Polymers as Materials

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Polymers as materials appear in myriad forms. Everyone is familiar with floor coverings made of polyvinyl chloride (PVC) and with Plexiglas windows (polymethyl methacrylate), and the latter's particularly successful version: the roof-top of the Munich Olympic Stadium. Many are equally familiar with the strengthening of polymers by compounding them with glass fiber. Polymers are also increasingly being used in medical applications, for instance as bone and organ prostheses. One can easily imagine that these must meet completely different requirements than, for example, an ordinary PVC tube in a chemical laboratory. These few examples amply demonstrate how diversified and partially contradictory the requirements for a material in its specific application are, and that an ideal material for all applications cannot exist.

The respective arguments for the application of plastics as an alternative to metals, glass, wood, or ceramic are multifarious. Often, weight advantages, thermal insolation, sound insulation, or electrical insulation are foremost. Depending on the size of the production series, polymer articles can have comparatively low manufacturing costs. Thermoplastics also offer a relatively large degree of design freedom. Complicated parts can often be produced from a single piece, for instance, by injection molding (▶ see Chap. 17). Synthetic materials are typically also relatively corrosion-resistant. Last but not least, the comparatively low temperatures at which synthetic materials are usually processed leads to energy and, consequently, cost reduction during processing.

As a result, many polymer researchers spend their time on the development of macromolecules that can be customized to particular requirements. This involves trying to incorporate as many desired attributes as possible into one polymer. Ideally, this would be, for example, a polymer that is as hard as steel, as clear as glass, as light as a feather, as heatproof as quartz, and as cheap as possible.

When searching for a suitable material, some basic requirements need to be considered:

- Mechanical and thermal resilience
- Resistance to chemicals, ultraviolet (UV) radiation, and electrical fields
- Appearance (inherent color/colorability, transparency, and printability)
- Cost of raw materials, production, rework, and assembly
- Weight
- Dimensional stability, and thus form constancy under different conditions
- Resistance to fire

Clearly, deciding on the right material is a complex process. Therefore, only the basic methods of customizing polymers are described in this chapter.

7.1 Fracture Behavior

As the material properties of polymers can be varied over a broad range, more than just one mechanism can lead to material failure. Figure 7.1 shows two characteristic cases.

The left curve (Fig. 7.1a) shows the dependence of the stress on the elongation for a brittle polymeric material. For stiff materials (with a high Young's modulus) a relatively minor elongation ε already requires a high stress σ. The curve is therefore rather steep. Even a relatively minor elongation leads to fracture. This fracture behavior is referred to as a brittle fracture. It is typical for brittle, rigid materials and is characteristic of polymers

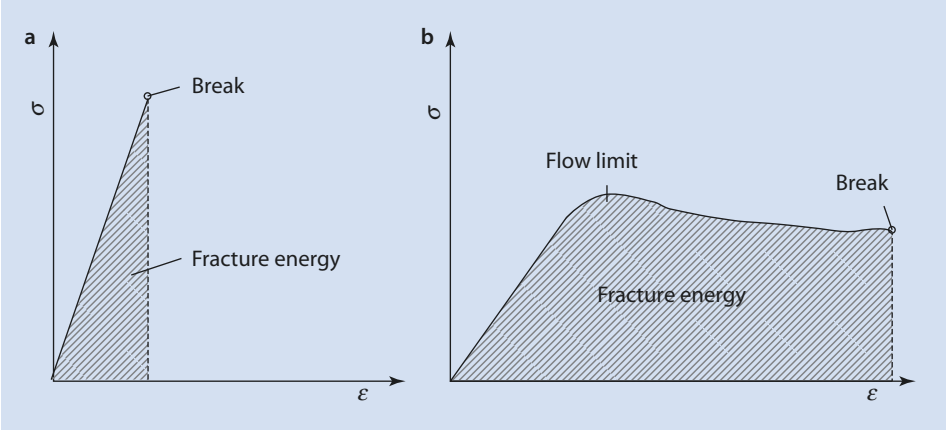


Fig. 7.1 Tension–elongation curves ($\sigma = f(\varepsilon)$) of (**a**) brittle and (**b**) viscoelastic polymers

below their glass transition temperatures. The Young's modulus is given by the initial slope of the curve shown and the energy needed for fracture by the area under the curve until fracture. An everyday example of such behavior is glass.

The other curve (Fig. 7.1b) shows the result of the same test for a tough, viscoelastic material. These materials are generally less stiff than crystalline polymers, or polymers at temperatures beneath their glass transition temperature. Thus, the curve becomes flatter. In such cases the material typically starts to flow under the external stress at a particular degree of elongation ε. This elongation is referred to as the yield point. The shape of the curve after exceeding the yield point is relatively poorly defined. Here, too, the material eventually fractures whereby the mechanism is referred to as ductile fracture. The energy leading to fracture is again given by the area under the curve. An everyday example of such behavior is chewing gum.

The fracture behavior of a polymer is strongly dependent on temperature. That way, for instance, a material that exhibits brittle fracture at low temperature can fracture in a ductile manner at higher temperatures. This is depicted in Fig. 7.2.

In Fig. 7.2, the transition from brittle fracture to ductile fracture is clearly recognizable. At low temperatures, only limited deformation is possible. The material is characterized by a high Young's modulus, i.e., the material is very stiff and a great deal of force is needed to stretch it. On the other hand, the material is able to sustain considerable stress before it breaks. The material becomes softer with increasing temperature (from T_1 to T_6), the Young's modulus sinks, and the curves become flatter. The *strength* of the material, the stress at which the material fractures, tends to decrease.

At even higher temperatures, the material reaches its yield point. Beyond the yield point, the form of the curve is no longer well defined. The material becomes progressively softer, which is reflected in a sinking Young's modulus and relatively flatter curves.

It is important to note that the maximum *toughness* of the material, i.e., the maximum energy required for fracture, is reached at an average temperature T_4. The area below the curve is smaller at lower temperatures because of a different fracture mechanism (brittle fracture). At temperatures above T_4, the curves are, taken as a whole, flatter, so that the integral of the curves are also smaller.

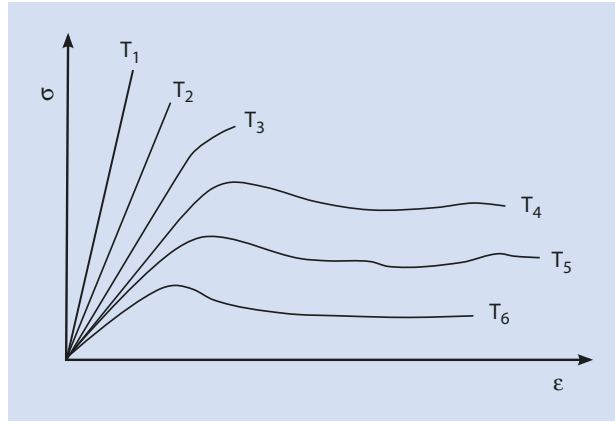


Fig. 7.2 Stress–strain curves for a polymer at different temperatures (increasing from T_1 to T_6)

7.2 Tailor-Made Plastics

7.2.1 Mechanical Characteristics

All polymers have approximately the same molecular main chain stability, no matter what their particular structure, because they consist of covalent C–C-, C–O-, C–N-, or C–S-bonds with bond strengths of between 330 and 420 kJ/bond. Important, distinctive differences are produced by intermolecular interactions or cross-links (Fig. 7.3).

