the proportion of reusable, pure-type substances (rubber, plastics, raw materials, etc.).

Collection of waste products in the form of pure types free of foreign substances has become the most important consideration regarding recycling and reuse, and thus reduction, of waste products.

1.7 Behavior of Material in Landfills

Most plastics show neutral behavior in landfills. Compostable plastics do not provide palpable relief in view of the continuing reduction of available waste deposit volume, since their substance volume is not appreciably reduced. Basically plastic materials are too valuable to dispose of as waste as neither their material qualities nor their energy content can be made use of.

Waste dumps are used to dispose of and store wastes. It is important to understand the difference between older dumps with mixed wastes, also known as “reactor landfills” because of the transformation processes taking place within them, and state-of-the-art landfills in which only pretreated wastes can be deposited. This pretreatment can be either thermal in nature (e.g., incineration) or of a biological–mechanical nature (sorting to obtain high calorific fractions, degradation of organic portions, and drying). At this level, larger shares of plastic materials should not end up in dumps since pretreatment would in most cases recycle them for their energy content.

Little is known about the behavior of plastics in reactor dumps, since these dumps are highly heterogeneous. As a rule, it can be assumed that most plastics will show neutral behavior in the dump. Within the dump corpus, however, peak temperatures of up to 80 °C can be caused by biological activity, with long-term temperatures of 40–50 °C, combined with an oxygen-free milieu with acidic or methanic fermentation, a process that may take decades. The resulting percolation fluids have pH levels of about 4–9 (Fig. 1), temperatures of up to about 30 °C, and high ionic concentration levels (conductivity 15–18 mS/cm). Depending on the material deposited, the percolation fluids may also contain for example organic solvents or organic degradation products, which in turn may interact with the plastics. Substances mobilized by such processes, for example plasticizers, are however also subject to degradation or adsorption processes in the dump corpus just like all the other substances and – once the percolation fluids have been collected – to percolation fluid treatment as well.

Detailed studies have been made on polymer barrier foil materials for combination barriers at the landfill base and surface (combination of plastic barrier foil and mineral sealing layer). Extensive stability studies were carried out regarding the

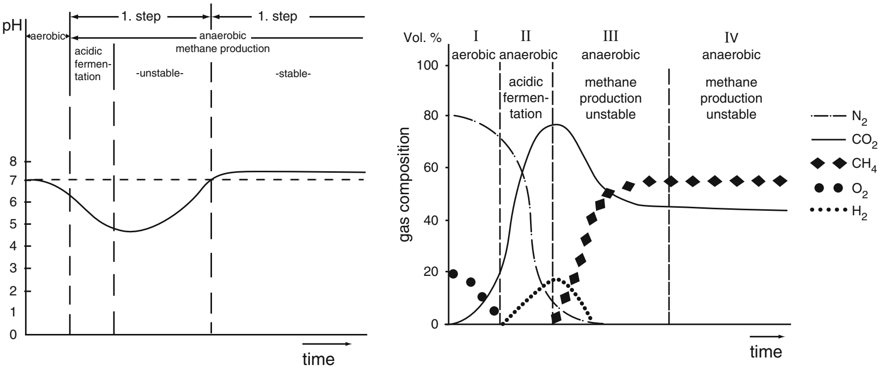


Fig. 1 Conditions in percolation water (*left*) and dump gas (*right*) during aging process in a settlement waste dump [2]

interaction of materials with liquids, for example fuels, alcohols, esters and ketones, organic acids, oxidizing mineral acids, lyes, salt solutions, and also with gas mixtures (methane/carbon dioxide) to simulate landfill gas. HDPE was selected as a suitable material for the 2.5-mm plastic barrier foil and was then used in numerous landfills. In addition to the mechanical requirements, for which stretching of approx. 3 % was assumed and weight load from the waste load could be up to 1,500 kN/m^2, the barrier/sealant qualities of the foil material was the main focus [3].

Compostable plastics provide little relief as to the increasingly rare landfill space available, since their substance is hardly reduced in the process: Anaerobic degradation processes in fermenters degrade about 35–60 % by weight of the mass placed in the system for fermentation. If the landfill corpus is considered to be a (nonoptimized) biogas reactor, degradation rates of the biodegradable materials (BM) on the order of 30 % would appear to be realistic.

1.8 Renewable Raw Materials, Degradable Plastics

The greenhouse gas carbon dioxide is emitted by the chemical breakdown of certain plastics, not using the energy content of the material which is not utilized. For this reason, such plastics are only used if their degradation process involves an additional utility factor. Examples of this are polyesteramide sacks for collecting plant material: the sacks rot together with the plant material (manufacturer: Ⓓ Bayer) and no toxic compounds are formed.

Thin-walled planting pots can be "planted" in the earth with the plant. The planting pot rots, allowing the roots to emerge. In surgical applications, interior sutures made of degradable plastics are used so that no additional surgical session is required to remove the interior sutures. Degradable plastic wastes should not be mixed with (recyclable) conventional plastic, since they may cause negative effects on the material properties during recycling.

Derivatives of cellulose, a renewable raw material, address only a minor market segment due to production expenses that are too high for mass articles. Flax is used as a reinforcing fiber, starch is used as a filler and plasticized starch can be used as a technical material [4]. The agricultural market regulations in the European Union inhibit industrial use of such materials. Many renewable raw materials could already be profitable at low world market price levels. Moreover, competition between materials applications and energy generation from renewable resources along with specific subsidies are interfering with the increasing application of renewables. Nonetheless, renewable resources are regarded to have the potential of replacing oil-based polymers in the long run. As of today, concepts like "bio-refineries" are under development, in order to use the synthesis processes of nature work as a basis for man-made materials. It can be expected that in future a remarkable portion of the materials carbon sources will be from renewable resources.

2 Product Lifecycles and Recycling

The demand for a "sustainable economy" includes economic, technical, social and ecological necessities, the aim being to ensure a balanced development that is "indefinitely self-sufficient," i.e., sustainable. The basic idea is to maintain the development potential of coming generations at the present level.

One aspect of ecological sustainability is the establishment of complete lifecycles of materials and products – recycling. The recycling qualities of materials cannot be defined in abstract terms, but always involve specific framework conditions, including for instance the purpose of use, possible alternative materials, material behavior during utilization and existing structures for recycling or disposal of used products: In the 1980s, plastics were often considered nonrecyclable. In recent decades, numerous methods have been developed and partly realized on a major technical scale, to recycle and reuse plastic materials in the areas of packaging, electrical and electronic products and used motor vehicles. Legal requirements have played a key role in these developments, increasingly demanding that manufacturers assume product responsibility before the products are marketed and also that they assume responsibility for final disposal of their products. This product responsibility includes informing users about how the products can be disposed of and establishing structures to collect, dismantle, sort, and reutilize the products (see "Decision of Residual Value" in Fig. 2). The aim of lifecycle completion was and is to preserve natural resources by reducing material consumption volumes and disposal volume requirements.

In addition to these considerations of the postuse phase, the steps of product design, production, and utilization are also relevant to sustainability. During product design, the potentials for sustainable forms of product use and disposal are determined. In the production phase, matters such as working conditions become relevant. During the use phase, the effects of a product on humans and the

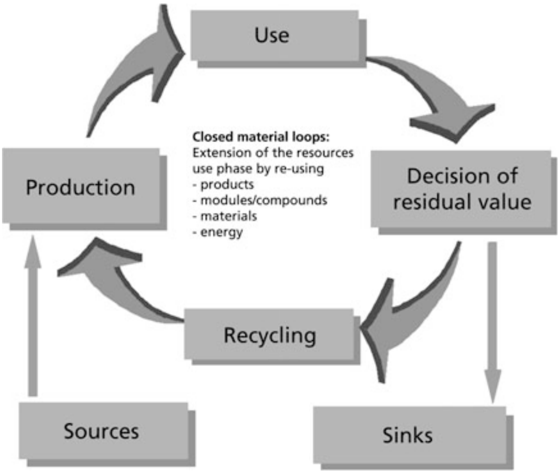


Fig. 2 Basic principle of a product lifecycle

Table 3 Opportunities and risks of product life cycles and recycling

Segment	Evaluation	
	Opportunities (advantages)	Risks (disadvantages)
Technical	– Material solutions that meet requirements by means of additives and compounding of used materials – Product responsibility results in product innovation	– Material variety reduces potential for material recycling – Recyclates often show different material properties than the corresponding new products – Recyclates require variation-tolerant processing methods or expensive processing
Economic	– Cost savings by means of recyclate use – Reliable regional material sources and no dependence on international raw materials markets	– Dismantling and processing of old products more expensive than new products – Separation of waste fractions increase recycling cost – Political framework cannot enforce economical solutions
Environmental	– Minimization of wastes and disposal requirements – Minimization of resource consumption	– Entrainment/spread of contaminants and pollutants in recyclates – In some areas, recyclate production and processing contaminates the environment more than new products
Social	– Job opportunities for persons with specific qualifications	– Work with wastes is of low social ranking – Waste separation requires additional household working hours – In some cases hygienically questionable jobs

environment are added to the considerations relevant to its overall sustainability. The standardized method of ecological balancing/lifecycle assessment in the standard series DIN ISO 14040ff can be used as a basis for detailed investigations of the environmental effects of a product.

Table 3 shows the opportunities and risks of product life cycles and recycling.

2.1 Component Re-Use

The reuse of parts or components closes a small product lifecycle with fewer process steps than production of new components. This puts reuse at a high level in the ecological ranking of the recycling methods. Plastic components are, however, often used as housings or external parts of different products, whereby their variability constitutes a major contribution to the stylistic design differentiation of product generations, so that old components can rarely be used in the following generation of products. On the other hand, reuse of plastic parts may make sense for products for which replacement parts are kept in a closing inventory, the scope of which can be supplemented by reuse of product returns. The total volume of such reuse is of course limited, as seen in the example of used cars: Currently, the parts from 10 to 20 % of deregistered vehicles are reused, with dismantling of plastic parts in a similar percentage, but only about 3 % by weight of old cars are recycled in the parts lifecycle. A wide variety of recycling options can be found with tires: The reuse of automobile tires requires general reconditioning for low and medium-level applications, for example in passenger cars (approx. 12 %) and trucks (68 %). Continued utilization of tires is seen in agriculture (weights for plastic sheeting), in harbors (as dampers along quay walls), on ships and as playground elements (also to dampen impact).

2.2 Potential Material Lifecycles

Table 4 illustrates the recycling options for polymer materials.

The reuse of production wastes (gates, flashes) is state-of-the-art practice to reduce material consumption. Grinders of different sizes are used and the ground material is reintroduced directly into the production process.

The quality of recyclates from recycling of old parts should be as high and uniform as possible. An important parameter for old parts with a thermoplastic polymer matrix is the chain length. Aging and processing influences the polymer chain length, resulting in poorer material parameters in thermoplastic polymers that

Table 4 Material options in plastic reutilization

Polymer system	Material recyclability
Thermoplastics and thermoplastic elastomers	1. Regranulation (use of recyclate only) 2. Compounding (mixtures with new material)
Glass fiber-reinforced thermoplastics	1. Regranulation (use of recyclate only) 2. Compounding (mixtures with new material) 3. In glass mat-reinforced thermoplastics (GMT) extrusion (secondary forming of the structural components)
Thermosets	Particle recycling: 1. Use of the finely ground mass as filler 2. Use of glass fibers in reinforced masses (SMC/BMC) in new material
Thermoplastic or thermoset polyurethanes[a]	1. Further processing as with thermoplastics 2. Extrusion 3. Grinding and use as PUR filler 4. Particle composite (comminute PUR and compress with bonding agents, with soft foam as a flocculated composite, with hard foam by means of adhesion molding)
Elastomers	Old tires rendered into pieces, granulate or ground material in grinder. Products for underbody, sound insulation board, insulating material, regrind for tires, conveyor belts, mats, soles

[a] This separate classification is standard practice in the automotive industry

have been processed repeatedly and aged. The influence of aging of duroplastic matrix materials on recyclate quality appears, on the other hand, to be minor.

Reuse of used materials without modification is rare. As a rule, new material is mixed in and additives and compounding are used to adjust the properties. Recyclate percentages up to 30 % by mass have proved useful in products in which parameters comparable to those of new material are sought.

An important element in thermoplastics recycling is melt filtration to separate out unmelted or unmeltable shares in the polymer. These particles are held back by metal textiles or perforated plates and flushed out of the poymer melt with a partial current . The loss of polymer melt mass amounts to about 3–5 % plus the mass of the separated particles.

The external causes of aging in exposed parts made of plastics include weather influences (UV radiation, water uptake, gas exposure, temperature changes) and continuous dynamic stress. In pigmented structural components, damage due to UV radiation only affects the outer layer to a depth of 300 μm, below which the material remains essentially unchanged. A coat of paint influences moisture and oxygen uptake, radiation absorption and mechanical stressing. Plastics are also attacked by, for example, high temperatures, oil, fuels, and acids. Reprocessing of the material also damages the polymer itself. Besides these signs of chemical aging, recyclate quality is also affected by contaminants such as incompatible polymers, paints, adhesives, or soiling (such as dust or adhesive labels). With paint in particular, paint particles can cause defects in recycled thermoplastic structural components that can reduce impact strength, for example, to a considerable degree.

Material compatibility is therefore an important precondition for material recycling. Even in tiny quantities, impurities in the form of incompatible material types may reduce the quality of recyclates, or components containing recyclates, to such an extent that recycling is hindered or even prevented. VDI Guideline 2243 [5], for example, provides information on plastics engineering compatible with recycling processes.

2.3 Recycling of Crosslinked Polymer Materials

2.3.1 Recycling of Thermosets: Particle Recycling

The fact that thermosets cannot be subjected to secondary forming calls for different material reutilization methods than those applied to thermoplastics. For example, the basic principle of SMC particle recycling is comminution. Table 5 provides an overview of possible reuses for SMC regrind fractions.

Particle recycling is the term used for integration of comminuted, chemically unchanged duroplastic particles or fibers in a duroplastic matrix consisting of primary material. The objective of particle recycling is either recovery of the glass fibers in order to make further use of their reinforcing qualities or use of all of the matrix and reinforcing material in finely powdered form as a filler substitute.

Table 5 Potential uses for comminuted SMC [6]

Particle size	Potential uses
> 25 mm	Building material, plywood, light concrete, insulating material, agricultural mulch
ca. 3–10 mm	Reinforcing or filling material in bituminous sealing masses, polymer concrete, roadbuilding material, glass fiber substitute in polymeric matrices
< 0.8 mm	Filling material in SMC, BMC and thermoplastics (particle recycling)

Particle recycling comprises the following steps:

1. Comminution,
2. Classifying,
3. Preparation of the molding compound including recyclate,
4. Forming and compression molding [7].

2.3.2 Recycling of Elastomeric Materials

The material recycling of rubber is only feasible within narrow limits. This applies above all to technical rubber articles such as bellows, sealing elements (radial shaft gaskets, O-rings, sealing profiles), tire tubes, rubber–metal dampers, etc. that are made up of a number of different types of rubber.

Besides the problem of type purity, the same problems apply as to other technical plastics, i.e., procurement of material flow volumes that have to “fit the bill” as to place, time, and costs. Aging processes and permeation of additives within the polymer material restrict material recycling of technical rubber components to very few special cases.

“On the other hand, it makes sense to use this material thermally, as a secondary raw material. The calorific value of “rubber” is about equivalent to that of lignite. Today, a major portion of rubber wastes is used in cement kilns as a source of energy. However, all types of rubber containing chlorine and fluorine are excluded from such applications. These types, to the extent small-scale material recycling is not possible, must still be disposed of in waste deposits” [1].

2.4 Biodegradable Polymers (Biodegradable Materials)

Biodegradable polymers are often (incorrectly) considered to be the same as polymers made from renewable raw materials, although the two properties are not necessarily coupled. BM can be degraded, under certain ambient conditions (temperature, moisture, presence of microorganisms), either aerobically by composting or anaerobically by fermentation. The appropriate method can be determined by means of tests such as those described in EN 13432 [8].

In synthetically produced polymers, biodegradability is achieved by reducing the stabilizer content and/or addition of initiators that accelerate biodegradation. Materials in this group include, for example, PHB (polyhydroxybutyrate) and PLA (polylactic acid) [9]. Other polymers use a blend of both types, for example a combination of polyethylene and starch.

Until now, BMs have only established niche markets, for example as tableware or plastic forks, knives and spoons for mass events, or in agricultural applications as pots or mulch foils. The technical and economic conditions in these areas are promising for BMs. Such advantages have not yet been realized fully, for example in substitution of BMs for mass-produced plastics, especially since they have some drawbacks as waste material. For instance, mixing BMs with mass-produced plastics is problematical due to incompatibilities.

2.5 Polymer Compatibilities

Obtaining pure-type plastics for recycling often involves significant effort and expenditure. In principle, however, material recycling is not impossible in such cases if the polymers in the mixture are compatible and miscible and can therefore be processed together. Compatibility matrices (Table 6) help assess the material compatibility of different plastic types in mixtures.