Intermolecular interactions between hydrocarbon chains such as in polyethylene and polypropylene are primarily caused by van der Waals forces. Polar groups, such as the nitrile groups in polyacrylonitrile, increase the stiffness and strength of the polymer through dipole–dipole interactions. Hydrogen bonds are the reason for the exceptional strength of polyamides. An interesting variant is the ionic interactions between carboxylate functions of a polymer and bivalent metal ions, such as Zn^{2+}. A considerable improvement in the mechanical characteristics can be achieved through cross-linking.

The mechanical characteristics of thermoplastics can be improved by increasing their molar mass and by avoiding or removing low molar mass moieties or by crystallization. When nonpolar sections along the chain are replaced by polar ones, for instance if a C–C- is replaced by a CO–NH-function (an amide function), the stiffness, strength, and viscosity of the polymer increase. Replacing nonpolar aliphatic groups by polar side groups, for example CI, CN, or OH, works in a similar way. These polar groups do not necessarily need to be part of every repeating unit, but can be introduced into the polymer chain by copolymerizing a nonpolar monomer with a polar monomer in a controllable manner (▶ Chap. 13), which can be seen as fine tuning of the polymer characteristics (Nuyken 1987).

As already explained in ▶ Chap. 2, because of entropy effects, polymers have limited solubility in low molecular solvents. Such effects are even more pronounced when two polymers are mixed so that chemically different polymers are not, as a rule, miscible. For this reason, when dealing with solid block copolymers, the two different polymer blocks usually form separate phases. However, because both blocks are chemically bonded, a macroscopic separation is impossible but the material is heterogeneous at a nanoscale. This can lead to different morphologies depending on the volume ratio of the polymer blocks whereby the minor component forms spherical or rod-like aggregates dispersed in

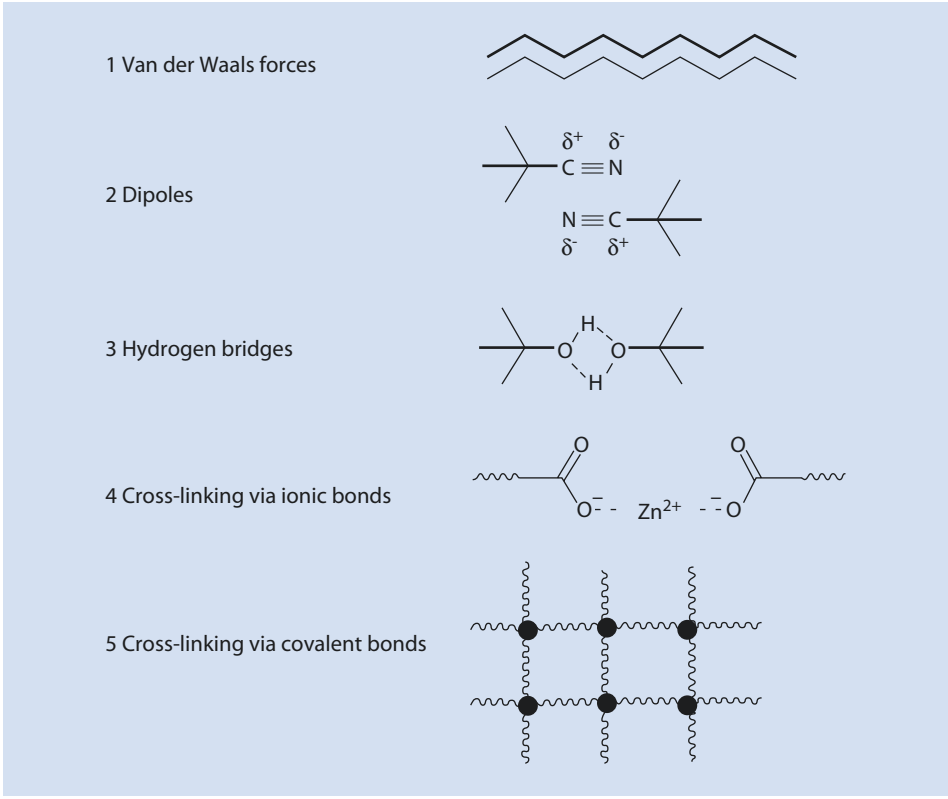


Fig. 7.3 Typical examples of intermolecular interactions or cross-links between polymer chains

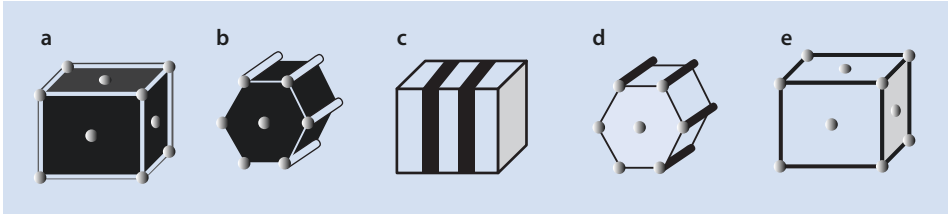


Fig. 7.4 Schematic depiction of the morphologies of block polymers having different compositions (see text)

a matrix of the major component. If both blocks are about equally distributed in the system, lamellae can form. These morphologies are schematically shown in Fig. 7.4.

Spherical aggregates arise for strongly segregated block copolymers when the weight fraction of the one component is less than ca. 15 % (Fig. 7.4a). When the portion is between about 15 % and 35 %, one-dimensional (rod-like) structures are formed (Fig. 7.4b). Between 35 % and 65 %, lamellae can be found (Fig. 7.4c). For even higher portions, the corresponding inverse structures are formed (Fig. 7.4d and Fig. 7.4e). Of course, these percentages should only be taken as a rough guide.

If the driving force for the phase separation of the blocks is relatively low, interpenetrating co-continuous networks can form at certain compositions because of surface area

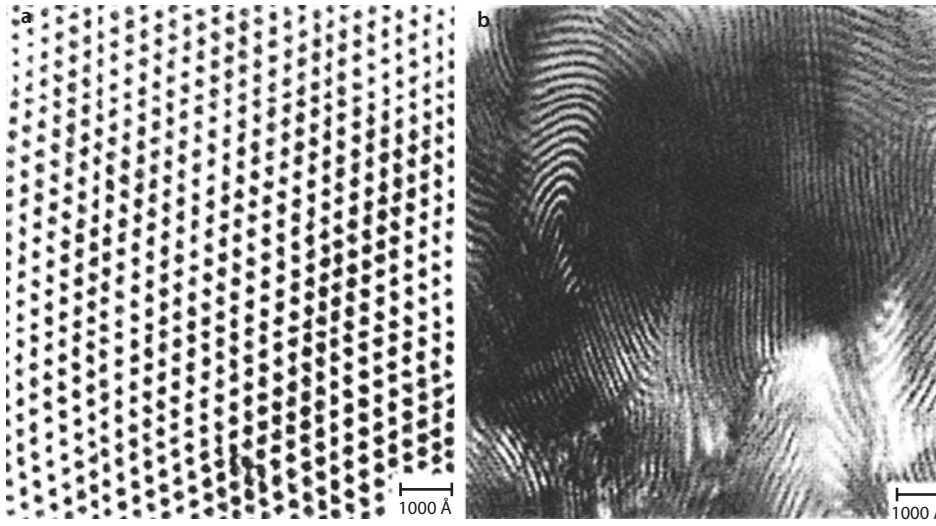


Fig. 7.5 Electron-microscopies (TEM) of (**a**) a rod-like and (**b**) a lamellar morphology (seen perpendicular to the plane of the page)