2.6 Raw Material Recycling

Raw material recycling goes back to the chemical base units of the polymers, which are reused, for example in polymer synthesis, production of other chemical

Table 6 Compatibility matrix for polymers [10]

Added material	PE	PP	PS	PVC	PET	PC	PA	PBT
PE	1	3–4	4	4	4	4	2–4	4
PP	2–4	1	4	4	4	4	2–4	4
PS	4	4	1	4	3	2–4	3–4	3–4
PVC	4	4	2–4	1	4	3–4	4	4
PET	4	4	4	4	1	1	3–4	4
PC	4	4	2–4	4	1	1	3–4	1
PA	4	4	3–4	4	3	4	1	3
PBT	4	4	2–4	4	4, 3	1	3–4	1

1 = readily compatible; 2 = miscible up to approx. 20 %; 3 = miscible up to approx. 5 %; 4 = incompatible

products such as paints or adhesives, or as substitutes for petroleum or its derivatives.

2.6.1 Taking into Solution

When polymers are taken into solution, they are not broken down into monomers, but rather the macromolecules are dissolved in a solvent while retaining their structure, so that solid fillers and additives can be filtered out. The polymers and the solvent are then separated by means of evaporation and distillation or precipitation [11]. The total energy requirement of the process, depending on the solvent content level, is between 1.5 and 3 kWh/kg of released polymer. Thermoplastics are soluble in given solvents depending on their polarity, and this principle is made use of, for instance, in paint production. PP is soluble, for example in xylene, acetone and tetrachloroethene [12]. The dissolution takes place above all in the amorphous regions of the polymer, crystalline regions being highly resistant. The problems involved include toxicity and handling (risk of explosion) of some solvents as well as the high levels of energy demand for solvent regeneration.

2.6.2 Solvolysis

The solvolytic processes hydrolysis, alcoholysis, glycolysis, and aminolysis are suitable for recycling of products of polycondensation and polyaddition [13]. Since these are balanced-reaction processes, the primary material can be broken down into its monomers at a high temperature and with appropriate additives. A differentiation is drawn between summative and selective solvolytic processes. These processes are applied to polyesters, styrenics, and polyurethanes on a large scale as of today, and other (selective) polymers solvolysis solutions are under development.

2.6.3 Input of Polymeric Materials into Petroleum Processing

Plastics must be pretreated to render them pumpable before they can be used in petroleum processing. The pumpability of thermoplastics is achieved by means of a reduction of the molar mass to 1,000–15,000 g/mol (chain shortening). Duroplastics can be reduced to less than 100 μm by means of mechanical comminution and slurrying with small amounts of petroleum intermediate products and introduced into the process via the classic “coal pathway” as a suspension [14]. This makes it possible to close the material lifecycle of polymers completely by breaking them down into low molecular products, which are then fed into refineries for polymer synthesis. When these materials are fed into a refinery, however, their chlorine content must not exceed 1 ppm.

Large-scale plants for cracking and compounding high-boiling, long-chained residue fractions resulting from petroleum processing are available. The methods for integrating polymer materials into petroleum processing include thermal and

Table 7 Overview of methods for integrating polymers into petroleum processing

Process	Starting materials	Products[a]	Brief characterization
Thermal cracking			
Visbreaking	Vacuum residue[b]	Middle distillate components	Pressureless method of reduction of molar mass at temperatures of 350–480 °C in a tube furnace at 1.4–1.8 MPa
Delayed coking	Atmospheric residue, heavy oil[b]	Petrocoke, gas oil, gasoline, cracking gasses	Discontinuous treatment with heatup to approx. 490 °C and coking in coking chamber at 2 MPa, 460 °C
Fluid coking	Vacuum residue[b]	Petrocoke, gas oil, gasoline, cracking gasses	Continuous treatment in fluidized bed at 480–560 °C
Steam cracking	Low-boiling fractions (ethane, light gasoline), naphtha[b]	Ethene, propene, other olefins	Conversion at approx. 600–900 °C, 2–3.3 MPa with addition of water vapor to increase olefin yield
Catalytic cracking			
Cat cracking	Distillate fractions, metal-/residual fractions low in heteroatoms[b]	Liquefied petroleum gas (LPG), gasoline, gas oil	Catalytic treatment in fluidized bed or moving bed reactor at 0.6–0.9 MPa, 450–510 °C
Hydrogenation			
Hydrocracking	Residual products (vacuum residue), naphtha[b]	Light heating oil, gasoline, synthetic crude oil made from residual products, LPG made from naphtha	Catalytic treatment at high pressures (7–25 MPa) and temperatures (250–450 °C) to crack the C chains
Degradative extrusion			
Degradative extrusion	Thermoplastic polymers with low unmeltable moiety	Oil-like/wax-like, atomizable melts	Polymer chain degradation in modified extruder at temperatures up to approx. 400 °C Optional addition of gasification mediums or catalysts[c]

[a] Boiling ranges (guidelines): up to 100 °C light gasoline, up to 200 °C heavy gasoline/naphtha, up to 250 °C kerosene/petroleum, up to 350 °C gas oil

[b] Addition of polymers to the starting material involves only a small partial current

[c] Since this cracking process is cannot be definitively categorized as either thermal or catalytic, it is listed separately in the table

catalytic cracking as well as hydrogenation (Table 7). A coal–oil plant in Bottrop/Germany, shut down for economic reasons, was used for pretreatment of polymers before returning them to refineries. In addition to this hydrogenation method, other technical operations for conversion of polymers have been tried in pilot processes and only with unreinforced polymers. Hydrogenation (liquefaction by application of heat and pressure) of rubber with attachment of hydrogen results in a synthetic oil for further refining.

2.6.4 Pyrolysis

Pyrolysis is the pressureless thermal disintegration of substances without a gasification medium. The starting materials are converted radically into hydrogen-enriched, volatile pyrolytic gasses and oils, water as well as low-hydrogen, solid pyrolytic coke. Three types are classified according to the treatment temperatures: low-temperature (up to 500 °C), medium-temperature (500–800 °C), and high-temperature pyrolysis (above 800 °C). Raising the pyrolytic temperature can shift the product type distribution from oil to gas [15]. A particularly advantageous aspect of pyrolysis compared to combustion is the lower gas flow volume, which accounts for approx. 5–20 % of the combustion smoke gas flow. The much smaller gas scrubbers required mean lower investment costs.

In the gas treatment phase, the pyrolytic gas is normally separated by cooling into one or more oil fractions with different boiling ranges and the permanent gas with the main components H_2, CO, CO_2, and CH_4. The condensable oils are chemically unstable and require treatment, for example hydrogenation or direct conversion in combination processes.

The coke, the solid product of pyrolysis, contains the mineral and nonoutgassable components of the starting material. It is brittle when cooled, so that mineral moieties can be separated out by means of mechanical comminution and classifying methods. Utilization of this material is still being worked out [16].

Fluidized bed and rotary drum reactors have been identified and tested as the best-suited aggregates for pyrolysis of plastics. Residence times in rotary drum reactors are between 20 and 90 min [17], in fluidized bed reactors up to approx. 90 s [18]. With plastics in particular, poor heat conduction and the high energy requirements of plastic disintegration do not speak in favor of pyrolysis (Fig. 3).

2.6.5 Gasification

In the gasification process, carbon is converted into gaseous products by substoichiometric oxidation. The process can be divided into the idealized partial stages of drying, outgasing and gasification. The partial oxidation of outgassing products releases heat that in turn contributes to the endothermic processes of drying and outgassing. The gasification temperature is set by adjusting the oxygen input.

Hydrocarbons are converted into synthesis gas in the presence of gasification mediums (oxygen, air, water vapor) at 1,350–1,600 °C and 15 MPa. This gas shows varying compositions depending on the process conditions and can be used in ammonia or methanol synthesis, Fischer–Tropsch synthesis of hydrocarbons, hydrogen production or as an energy source [15]. The high pressures and temperatures involved reduce all higher molecular structures to CO and H_2. Inorganic pollutants (hydrogen chloride, ammonia, sulfur compounds, dust) can be separated by the gas treatment and in some cases utilized.

In Germany, the Secondary Raw Material Utilization Centre *Schwarze Pumpe* formerly ran a gasification process for a variety of wastes.

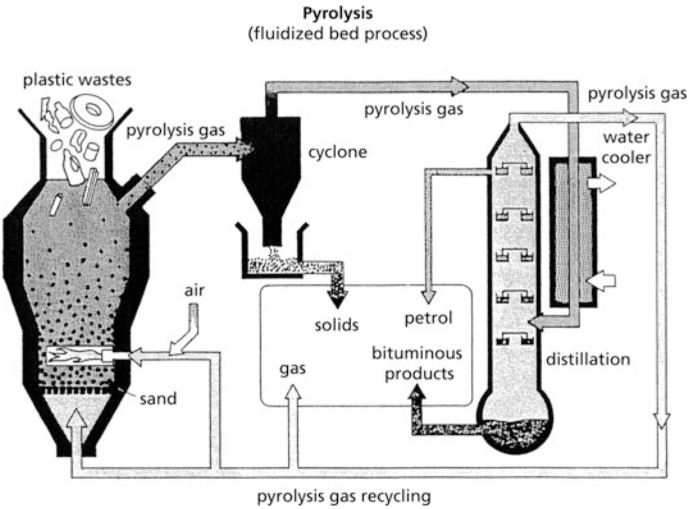


Fig. 3 Pyrolysis of plastic wastes at 600–900 °C under exclusion of oxygen in a reactor with a fluidized bed of sand that behaves like a high-density liquid, keeps the plastic waste suspended and makes heat transfer more efficient (photography by: Plastics Europe)

2.6.6 Blast Furnace Injection

Fractions with high calorific values can be used in cupola or blast furnaces in production or processing of iron. Cupola furnaces are used mainly to melt scrap metal with coke. In blast furnaces, metallic iron is melted in iron ore reduction. For this purpose, along with the coke highly sulfurous heavy oil or coal is injected and gasified with the hot blast. Plastic material can substitute the heavy oil to a certain extent [19]. Use of plastics in blast furnaces require prior comminution to a diameter of max. 5 mm, since this granulate is introduced into the lower section of the blast furnace out of a pressurized container at 0.4–0.5 MPa through a lance.

2.6.7 Use in Rotary Cement Kilns

In the rotary kiln of cement works, clay and lime are sintered or burnt into cement clinker. The reactor is run in counterflow: Primary firing heats the material to approx. 1,400 °C, secondary firing in the loading area ensures calcinations at approx. 900 °C. Approximately 3.3 GJ energy are required for production of 1 Mg cement [20]. To reduce the energy costs, which account for approx. 50 % of the production costs, substitute fuels such as old tires, used oil, paint sludges, sawdust or refuse-derived fuels are used. As much as 30 % of the total heat requirement of a plant have been covered by these secondary fuels [21], the solid residues of which are integrated into the product [19].

2.7 Incineration

The materials properties of the material used is lost in incineration, so that this method cannot be considered material recycling in any real sense.

The incineration process can be subdivided into the partial processes drying, outgassing, gasification, and complete oxidation (Fig. 4) [17]. These idealized processes may overlap both spatially and in time and influence each other. Pyrolytic and gasification methods involve adjustment of the framework conditions so as to favor selected processes.

2.7.1 Incineration Concepts and Aggregates

Feasible incineration concepts:

- Monoincineration of plastics only
- Coincineration systems with combined incineration of at least one fraction besides plastic [22].

Drying:	Evaporation of water	
Outgassing / pyrolysis:	Endothermic disintegration reaction without gasification mediums at 150 – 650°C:	
	Organ. compounds $\leftrightarrow$ pyrolytic gas + pyrolytic coke	
	$\Delta H > 0$ kJ/mol	
Gasification:	Conversion of solid carbon by means of partial oxidation with a gasification medium at 650 – 900°C:	
	$C + \frac{1}{2} O_2 \rightarrow CO$	$\Delta H = -123$ kJ/mol
Incineration:	Conversion of all gaseous compounds by means of complete oxidation to CO_2 and water vapor at 750 – 1.100°C:	
	$C + \frac{1}{2} O_2 \rightarrow CO$	$\Delta H = -123$ kJ/mol
	$\underline{CO + \frac{1}{2} O_2 \rightarrow CO_2}$	$\underline{\Delta H = -283 \text{ kJ/mol}}$
	$C + O_2 \rightarrow CO_2$	$\Delta H = -406$ kJ/mol
Secondary reactions:	$C + H_2O \leftrightarrow CO + H_2$	$\Delta H = 119$ kJ/mol
	$C + CO_2 \leftrightarrow 2\,CO$	$\Delta H = 162$ kJ/mol
	$C + 2\,H_2 \leftrightarrow CH_4$	$\Delta H = -87$ kJ/mol
	$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H = -42$ kJ/mol
	$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O$	$\Delta H = -206$ kJ/mol

Fig. 4 Idealized partial chemical processes in incineration

Monoincineration of plastics in special aggregates is not yet state of the art. The relevant incineration aggregates used for solids include:

- Grates (mainly bar and roller grates),
- Drum furnaces (with uniflow or counterflow air feed),
- Fluidized bed (with stationary, rotating, or circulating fluidized bed)
- Dust firing.

2.7.2 Incineration in Power Plants

Fluidized bed or dust firing is used to incinerate high-calorific fractions in power plants [19]. In dust firing, the starting material is ground, then injected through a burner into the furnace chamber, where it is incinerated.

As a preparation for pneumatic furnace chamber injection, the plastics must either be melted or ground before they can be fed into the furnace chamber. Coal is ground to grain sizes below 100 μm to ensure complete incineration. Such fine comminution poses problems with thermoplastics in particular due to heating of the polymer from the mechanical stress. With cyclone furnace chambers, larger grain sizes up to several millimeters are possible, since the furnace chamber geometry enables a much longer residence time [15].

2.7.3 Incineration in Waste Incineration Plants

Unfilled and unreinforced plastics have high calorific values, low moisture contents and therefore gasify, ignite quickly and incinerate at low temperatures [22]. The calorific value of reinforced plastics depends on their chemical composition and the portion of mineral filling and reinforcing materials. Table 8 provides an overview of the calorific values of different materials.

In addition to the calorific value, the moisture and ash content of a material are essential parameters for self-perpetuating incineration in waste incineration plants: Self-perpetuating incineration can be expected beginning at approx. 3.4 MJ/kg, a water content under 50 %, and an ash content level below 60 % [17].

2.8 Perspectives

A wide variety of technical options are available for the recycling of plastics and products containing plastics, although only a small number of these methods have actually been implemented in pilot and production scale. In addition to the technical suitability of the methods, economic and political conditions are decisive for development and operation of recycling processes. In areas in which direct advantages (mainly economic in nature) are generated from the start, for example in

Table 8 Calorific values of different materials

Material	Calorific value H_u (MJ/kg)
PP (unreinforced)	44
PE (unreinforced)	43.3
PS	40
PVC	18–26
Glass mat reinforced thermoplastics	30
Duroplasticics (in general)	20
SMC/BMC (UP-GF)	10–12
Petroleum/heating oil	42
Hard coal	29–30
Wood	15–17
Paper	13–15
Household wastes	8.5

recycling of production waste material, such new processes have always been implemented rapidly and then run continuously. For some time, additional steps to complete ecological lifecycles received considerable political support with a focus on the ecological dimension of sustainability. Currently, some aspects of sustainability appear to be the subject of a reevaluation: Economic aspects of sustainability in particular are beginning to influence the discourse. In future specific “island solutions” for minor material flow volumes from individual applications can hardly expect to be implemented unless society at large shows support, or the economics favor this solution. Instead, large uniform material flow volumes from various different applications will be combined, utilized, or disposed of by the cheapest means available (e.g., blast furnaces, gasification or incineration plants), wherever capacities are sufficient and the basic ecological regulations can be satisfied.

3 Example: Recycling of Vulcanized Elastomer Wastes and/or Products, in Particular from Used Vehicles

The term “balancing” is reminiscent of ledger-sheet economics, plus and minus columns, costs and benefits. Balance sheets are used as a basis for making decisions and a control instrument and are, as a rule, geared toward expenditures and costs. In the past, decisions concerning materials, processes and products were usually made according to technical and economic parameters. Ecological aspects were only integrated in isolated projects. Now, effective and proven tools for these tasks, standardized in ISO 14040 ff., are available in the form of the instrument for ecological balancing (or lifecycle assessment (LCA)) and its further development holistic balancing (or lifecycle engineering (LCE)). A further advantage of this method is that its application does not depend on certain materials or products, so that it can be used to compare, and improve, competing materials (e.g., plastics vs. metals, renewable raw materials vs. fossil materials, etc.) and technologies.

Development of professional software tools with extensive background databases has continued over the past 15 years and provides a basis for efficient realization of studies covering both industrial product and process development and detailed analysis in the context of scientific research.