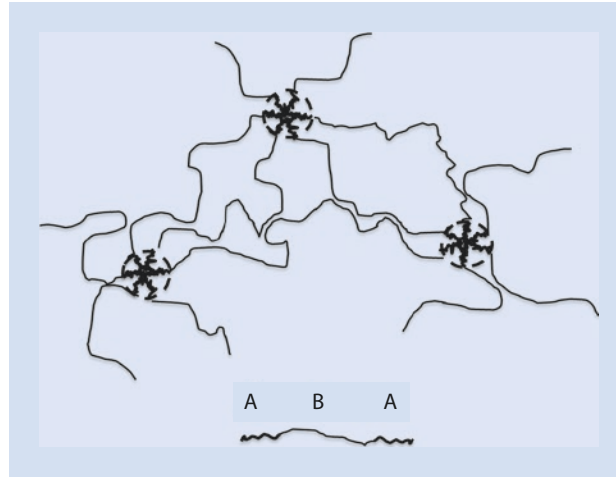


Fig. 7.6 Schematic depiction of a spherical morphology with a stiff polymer as the continuous phase

considerations. These are also referred to as *gyroide* phases and lead to a minimum in the surface area between the two phases.

The morphology of block copolymers can be very well visualized by transmission electron microscopy (TEM) (Fig. 7.5).

The mechanical characteristics of block copolymers are very interesting and make them useful for a wide variety of applications. One example would be the spherical morphology as shown in Fig. 7.6.

If we assume that the continuous phase consists of a stiff polymer but that the dispersed spheres are composed of a soft, elastic material, then the combination of these two

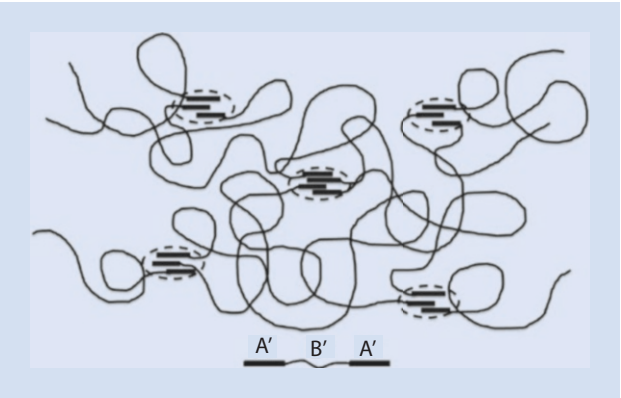


Fig. 7.7 Phase separation in an A′B′A′-block copolymer via physical cross-linking. Example: A′ polystyrene segment, B′ polybutadiene segment

materials exhibits very interesting characteristics: The continuous, so-called *hard phase* makes the material seem stiff macroscopically. Stiff materials are characterized by a high Young's modulus, but often suffer from their brittleness. If a so-called *soft phase* made from a soft, elastic polymer is embedded in such a stiff material, this phase can dissipate energy, for example, impact energy. Thus, the material becomes substantially less brittle. This principle is used industrially and is referred to as *impact modification*. It enables the production of materials that are not only stiff, but tough.

This principle is applied technologically, for instance to styrene copolymers. Non-transparent (opaque), high impact polystyrene (HIPS) consists of a mixture of neat polystyrene with a graft copolymer having a polybutadiene backbone and polystyrene side chains. The incompatibility of these two components leads to phase separation whereby the polystyrene forms the continuous (coherent) phase. Under stress cracks are generated which propagate through the polystyrene phase until they meet a softer, polybutadiene phase where the propagation halts. As a result, the mechanical resilience of the material is considerably greater than that of pure polystyrene, which is relatively brittle at room temperature because of its relatively high glass transition temperature of 100 °C.

One class of *thermoplastic elastomers* (*TPE*) is A′B′A′-block copolymers where A′, for example, is a polystyrene segment and B′ a polybutadiene segment. The incompatibility of these polymers also leads to phase separation. In this case, the continuous phase is generally the elastic polybutadiene (similar materials are also made using polyisoprene as the elastomeric phase). Because of the hard polystyrene domains that are glassy at room temperature, the polybutadiene behaves as if it were cross-linked (Fig. 7.7). However, the physical cross-links are only stable up to the glass transition temperature of the hard phase, in these examples the polystyrene. The polystyrene transitions into a plastic state when heated above its glass transition, and the material becomes malleable.

The thermal characteristics of block copolymers are different from those of homopolymers or statistical copolymers. Because of the phase separation in the solid state, the material has two melting and two glass transition temperatures at which the respective, separate polymer blocks undergo the corresponding phase transitions. These can be observed, for example, by DSC.

However, practically, only two of these four transitions are important. The material starts to flow and loses its form only if the temperature exceeds the highest of the melting temperatures. In other words, it can be thermally strained up to the higher melting

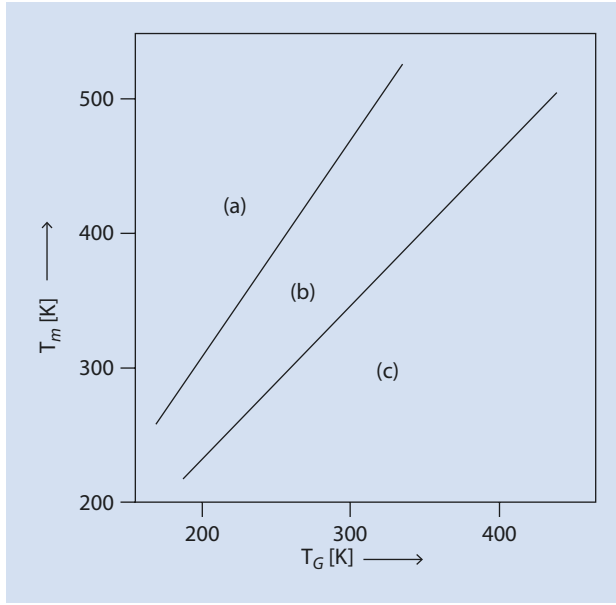


Fig. 7.8 Schematic representation of the relationship between melting temperature T_m and the glass transition temperature T_G for (**a**) block copolymers, (**b**) homopolymers, and (**c**) statistical copolymers having identical or similar chemical compositions

temperature without losing its form. This temperature is relevant for processing, and defines the highest temperature at which the polymer can be used.

On the other hand, if the desired property is impact modification, it is the low glass transition temperature of the soft phase that is critical and this defines the temperature at which the article becomes brittle.

By combining a polymer with a very high glass transition temperature or melting point with a polymer having a low glass transition temperature, a material can be obtained with a broad range of useful impact resistant properties.

In summary, by using the concepts of statistical copolymers (▶ Sect. 5.1.8) and those of block copolymers, the practically relevant melting and/or glass transition temperatures can be adjusted by using the rules of thumb mentioned in ▶ Sect. 5.1.8 over a wide range. This is shown schematically in Fig. 7.8.

Another interesting way to influence the mechanical properties of a polymer is to mix it with a solid filler such as carbon black, graphite, silica gel, glass fiber, or aluminum oxide (▶ Sect. 17.2). If unsaturated polyesters, epoxy resins, phenol formaldehyde resins, and other materials are reinforced with minerals or chopped glass fibers, they can be processed, for example, by injection molding as long as the polymers are not cross-linked.

As an example, the effect of short and long glass fibers on the tensile strength of polyamide and polypropylene is shown in Table 7.1.

The mechanical characteristics of polymer/GF-compounds can be further improved by replacing the fiber by glass mats and three-dimensional structures. However, the properties also depend on the fiber material (diameter, kind of glass), the kind of polymer, and the interaction between the polymer and the fiber. As well as the examples mentioned above, among others, polystyrene, polyoxymethylene, polyester, polyether ether ketone (PEEK), polycarbonate, and epoxy and phenolic resins are also used in such composites. Such composites are perfectly able to compete with metals in terms of their tensile strengths.

Table 7.1 Comparison of the effect of short and long glass fibers (GF) on the tensile strength of polyamide 6 (PA) and polypropylene (PP). (Data kindly provided by G. Heinrich, IPF/Dresden)

Material	Source	Tensile strength (MPa)
PP + GF, short fibers (30 wt% GF)	IPF/Dresden	90
PP + GF, UD[a] (50 wt% GF), 17 mm	IPF/Dresden	884
PP + GF, UD[a] (50 wt% GF), 12 mm	IPF/Dresden	964
PP + GF, UD[a] (60 wt% GF)	Twintex® R PP 60	760
PA + GF, short fibers (30 wt% GF)	IPF/Dresden	183
PP + GF, UD[a] (50 wt% GF)	IPF/Dresden	983

[a] *UD* unidirectional

Alternatives to glass fibers are carbon fibers and SiC fibers. Spectacular applications of such composites are the tail of the Airbus A380, the gripping arm of the Space Shuttle, and various items of sports equipment.

Aramid yarn can be seen as a "self-reinforcing system". The stiff chains of the aromatic polyamide interact via intermolecular hydrogen bonds to give a composite-like system with a very high tensile strength. Here, the stiff aramid yarn corresponds to a high-modulus fiber (for instance, glass or carbon fiber) embedded in soft resin.

7.2.2 Optical Characteristics

Amorphous polymers usually appear optically transparent, whereas crystalline polymers are generally opaque. This is because the light that falls through a crystalline polymer is scattered by the crystal lamellae; it is unable to pass straight through the sample. Only a few crystalline polymers, such as polycarbonate and poly(4-methyl-1-pentene), are transparent because the crystallites are smaller than the wavelength of visible light. In addition, the refractive indices and densities of the crystallites and the amorphous phases are almost identical so that the light is not scattered and they appear transparent.

However, there are exceptions to this basic rule: amorphous polymers naturally appear opaque if they contain chromophores that absorb the incoming light. Crystalline polymers, on the other hand, can be optically transparent if the crystallites they contain are so small that they do not scatter visible light. This can be achieved by strongly increasing the formation of crystal nuclei by adding additives. Hereby, the number of crystallites increases to such an extent that their size becomes limited. If the crystallites are made substantially smaller than the wavelength of the incoming light, no scattering occurs.

Amorphous thermoplastics, such as polystyrene, polymethyl methacrylate, polyvinyl chloride, or cellulose ester, are thus transparent, and used for glasses, frostings, photographic materials, and packaging. However, crystalline polymers, such as polyethylene, polyamides, and polyacetals, are not suitable for glass production. To make such polymers transparent the crystallization has to be prevented. This can be accomplished by, for

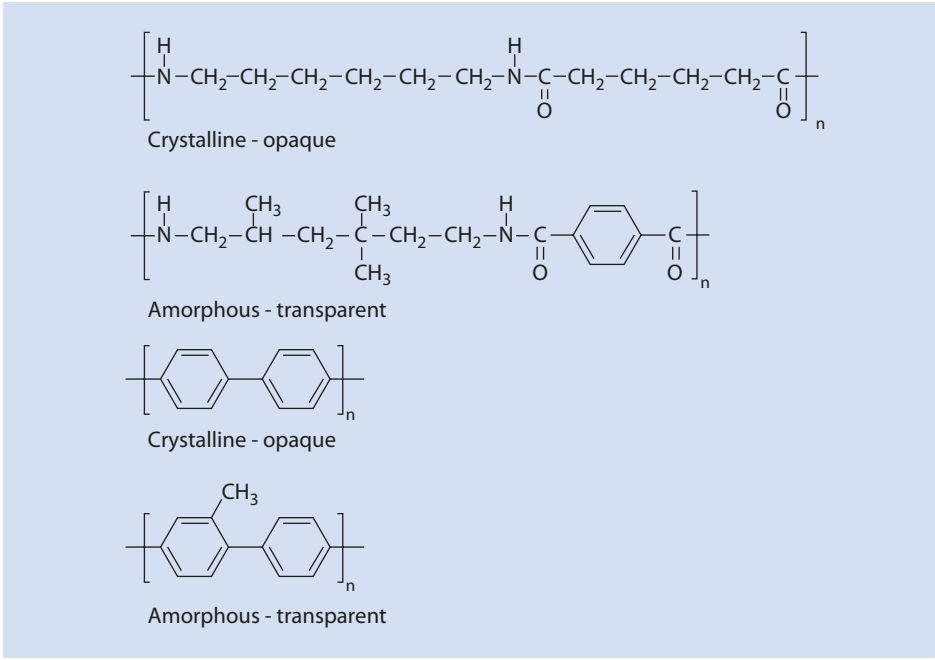


Fig. 7.9 Examples of crystalline and amorphous polymers

example, introducing side chains; CH_3-functions are often sufficient. In Fig. 7.9 crystalline and amorphous polymer structures are compared to each other.

7.2.3 Materials for Lightweight Construction

Synthetic materials are usually specifically much lighter than metals. If the mechanical strength is less critical than a lower specific weight for an article, polymer foams are a suitable solution, for example, for sound and heat insulation, foams have special advantages (▶ Chap. 17). Mechanically more demanding foams, such as furniture cushions, are also available. Polymer foams can be obtained from many polymers, for instance, from polyvinyl chloride, polystyrene, urea-formaldehyde and phenol-formaldehyde resins, poly-urea, as well as from polyurethanes. Foams can also be obtained from polyvinyl acetal and polyethylene.

Polymeric foams can be prepared by mixing at high shear and introducing gas by adding low molecular mass additives which are then allowed to evaporate or chemically. For more details, refer to ▶ Sect. 17.3.

Foaming a natural rubber is successful if a foaming agent, such as soap, is added to an initial volume of a mixture of latex rubber, extender, and vulcanization accelerator. The mixture is then vigorously stirred, expanded, and afterwards solidified using foam stabilizers. In this way, the density of the material can be reduced by up to 90%.

Viscose sponges can emerge when Na-cellulose xanthate is mixed with coarse grained salts, such as Glauber's salt, and coagulated in electrolyte solution. The material

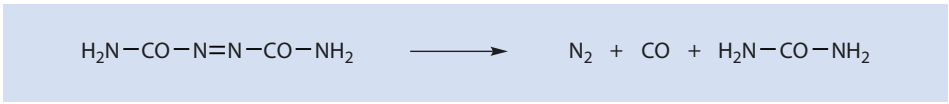
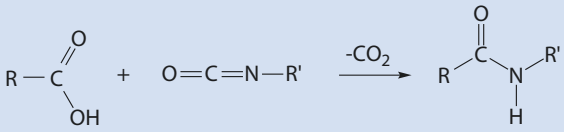


Fig. 7.10 Example of a chemical blowing agent

Fig. 7.11 Reaction of a carboxylic acid with an isocyanate



attains it porous structure because of the multiple salt inclusions which are later washed out.