In contrast to thermoplastic materials, crosslinked (vulcanized) elastomer products cannot be remelted. This puts narrow limits on material recycling or reuse. The case is different with the recycling and reuse of tires, the main elastomeric product.

For decades now, car and truck tires have been retreaded on an enormous scale (recycling). Their reuse, above all in agricultural applications as foil weights/covering, etc. is also widespread.

Figure 5 lists general recycling alternatives for used rubber [23].

Figure 6 lists the enormous amount of used rubber wastes, approx. one million tons annually in Germany, according to application.

The percentage of tire retreads for cars is approx. 21 %, for light trucks 4 %, for trucks 75 %. The difference in price compared to new tires is 30–40 %.

In view of German used care recycling (used vehicle regulations) and the European Directive EU-DIR 2000/53/EC with all of its time and recycling provisions, Fig. 7, vehicle manufacturers are under considerable pressure to undertake something.

This pressure hardly exists for used car tires, as seen in Fig. 8.

The problem of how to recycle or dispose of vulcanized elastomer wastes/products is therefore acute for the approx. 0.4 million ton p.a. of technical products, especially profiles, tubes, and molded articles.

The annual volume of used rubber parts that can usefully be removed from the vehicles is estimated at approx. 160,000 ton, of which approx. 50,000 ton come from used vehicles and the rest from other application areas (seals, tubes, profiles, shoe soles, vibration dampeners, drive belts, etc.) [26].

Economical dismantling and removal of elastomeric parts such as seal elements (flat and radial shaft, door, trunk and window seals, roof strips), tubes and hoses (brake, cooling water, refrigerant, fuel hoses), vibration dampeners (engine mounts), drive elements (v-belts, toothed belts, ribbed v-belts), moldings (bellows, sleeves, membranes) or air-charged spring systems, etc. is feasible to a limited extent only as far as material recovery and recycling are concerned.

Another aspect is that modern elastomer parts are made of a wide variety of elastomer types and/or are combined with metals or other plastics in material composites for the purpose of realizing additional functions such as sensory aspects, insertions, strength elements, textiles attached by gluing or vulcanization, lubricant coatings, installation elements, flocculation applications, paint coats, etc.

As far as material recycling is concerned, the opportunity represented by plastics (including elastomers), i.e., the integration of various additional functions, can quickly become a disadvantage. The objective of using as many monosubstance systems as possible so that a product can be separated into pure material types after

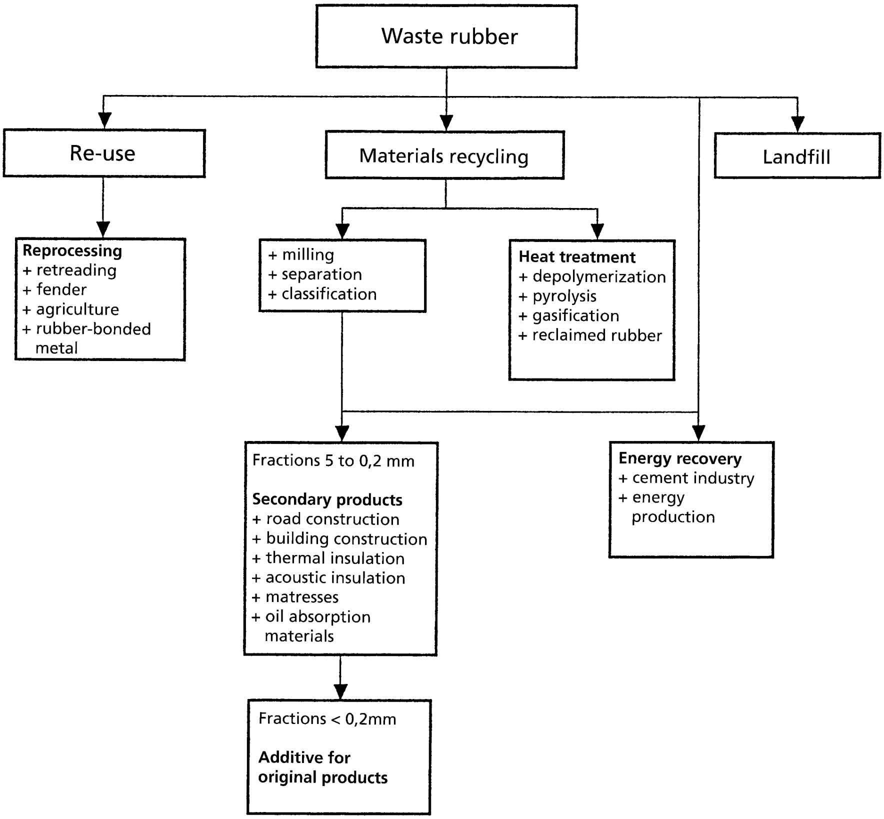


Fig. 5 Recycling alternatives for used rubber [23]

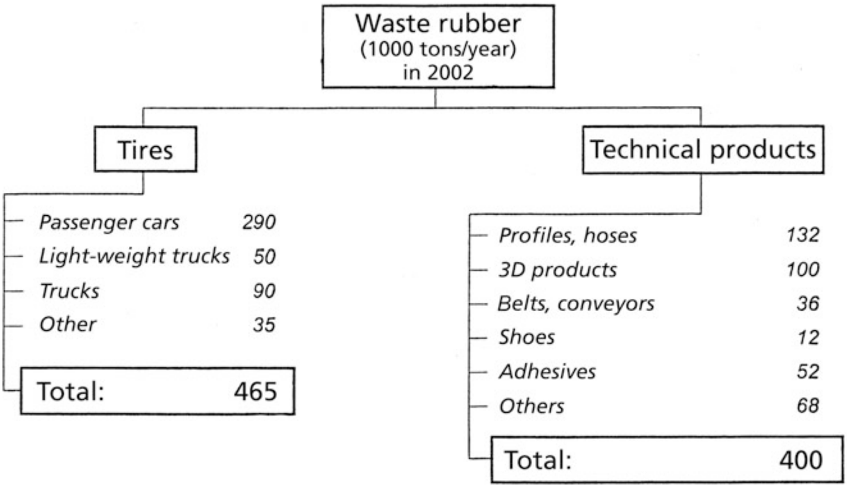


Fig. 6 Volumes of used rubber for 2002 (updated acc. to [23])

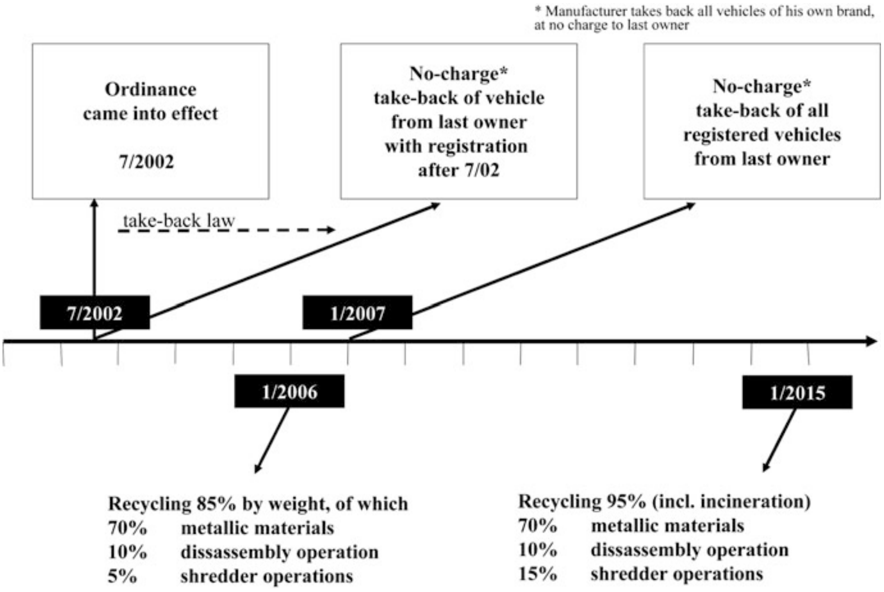


Fig. 7 History of implementation of used car recycling law in Germany (acc. to [24])

Annual amount: approx. 650,000 t/a

Recycling

- **approx. 265,000 t recycled as energy, usually in cement works**
- **approx. 180,000 t recycled as material, e.g. in**
  - **granulate production (90,000 t)**
  - **retreading (84,000 t)**
- **about 50 – 60,000 t exported for reuse**
- **approx. 10,000 t for further use in agriculture and coastal protection**

Proportion from used vehicles relatively small.