In many cases, chemical agents such as NH_4NO_2, $NH_4Cl + NaNO_2$, azo compounds, sulfohydrazides, or azides that produce nitrogen when heated are employed as blowing agents (Fig. 7.10).

Chemical and physical agents are also used in the production of foams from isocyanates. For instance, the reaction of a carboxylic acid with an isocyanate to an amide, with the elimination of CO_2, is depicted in Fig. 7.11. To enhance foam formation, physical agents, such as volatile solvents, are frequently added to these systems.

The reaction of water with isocyanates to form a polyurethane foam also needs to be mentioned here. More details of this reaction are given in ▶ Sect. 17.3.2.

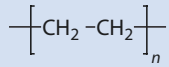
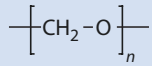
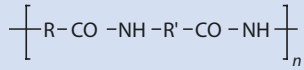
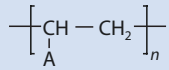
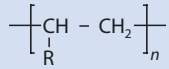
7.2.4 High-Temperature Materials

One of the biggest disadvantages of plastics compared to other materials such as steel and ceramic is their usually limited shape retention at higher temperatures. Crystalline polymers keep their shape at temperatures approaching their melting point whereas amorphous polymers tend to soften at much lower temperatures and over a wide range of temperatures. Thus, syndiotactic and isotactic polymers which can crystallize can be used at higher temperatures than their atactic or amorphous analogs.

Another way to improve the shape retention of polymers when they are heated is to introduce intermolecular interactions or links (Fig. 7.3) between functional components of the main chains and the side chains. Such functions have a distinct influence on the melting temperature and can be seen as a criterion for estimating heat stability as a first approximation (Table 7.2).

If every second CH_2-group in polyethylene is replaced by O, the polymer becomes more polar, and the melting temperature rises from 137 °C (polyethylene) to 175 °C (polyoxymethylene). CONH-moieties in the main chain of polyamides lead to a further increase of the melting temperature to 255–267 °C. Some side groups, e.g., CH_3, Cl, C_6H_5, or CN, also increase the polymer's melting temperature. In contrast, the melting temperature is decreased by longer alkyl side chains (▶ Chap. 5) (Brandrup et al. 1999). An important means of increasing the temperature at which a polymer can be used is to include aromatic structures in the main chain. Some typical examples are shown in Fig. 7.12.

Table 7.2 Influence of the polymeric structure on the melting temperature (comments ▶ Chap. 5)

Structure		Name	Melting temperature (°C)
		Polyethylene	137
		Polyoxymethylene	174–180
		Polyamide	255–267
	A = CH_3	Polypropylene	170–180
	A = Cl	Polyvinylchloride	180–240
	A = C_6H_5	Polystyrene	240–270
	A = CN	Polyacrylonitrile	317
	R = C_2H_5	Poly(butene-1)	126

Polyimides are synthesized in a two-step process and are particularly well researched (Fig. 7.13).

These polymers are resilient until ca. 500 °C for short periods of time and can be used long-term at temperatures of up to 270 °C.

Another concept for developing heat-stable polymers, which has proved successful, is the systematic replacement of carbon atoms by heteroatoms, such as Si, Sn, Al, Ti, etc. (Fig. 7.14).

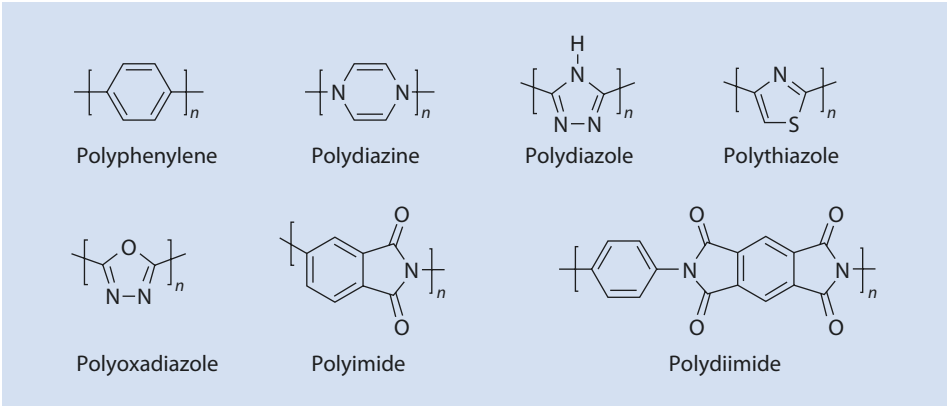
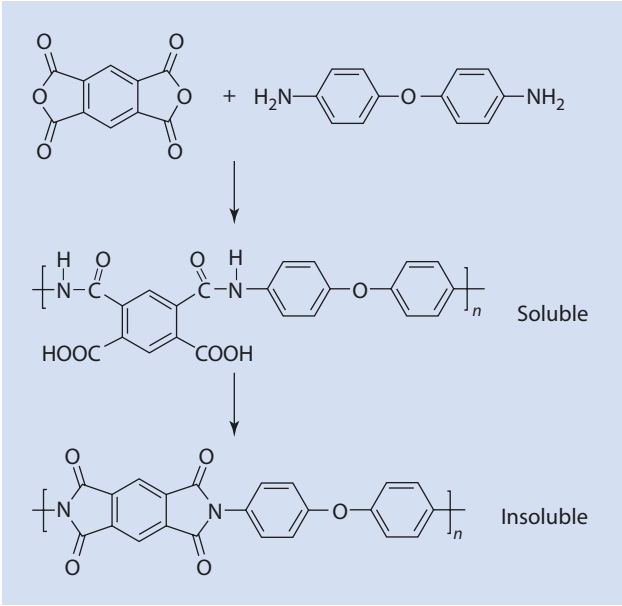


Fig. 7.12 Polymers with aromatic rings in the main chain

Fig. 7.13 Synthesis of polyimides



The transition from single-chain polymers to *ladder polymers* (Fig. 7.15) is particularly interesting. Evidently, polymers with a single main chain only sustain a decrease in their molar mass if one bond of the main chain breaks, and thus their mechanical and thermal characteristics deteriorate. In contrast, breaking a single bond in a ladder polymer does not change the molar mass. Indeed, there is a good chance that the breakage heals because the radicals initially formed by the bond breaking are held in close proximity by the rest of the molecule and they can recombine.

Ladder polymers such as those depicted in Fig. 7.15 can have thermal distortion stabilities close to that of quartz. Carbon fibers (▶ Chap. 4) also exhibit excellent heat

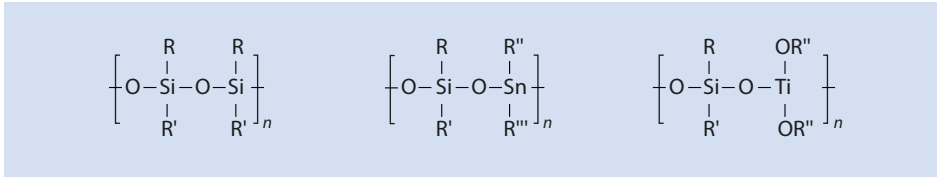


Fig. 7.14 Thermally stable heteropolymers

Fig. 7.15 Siloxane-based ladder polymer

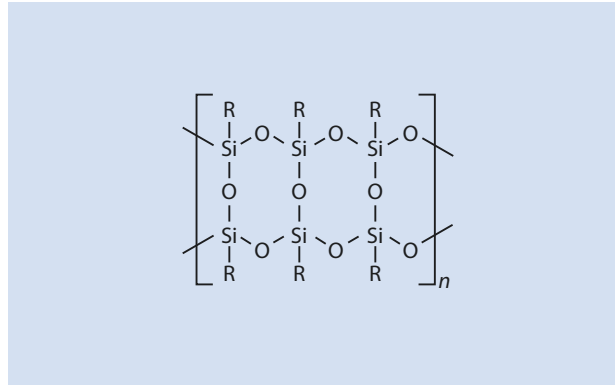
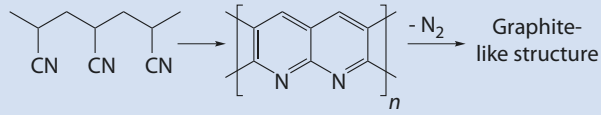


Fig. 7.16 Simplified depiction of the formation of carbon fibers



resistance. Crucial characteristics of carbon fibers are their extraordinarily high mechanical strength and their heat stability. Their manufacture is complex, and they are made mainly from polyacrylonitrile fibers (Fig. 7.16). They can also be made from pitch or cellulose fibers. At 150–350 °C an oxidation and partial cyclization takes place. In a second stage the fibers are carbonized at temperatures up to 2000 °C and ever more highly organized structures similar to graphite, which can be considered simplistically as ladder structures, are formed. The strength and low density of carbon fibers can best be exploited as composites with, e.g., epoxy resins or polyesters. They are extensively applied in aircraft construction but also, e.g., in high performance sports equipment.

7.3 Cross-Linked Materials

Connecting several polymer chains together via covalent bonds leads to 3D network structures. These consist theoretically of a single molecule of which the molar mass is essentially infinite. Cross-linking is one of the most important means of modifying the material characteristics of a polymer. Cross-linking can take place either during the synthesis of a polymer by copolymerizing a multi-functional monomer (▶ Chap. 8) or by subsequent reaction of a pre-prepared polymer (▶ Chap. 15).

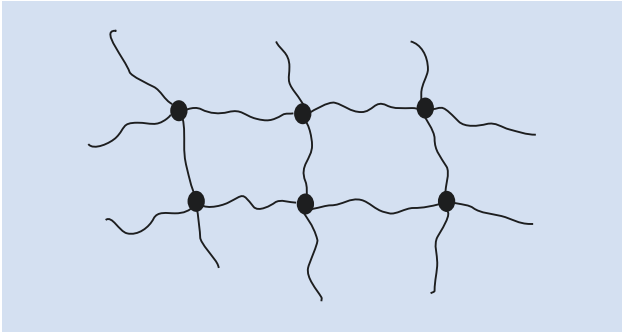


Fig. 7.17 Schematic depiction of a polymeric network

7.3.1 Structure and Application of Networks

A network is characterized by network points of specific functionality f ($f = 3, 4, \ldots$) connected to other network points by f chains (Fig. 7.17).

Polymeric networks can be soft, rubber-like materials (elastomers, ▶ Chap. 18) but also very hard materials. They can also form swollen gels with solvents. The thermo-reversibly cross-linked thermoplastic elastomers, discussed above, also belong to the class of polymeric networks.

Examples of applications for covalent networks include:

- Vulcanized rubbers (elastomers, for example car tires)
- Composite materials
- Organic coatings, such as car paints
- Separation media (ion exchange resins)
- Prostheses, contact lenses
- Carriers for the controlled release of active ingredients
- Electronic systems for printed circuits
- Biological gels, for example the lens of human eyes

This short list of examples emphasizes the numerous material requirements and particularly that these requirements can differ greatly. To fulfill these requirements the materials need to be specifically adapted.

Generally, one can say that networks can be differentiated from their linear analogues by their insolubility and infusibility.

7.3.2 Mechanical Characteristics of Networks

Cross-linked materials are similar to semi-crystalline systems in some of their properties; neither semi-crystalline nor cross-linked polymers are viscoelastic. A macroscopic flow of the material is either hindered by the crystal lamellae or by the cross-links. The lamellae or cross-links act as anchor points and fix the macroscopic form of the article even for temperatures above T_G. However, the material appears softer and is tougher at temperatures between T_G and T_m because the amorphous phase dissipates impact energy (▶ Sect. 7.2.1).

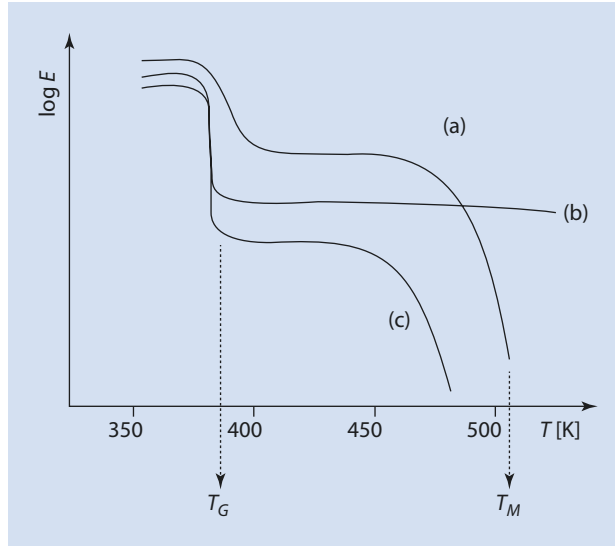


Fig. 7.18 Changes in the E-module of an (**a**) isotactic, (**b**) cross-linked atactic, and (**c**) linear, non-cross-linked atactic (high molecular) polystyrene with temperature

With an increasing number of network points in an amorphous material:

- The relaxation time and module increase
- The yield point rises until it disappears when cross-linking is complete
- The viscous flow and stress relaxation decrease; both these processes also cease when cross-linking is complete

Both crystalline and amorphous polymers can be cross-linked whereby, to a first approximation, cross-linking does not change the morphology of the material.

Figure 7.18 shows the influence of the temperature on the mechanical characteristics of the material using polystyrene as an example. In this diagram isotactic, atactic, and cross-linked, atactic polystyrene are compared with each other.

The curve of the E-module with temperature for atactic polystyrene has already been discussed above. If the material is cross-linked, the material characteristics—for instance, the module—below the glass transition temperature are relatively independent of whether the material is cross-linked or not. The module drops for both materials at the glass transition but for the cross-linked material the module stabilizes at a higher level (to a first approximation) until the material thermally decomposes. This happens because the material cannot flow. The semi-crystalline, isotactic polystyrene also passes through a glass transition but, because only the amorphous part of the material undergoes a glass transition, the module decrease is not as large as that of the amorphous material. Between T_G and T_m the module is determined by the crystalline portion of the material and changes very little with temperature; this also leads to a plateau in the log E vs. T curve. The module only drops again significantly when the melting temperature of the crystalline portion is reached.

The industrially very important, so-called elastomers are more or less soft, cross-linked polymeric materials. Because of their considerable importance they are discussed separately in ► Chap. 18.

7.3.3 Network Synthesis

To form stable polymeric networks, any reaction in which covalent bonds are formed can be used. The number of organic reactions that could be used is nearly infinite. In practice the following inter alia are employed:

- Reactions of epoxides
- Reactions of isocyanates
- Hydrolysis and condensation of alkoxy silanes and hydrosilylation
- Reactions of phenol and formaldehyde
- Reactions of urea, thiourea, and melamine with formaldehyde
- Addition of SH- or NH_2-terminated molecules to C=C-bonds
- Vulcanization of rubber by sulfur, peroxides, or phenol-formaldehyde resins
- Radical copolymerization of poly-unsaturated monomers
- Radical polymerization of α,ω-telechelics

Because the direct synthesis of polymeric networks is independent of the mechanism of the polymerization, some selected reactions are discussed here. The subsequent cross-linking of pre-formed polymers is discussed in Chap. 15.