Recycling functions relatively well.

Fig. 8 Waste volume and recycling of tires from used vehicles [25, 26]

utilization takes second place to the demand for lower prices – and is often forgotten entirely.

Table 9 summarizes recycling methods and provides brief assessments.

Brief summation of information in Table 8:

Under the current application framework conditions (technical, economic, environmental), used rubber should be fired to recover its calorific value.

Table 9 Recycling methods for used rubber (technical moldings)

Segments	Recycling method				
	Pyrolysis (disintegration at 500–800°C)	Regeneration Heat, mechanics, chemistry dissolve crosslinking	Particle recycling	Thermal recycling	Dump
Technical	Waste rubber materials converted into gasses, oils, soot	40 years ago 20–25% regenerate in crude rubber, new technologies (Vredestein!) could make a difference	Rubber particles $<$ 50 mm rubber granulate $<$ 5mm rubber meal $<$ 0.5 mm Fine rubber meal $<$ 0.1 mm (cold comminution requires high energy levels)	Special ovens with smoke gas washing required technical solutions found for cement industry and power plants	Technical solution applies if current regulations are complied with
Economic	Not economical	Still not economical	Usually too expensive	Feasible	Too expensive
Environmental	Controllable at considerable expense, but usually not as efficient as thermal recycling	Old methods do not qualify for permits new technologies required	Depends on application whether advantageous or not (see Chapter 8, 3.1 Holistic balancing)	Currently often the best solution, but in some cases should be compared to particle recycling and new methods of material/ raw material recycling methods	Unfavorable, since resources are wasted. Monodumps can serve as future raw material storehouses for recycling technologies that will be economically feasible in the future; risk of dump fires
Summary	Too expensive, suitable for niches	Still too expensive	Too expensive, suitable for niches	Feasible	Not feasible

If applying new technologies makes regeneration a feasible option for large series, this material recycling method would have its opportunity.

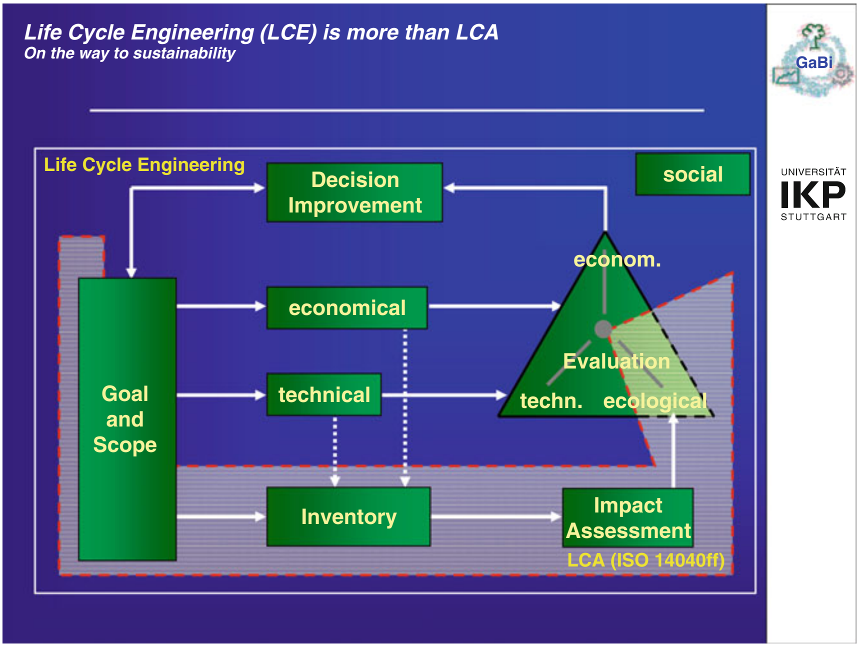
For further reading see the end of this chapter.

3.1 Holistic Balancing (Lifecycle Engineering)

Assuming the goal is sustainable development, it is important, when making ecological decisions, not to ignore economic aspects such as value added and profit use, whereby the profit earned could be put to either technical, social, or economic use.

A holistic lifecycle approach therefore aims to support or find solutions that are technically feasible, ecologically and socially defensible, and economically rational. A definition of the overall optimum must always take into account the interactions between ecology, economy, and technology. Ecological optimization must not, for instance, be purchased at the cost of failing to satisfy minimum technical specifications or designing a project that cannot be financed as a whole.

Holistic balancing (or LCE) must be conceived as a combination of the three dimensions technology, economy, and environment, Fig. 9. It is, essentially, a method of collecting, documenting, and compounding environmental parameters of products, processes, systems and services on the basis of technical and economic specifications.



Life Cycle Engineering (LCE) is more than LCA
On the way to sustainability

Fig. 9 Phases of an ecological balance sheet (IKP, Stuttgart University)

The ecological considerations involved cover what is referred to as the ecological balance sheet, which is therefore a subcategory of LCE.

The concept of an ecological balance sheet is based on the following principles:

- Consideration of the entire lifecycle from raw material derivation and processing to production and utilization, thence to recycling and final disposal.
- Inclusion of all influences on the environment emanating from the product lifecycle: in the air, water and soil, wastes, raw material consumption, use of natural space.
- Summary of environmental contaminations in terms of potential effects and evaluation, the objective being a basis for environmentally oriented decision-making.

The series of standards DIN/ISO 14040 ff. placed a number of procedures for formulating ecological balance sheets on an international basis.

3.2 Structure of an Ecological Balance Sheet

As shown in Fig. 10, an ecological balance sheet must contain definitions of the objective and the framework of the investigation, the databased balance, the impact

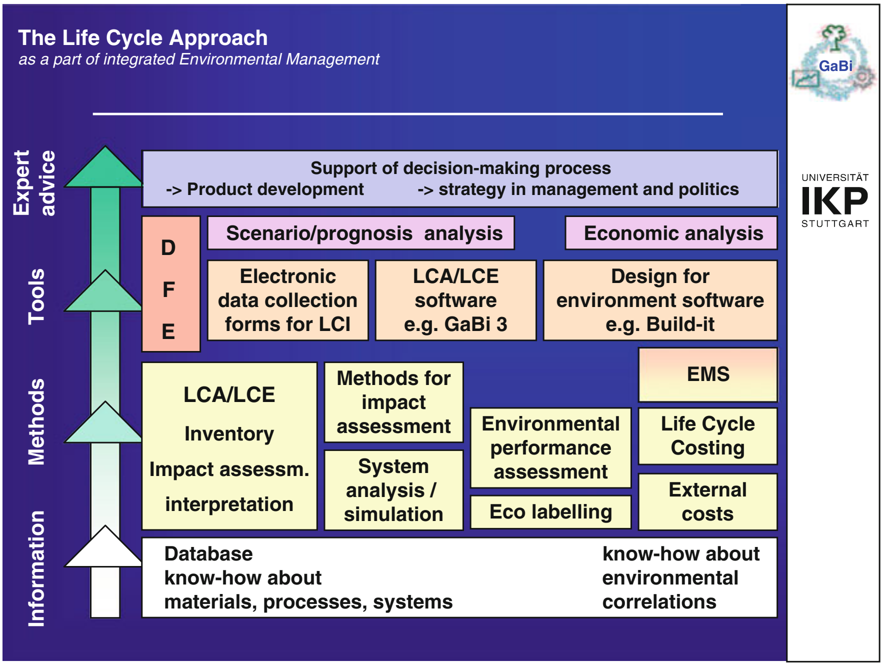


Fig. 10 System of holistic balancing (or lifecycle engineering (LCE)) (IKP, Stuttgart University)

assessment (impact of the databased balance on the environment), and the evaluation of the results. Applications of ecological balance sheets.

3.3 Definition of Objective and Framework

The first step, that also sets the course for the entire balance sheet, is to define the objective and framework of the investigation. Some of the framework conditions are not rendered transparent until the task and objectives have been clearly defined in terms of what one wants to find out.

The definition of the objective must cover the following points:

- What is to be learned
- Reasons for realization
- Target group

The description of the investigative framework covers the following points:

- Description of the system
- Definition of the functional unit
- Definition of the system limit
- Data quality specifications
- Explanation of basic assumptions
- Allocation methods
- Impact categories and impact assessment method

3.3.1 Functional Unit

The functional unit defines the function of the product under consideration and its performance capacity. At the same time, the functional unit serves as a reference unit for the environmental impacts as determined. Its purpose is to ensure that different balancing sheets will be comparable. The functional unit may characterize services as well as products.

3.3.2 System Limits

As a rule, a number of “materials” are required for product production. These may be resources, intermediate products, operating supplies, fuels, etc. All of these materials or products have been compounded and produced in preliminary steps, once again requiring material and energy at every stage. Every link in this chain has an impact on the environment and must find its way into the balance sheet. Of course some input flows will not influence the balance sheet outcome. Exclusion criteria must be formulated to keep from overloading the balance sheet with irrelevant data that do not add to its quality but make it more expensive to realize.

These criteria must be formulated so that no important aspects of environmental impact are ignored.

3.3.3 Data Quality

Data quality must be ensured for all of the modules investigated. On the basis of the input materials for a process and the specific process type, an analysis of data completeness and plausibility can be carried out, for example by means of stoichiometric calculations or by comparing the data with published statistics. If substitute values or estimates are used, they must be labeled as such and their use explained. Assumptions made must be explained.

3.4 Databased Balance

Before actual data collection is carried out, the regulations for data calculation and balancing must be fixed and documented as necessary. Important items that may influence the results significantly and enter into a balance sheet in a variety of different ways include treatment of secondary raw materials, data on coupled and secondary products as well as application of allocation rules.

The main task of a databased balance is to quantify input and output flows over the entire lifecycle of a product. Figure 11 presents a selection of input and output flows of frequent significance. A difference is drawn between coupled and uncoupled material flows:

Uncoupled flows (elementary flows) represent the flow of materials from the source “crust of the earth” or into the sink “environment.”

Coupled flows must be seen in relation to “upstream” production processes or “downstream” processing until only uncoupled material flows exceed the balance sheet limit.

Modular subclassification makes it possible to allocate these material flows, and thus the environmental impacts, to individual process steps, facilitating identification of the “polluter” or source of contamination. When this basis has been established, and not before, an analysis of weak points and recognition of improvement potentials is possible. In some cases, initial conclusions concerning the defined objective can even be drawn on the basis of the databased balance.

3.4.1 Allocation

The question of allocation always become relevant when, in a production process or process phase, several products are produced, or secondary products, or wastes, are produced in addition to the primary product and must be used or

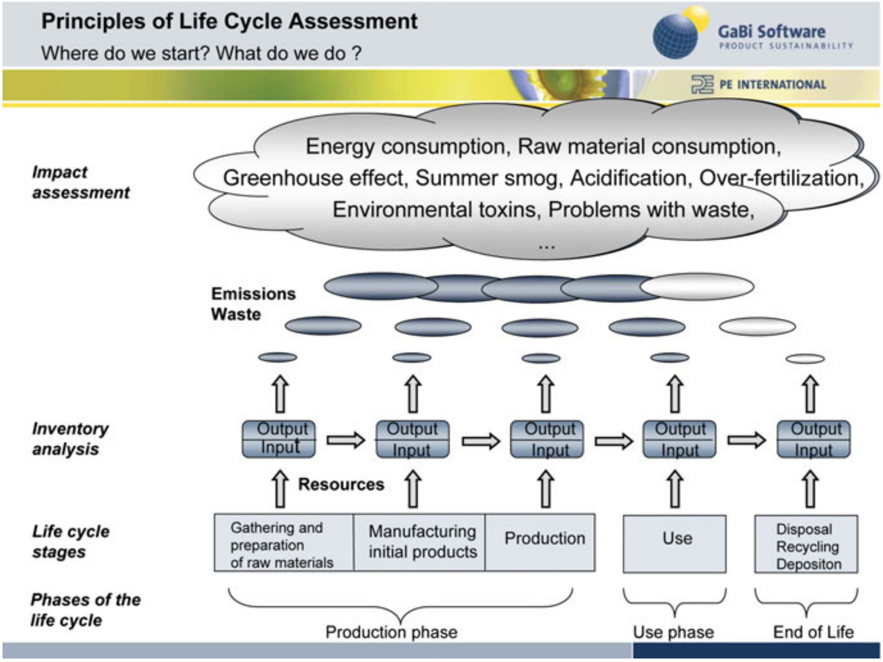


Fig. 11 Examples of input and output flows along the product lifecycle (IKP, Stuttgart University)

disposed of. The task is then to allocate the expenditures, and thus the environmental impacts, of production to the individual products or secondary products. The allocation method chosen should reflect the intention or purpose of the process being assessed. That way, the main environmental burdens will be allocated to the primary product. The allocation method selected must in any case be documented.

If individual product lines can be separated from a product system into modules of their own, allocation is not done, assuming, that is, that all input and output flows can be matched unequivocally to the individual processes.

Allocation is always a form of evaluation that influences the balance sheet results. If it is not readily apparent which allocation method is best suited, the possible methods should be applied and the resulting impacts presented in terms of a sensitivity analysis.

3.4.2 Recycling

How recycling flows are treated in an ecological balance sheet is basically a question of allocation, since every recycling process influences whether and to what extent burdens resulting from the primary production of a material can be allocated to the recyclate, effectively "passing on" part of the primary expenditure to another lifecycle. Generally speaking, all material flows that exceed the system limits must be taken into account.

A method that is often used to free the system "space" of other lifecycles of secondary raw materials is to issue credits for all materials and units of energy that are processed and enter into a new lifecycle. The secondary raw materials from recycled materials and energy provide these substitutes that would otherwise have been produced from primary raw materials. That way, production from the primary raw materials is obviated and can be credited to the system under consideration. This essentially constitutes an extension of the system space.

3.5 Impact Assessment

The impact assessment presents the databased balance in terms of environmental impact so as to derive conclusions concerning the overall impact. The databased balance thus provides the basis for the impact assessment. The aspects under investigation include the potential environmental impacts (e.g., climate change, ozone depletion, acid rain) caused by the input and output flows over the entire lifecycle.

The steps classification, characterization, and weighting are differentiated within the impact assessment. Classification and characterization constitute the objective part of impact assessment based on principles of natural science. In classification, the materials acting upon the environment are placed in impact categories in accordance with their potential effects. Within the impact categories, the databased balance is applied so as to determine the characteristic impact potential of the material or substance under consideration, which is then assigned to the specific impact category. This step is called characterization.

Weighting means that, in special cases, results may be grouped and prioritized as to their environmental impacts so as to facilitate comparability with other results. This is a matter of subjective evaluation.

3.5.1 Selection of Impact Categories

The standard ISO 14042 does not prescribe which impact categories have to be used. What it does define are the criteria for selecting the categories. The selection of impact categories should generally reflect the protective objectives of sustainability, resource preservation, global ecosphere protection, preservation of human health, and the stability of the ecosystem.

As was mentioned above, the methods of impact assessment are still in the development phase for some environmental impacts. This applies in particular to toxicity potentials (human toxicity potential HTP, aquatic ecotoxicity potential AETP, terrestrial ecotoxicity potential TETP) as well as use of natural space or surfaces.

Therefore, the following impact categories, recognized as essential to the international discussion, are currently considered a useful practical basis for formulation of ecological balance sheets:

- Greenhouse effect, global warming potential (GWP) in kg of CO_2 equivalent
- Stratospheric ozone depletion, ozone depletion potential (ODP) in kg of R11 equivalent
- Acidification, acidification potential (AP) in kg of SO_2 equivalent
- Excessive fertilization, eutrophication potential (EP) in kg of PO_4 equivalent
- Summer smog, photochemical ozone creation potential (POCP) in kg C_2H_4 equivalent
- Resource consumption, abiotic depletion potential (ADP) in kg of Sb equivalent (antimony equivalent)

The treatment of wastes (waste incineration, deposition, etc.) should be integrated in the system under consideration for ecological balance sheets and their environmental effects should be described in terms of the known impact categories. If this is not possible, the wastes can be documented in the groups spoil, ore compounding residues, household wastes, and special wastes.

3.6 Evaluation and Interpretation

In the evaluation, the results of the impact analysis and databased balance are analyzed, leading to conclusions and recommendations. A further aspect is the transparent presentation of the ecological balance sheet results.

The standard ISO 14043 divides the interpretation phase into three sections:

- Formulation of core statements
- Evaluation
- Presentation of results

To obtain the core statements, the main contributions of each impact category (which processes and which emissions are dominant in each category?) must be determined. Relevant databased balance information not included under any specific impact category must be integrated in these considerations. The core statements can then be formulated on the basis of the results, since it should have become clear which processes or lifecycle phases are predominant.

According to the standard, the completeness, sensitivity and consistency of the recognized processes or lifecycle phases must be reviewed. Completeness can be checked on the basis of mass or energy balances. Sensitivity can be determined by working out scenarios for different processes and parameter selections. The effects of the different assumptions on the final result then represent the sensitivity factor.