7.3.4 Typical Cross-Linking Reactions

Multi-functional Monomers

The stoichiometric reaction of bifunctional alcohols with trifunctional isocyanates results in cross-linked polyurethanes (Fig. 7.19).

In a similar way, networks can be formed directly from monomers by radical chain reactions. One example is the copolymerization of styrene with 1,4-divinyl benzene (Fig. 7.20).

When the two vinyl groups of 1,4-divinyl benzene are incorporated into different chains and when their incorporation exceeds a certain critical level, the resulting copolymer consists (ideally) of a single macromolecule network.

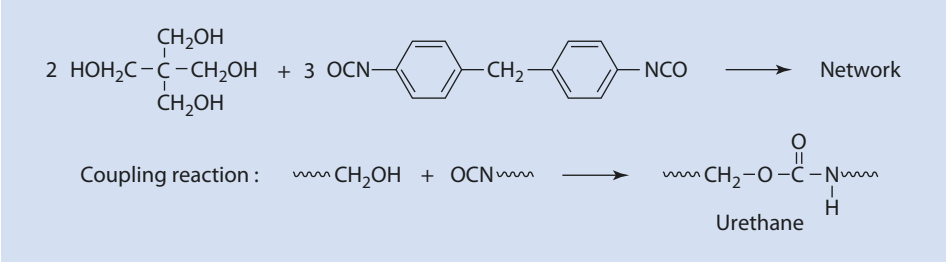


Fig. 7.19 Example of the formation of a network via a step-growth reaction

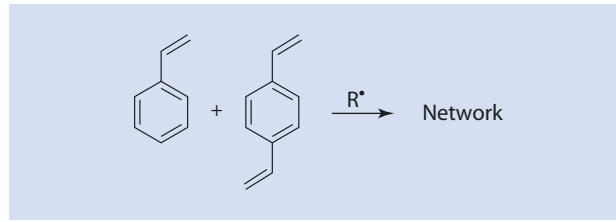


Fig. 7.20 Cross-linking during radical copolymerization

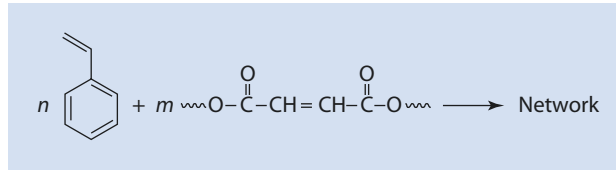


Fig. 7.21 Cross-linking via copolymerization of a monomer with a multi-unsaturated polymer

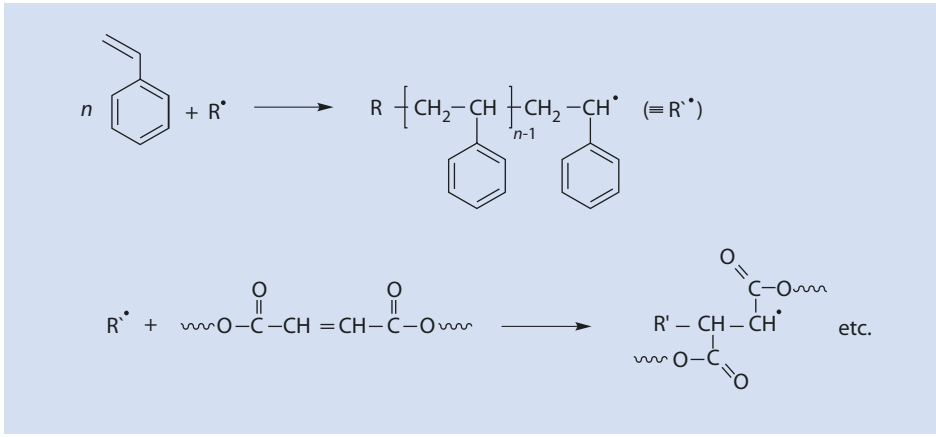


Fig. 7.22 Elementary steps of the reaction of styrene with an unsaturated polyester

Reaction of Monomer with Polymer

A polymer network results from the radical polymerization of styrene in the presence of unsaturated polyesters. Redox initiators are often used for such polymerizations so that they can be started at room temperature (Fig. 7.21).

Here, the growing polystyrene chain reacts with a C=C-bond of the unsaturated polyester. Thereby, it is connected with the polystyrene chain in a sort of copolymerization. When several C=C-groups of the unsaturated polyester react in this way, a network inevitably forms (Fig. 7.22).

The addition of an α,ω-dithiol to an unsaturated polymer belongs to this category of network formation via reaction of a monomer with a polymer (Fig. 7.23).

In place of the thiol in Fig. 7.23, SiH- or NH_2-functionalized molecules can be employed.

A cross-linking reaction frequently used is the stoichiometric hardening of α,ω-diepoxides with amines (Fig. 7.24) or acid anhydrides.

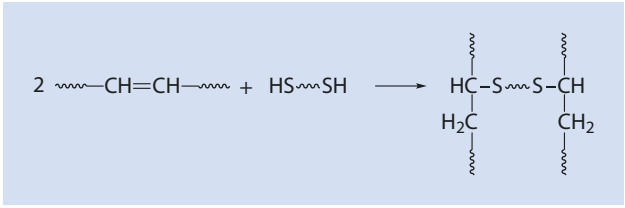


Fig. 7.23 Reaction of an *α,ω*-dithiol with an unsaturated polymer

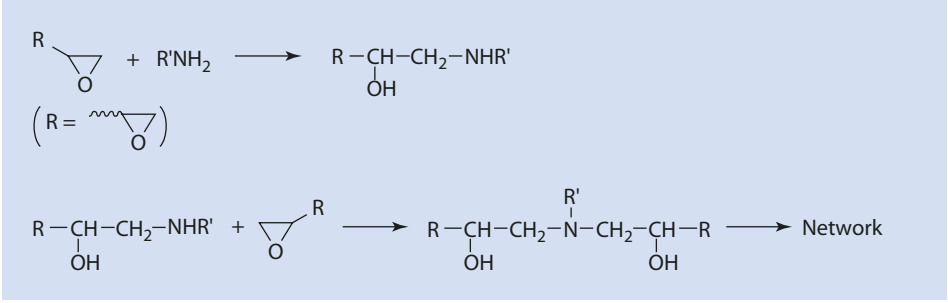


Fig. 7.24 Fundamental step of the cross-linking of an epoxy resin with a primary amine

7.4 Polymer Additives

Polymer additives are substances that improve the characteristics of a polymer, often in very small amounts. They are often necessary to convert a polymer into a useful material. Such additives:

- Improve the processability of the polymer
- Improve the mechanical properties of the polymer
- Reduce the costs
- Modify the surface of the polymer
- Influence the optical characteristics
- Improve the aging resistance of the polymer (▶ Chap. 15)

In addition, there are other additives which induce fire resistance or which act as foaming agents (blowing agents).

7.4.1 Technological Requirements on Polymer Additives

Additives need to be effective and cost effective. They must be compatible with the polymer matrix and not be removed from the polymer during processing. In addition, they should not be hazardous to health. These requirements vary depending on the application. Particularly strict requirements naturally exist for application in polymers for medical engineering or for food packaging.

An inevitable side effect is a deterioration of the electrical insulating effect because additives are usually more polar than the polymer. For the same reason, the absorption of water, and thus the hydrolysis susceptibility, can increase. The polymer and the additives are compounded by solution, solid suspension, and melting, but also by mixing as dry powders. The chosen mixing method depends on the inherent characteristics of the materials, the requirements of the compound quality, and the mixing plant's available equipment.

7.4.2 Function of Selected Additives

During processing, polymers experience both thermal and mechanical stress (▶ Chap. 17). Depending on the structure, bonds break or low molar mass entities are eliminated. For example, HCI can be eliminated from polyvinyl chloride. *Stabilizers* (▶ Chap. 15) help to hinder or repress undesirable reactions. Their main task is to maintain the desired characteristics of polymers over a longer time and to prevent the harmful influence of atmospheric oxygen. Lubricants help to reduce friction between the polymer and the reactor wall, or the inner wall of processing tools. These additives are similar to soap and accumulate on the polymers surface.

Equally important are *UV-stabilizers*, which protect the organic material from the negative effects of visible and UV light (▶ Chap. 15). One of the most effective additives against the negative effects of light is *carbon black*. The mechanical characteristics of the polymers are influenced by *plasticizers* or *reinforcing fill*ers (glass fiber, ▶ Chap. 17). Fillers can also be used simply to stretch the polymer and make it more cost-effective, and to modify the polymer's specific weight. The surface characteristics of polymers are improved by *antistatic agents*. In this way, the danger of the electrostatic charge on PVC-floors, for instance, can be reduced. The optical characteristics are influenced by *dyes* and *pigments*, and the above-mentioned *carbon black* also plays a role here.

Depending on their structure, polymers are more or less susceptible to attack by unwanted microorganisms. To prevent this, *fungicides*, for example, are added to the polymer. Because polymers are usually organic substances, their flammability needs to be reduced by adding *fire retardants. Blowing agents* are used to transform the polymer into a foam.

The weakening of the polymer by radiation, temperature, oxygen and other reactive gases, water, microorganisms, and by mechanical stress leads to discoloration, the loss of optical clarity, the loss of insulation quality, and/or the deterioration of the mechanical properties. The above-mentioned additives can delay the deterioration, but, as a rule, they cannot prevent it, because they are used up as they act (for example, antioxidants react with oxygen) or slowly diffuse out of the polymer.

7.4.3 "White Carbon Black"

Quartz powder has become a proven filler for casting resins. Casting resins are relatively low molecular, uncross-linked precursors which usually consist of one or two components to which, before being processed (hardened) to cross-linked polymers, an additional reactant and fillers are added. The addition of quartz powder reduces the heat development during the hardening (dilution effect), the volume shrinkage is decreased, and the thermal conductivity is increased. Particularly those fillers that bind chemically to the polymer influence its properties favorably, because a separation of the components is thereby prevented and the problems that often result from the

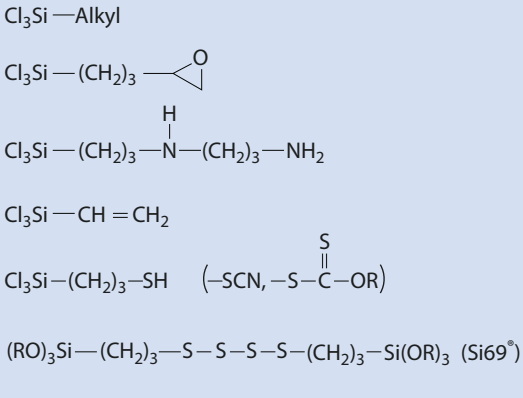


Fig. 7.25 Selected silanes for the modification of silica

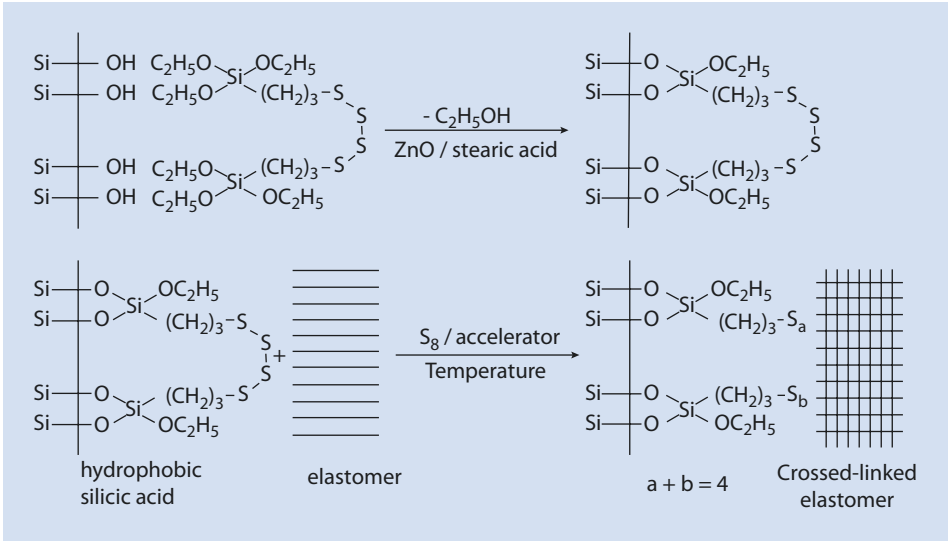


Fig. 7.26 Si69® as a coupling agent between silica and a rubber matrix

interface between the polymer and the filler are reduced. Free OH-groups on the surface of silica, for example, can take part in the hardening process of cast resins. Furthermore, reacting these groups with silanes modifies the silica surface and increases the range of applications where it can be usefully employed. Thus silica can be specifically modified depending on which polymer it is to be compounded with. A selection of modification reagents is listed in Fig. 7.25.

Attempts have been made for quite some time to replace carbon black, at least partially, with quartz, i.e., to develop a "white carbon black." This initially rather unsuccessful research was given a renewed fillip by the large increase in the raw materials for carbon black during the oil crisis. Because of their polarity difference, rubber and silica are incompatible. The surface of the silica can be made hydrophobic by reacting it with coupling agents such as Si69® (Fig. 7.26). Subsequently, the tetrasulfan group of the Si69® reacts with the double bonds of the elastomer matrix. The partial substitution of carbon black as filler by silica, combined with the use of such

Table 7.3 Example of a recipe for the tread of an automobile tire

Components	Weight amount (phr)[a]
Styrene-butadiene rubber (SBR)	70
Butadiene rubber	30
Carbon black	55
SiO_2	49
Specific coupling agent	12
ZnO	6
Stearic acid	2
Vulcanization accelerator	1–3
Sulfur	1–2
Stabilizers	1

[a]*phr* parts per hundred rubber; weight amounts based on the total amount of rubber

silanes, leads to an improvement of the rolling resistance and the wet traction, at the same time maintaining acceptable abrasion resistance. Because of the fuel-saving potential of reduced rolling resistance, the term "green tire" has been coined for silica-silane-filled tires.

The recipe for the tread of an automobile tire shows how complex the transformation of a polymer into a useful material can be (Table 7.3).

The additives have specific functions, which need to be carefully tuned (Eyerer et al. 2008). Table 7.3 shows that one cannot do completely without carbon black in this recipe. Carbon black not only improves the mechanical characteristics but is also an established protection against UV-light (▶ Chap. 15).

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