It is important that the information and data required for interpretation be complete. Another aspect that must be checked is whether uncertainties, for instance due to estimated data used to fill data gaps, might influence the result. Such uncertainties can be determined by calculation of a minimum–maximum interval covering the potential extremes, then determining its effect on the final result.

The purpose of checking for procedural consistency is, on the one hand, to ensure consistency with the defined objective and, on the other hand, to ensure that the methods and rules are applied consistently.

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Perspectives: Polymer Engineering

Peter Eyerer

Abstract Herein we discuss once again the importance of the engineering point of view and provide and overview of all the different steps influencing the engineering of components.

Keywords Perspectives in polymer engineering

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1 Material Production, Synthesis

The trend observed in recent decades is now continuing in view of the general winding-down tendency in polymer chemistry: Hardly any new plastics are being synthesized. Major sales volume opportunities will involve mainly mixtures of

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known polymers (copolymerizations, blending). New catalyst systems, for instance metallocene technology and its further development, can be expected. In the medium term, more polymerization processes will be designed to take place in water and in mass or, further down the road, in supercritical fluids (SCF), instead of in solvents. The reduction of residues of monomers, solvents, and additives such as emulsifiers will be the declared goal to the extent the costs of synthesis can also be reduced by these means. The method of continuing process analysis keeps this development on track anyway.

Another general theme in product development will be the reduction of secondary products (100 % conversion) or their utilization. What the chemical engineers will be looking for will be polymer formulae that produce migration-free, halogen-free, reusable products (additives free of heavy metals).

A big step in the direction of biobased polymer synthesis – moving away from petroleum and toward sugar, cellulose, starch, oils and fats, or lignin for raw materials – will definitely change the face of polymer chemistry.

Thermoplastics – long fiber-reinforced, textile-reinforced, woven mat-reinforced or with local hybrid fiber reinforcement – will gain ground in the direction of large-scale production series and structural parts production.

Nanocomposites and nanoparticles will contribute to these developments for higher levels of strength, rigidity, conductivity, etc. in transparent plastics as well.

2 Material Properties

The vision of variable plastic properties, sensor-adjustable in production, will become reality over the medium and longer terms. The fields of application of functional, structural, and gradient materials in polymer engineering are growing wider. [8, 9, 11, 12, 14]

Other developments, in the automotive industry in particular, are aiming at

- Materials with higher energy absorption capacities when exposed to cold
- Contaminant-resistant materials
- Improved combustion behavior (toxicity, smoke gases)
- Foaming systems that are more environmentally compatible
- Material combinations (hybrid systems)
- High levels of local electrical conductivity
- Emission-free plastics
- Plastic disks with scratchproof coatings
- Polymeric LEDs
- Large-surface illuminated diodes
- Applications in liquid crystal displays
- Improvement of properties with nanoparticles and nanocomposites

3 Processing, Process Engineering

The cost-driven trend toward combination of different processing techniques and functional integrations in plastic and hybrid components will continue in a dynamic fashion. Large-scale processing of thermoplastic, long fiber-reinforced composites with local textile or carbon fiber reinforcement will soon also make itself felt in series production. More economical processing of duroplastics (SMC), with improved quality assurance, can be expected within 3 years' time. Other reactive processes, such as production of polyamides from caprolactam, PUR-RIM/RRIM (polyurethane reaction injection molding/reinforced RIM) and SRIM (polyurethane reaction injection molding/structural RIM), RTM [resin transfer molding (duroplastics)] and TRTM (thermoplastic RTM), as well as extrusion will surely show considerable advances.

Integrated processes (reaction + compounding + forming), based on a combination of different process steps, will also certainly become more and more important, since these methods do not require the multiple heatup and cooling steps. The importance of microwave technology in drying, welding, adhesion, heating and melting, including plasma techniques for cleaning and coating, will also increase due to advantages in terms of function, costing, and environmental impact.

4 Mold Engineering

Inmold-assembled products and components (integration of sequential production steps in the primary or secondary molding tool) such as dashboards, headlights, door designs, bumpers, etc. will move from conceptual vision to small series and thence to large-series production. This will include mold systems requiring no afterprocessing, including precalculations of prototypic mold-filling processes in newly developed (combined) processing techniques.

5 Design, Calculation

Further refinement of dimensioning and designing methods in the field of simultaneous engineering can be expected.

For example, the calculation of shrinkage and warpage in (long) fiber-reinforced plastics can be worked out ahead of time and the data can be provided to the processor as well as the structural component development engineers. The same applies to improved integration of anisotropic and viscoelastic material behavior. The generation and expansion of FE calculation models (with rational transition from CAD to FE models) will be the result, including IT-supported searches for mass-optimized designs based on input of design variables. The miniaturization and modular construction of components are making progress in the areas of reduction of wall thicknesses, noise dampening, and soluble compounds. Precalculation of the acoustic behavior of moldings and components will become standard procedure. Low-cost assembly and bonding techniques are still in demand.

Rapid prototyping (functional parts parallel to series production) and rapid tooling continue to gain ground.

The following customer demands will determine automotive developments in the coming years:

- Light construction (fuel consumption will drop off towards 3 l/100 km) which will mean
  - More plastic applications in the engine compartment, drive train, running gear
  - Roof modules
  - Underbody modules with thermal protection
  - Cable harnesses replaced by on-board networks (drive-by-wire)Hybrid designs incorporating metals and plastics/fiber composites
- Improved crash safety (as in Formula 1)
- Improved all-round view
- All car windows made of polymer materials
- Integrated variation, e.g., convertible in summer, sedan in winter
- Protection from vandalism
- Plastic fuel cell

6 Surfacing Techniques

Surfacing techniques that are more economical and more environmentally compatible, for example through-colored products, back-injected or inmold-laminated films (external surface polishable) will see large-scale series production.

Customers will no longer be willing to pay for the exaggerated demands made of class A surfaces. The integration of the painting process in the molding system is a plus for cost-conscious consumers.

Visions yet to come:

- Film coating to replace painted surfaces
- Self-cleaning surfaces
- Sensor-controlled color variability of the external surface to go with surroundings (light colors at dusk, reflective films at night, flashy elements in a potential accident situation)
- Self-healing surfaces.

7 Quality Management

Inline testing techniques (preferably nondestructive) during synthesis and above all during the processing phase, will guarantee zero-error quality and reduce series deviations to a minimum (with more intelligent control and regulating systems for processing and assembly).

Above all, this will minimize expensive recalls and push down repair costs. The useful life of the products will become more predictable.

The use of fiber composite elements in the load-bearing structure of automobiles (light construction) will mean practical, nondestructive testing methods for repair workshops. Considerable research remains to be done in this field.

8 Series Production

For decades, series production has been the litmus test for every new design. More recently, time and costs have become decisive factors in competitive success, making simultaneous engineering more and more important in shortening of development times and reduction of runup costs.

Self-regulating groups remain an important organizational and management principle. This concept is characterized by input of objectives, after which the pathway to the objective is delegated to the responsible group, which must also exercise stringent self-control.

Production-integrated environmental protection, combined with maximum process reliability and safety, for products and humans, remains the top German standard. Rationalization of new and older technologies was, and still is, necessary for survival in global competition. [10, 13]

9 Environmental Aspects, Recycling, Disposal

Holistic balancing (lifecycle engineering of technical, economic, and environmental aspects) is now the established method used by major producers as a method of weak point analysis *during* the product development phase.

Small and medium-sized businesses still have to be won over. To this end, the costs and handling of the method of holistic balancing must be reduced and improved respectively. Risk management, economic aspects, in particular costs, and social aspects are all integrated in the system.

Product development must concentrate more on simplifying logistics, i.e., volume flows.

In view of the high price of crude oil, economical material recycling appears feasible. Control over critical contaminants, in particular during firing to obtain energy and deposition (additives, dust, emissions) requires further optimization. Materials and methods must in future be measured against the necessity of sustainable development on a global scale.

10 Education

Any treatment of the perspective of polymer engineering would of course be incomplete if the educational aspect were to go unmentioned, hence this brief aside. Here is a summary version of replies received in a recent survey by the *Technische Akademie Baden-Württemberg* [1, 2] to the question “Now that you have finished your education, how would you evaluate its quality?”:

The courses of education at German schools and universities is

- Unrealistic in terms of practical realities and professional applications
- Too abstract and theoretical
- Not team-oriented.

To counter these drawbacks, TheoPrax® [3, 4] has, since 1996, been active in the integration of real business and industrial projects into school and university courses and also provides advanced teacher training programs [5–7].

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