Amorphous Polymers

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The fundamental principles of "amorphous" polymers were introduced in ▶ Chap. 4. Some of their particular properties are described in more detail in this chapter.

6.1 Dependence of the Mechanical Properties of Amorphous Polymers on Temperature

To understand the unique behavior of amorphous polymers, let us first consider their behavior when they are heated. The change of the E-module of an amorphous polymer with a large molar mass when heated is shown in Fig. 6.1.

The polymer chains are frozen at a low temperature (Fig. 6.1, temperature range I); that is, the molecules are immobile. If an applied force acts upon them, they cannot change position, and the E-module, the force needed to stretch the sample, is very large. The material behaves as if it was a glass-like solidified liquid. Even though the polymer is not crystallized, its shape is macroscopically stable over this temperature range; it does not flow. If the deformation force is large enough, the material simply breaks.

The first chain segments start to move as the temperature approaches the glass transition temperature (Fig. 6.1, temperature range II). At this temperature the material can react better to an external force; the polymer chains can rearrange and the material is less brittle. The tenacity, the opposite of brittleness, of the material, increases. The material behavior is similar to that of leather. Therefore, this temperature range is also referred to as the *leathery state*.

The material can, theoretically, be considered as a melt above the temperature T_G. Because of its high viscosity, however, and especially the numerous entanglements of the polymer chains, the material (as long as the temperature is not that high) does not, macroscopically, behave as a liquid. Instead the material appears, at first glance, to be a solid. This changes, however, if mechanical force is applied to the material over a longer period of time. In this case, the polymer chains have enough time to yield to the forces being exerted upon them and to rearrange. The material flows and takes on a different shape.

The amount of time during which a force is applied to a sample determines whether the material irreversibly changes its shape, whether flow actually takes place or not. A single blow or other short application of force does not give the polymer chains time to yield to the forces by flow. After the application of force, the material can, as long as it is not broken, regain its original shape. If, however, the force is applied for a longer time, the material can flow irreversibly. In this temperature range (Fig. 6.1, temperature range III) the material

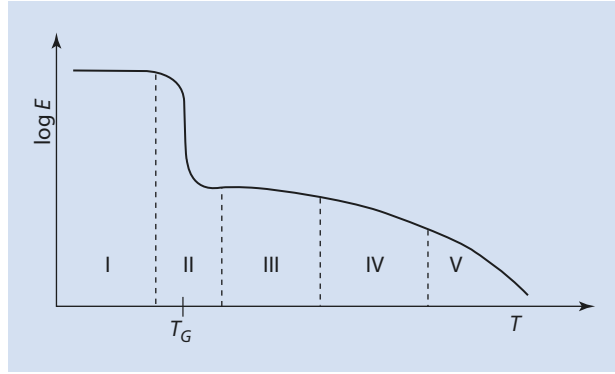


Fig. 6.1 Change of the E-module of an amorphous polymer with a large molar mass as a function of temperature

exhibits both viscous and elastic mechanical behavior. This type of behavior is called viscoelasticity and is discussed in more detail in ▶ Sect. 6.6. Over temperature range III the material is, theoretically, an extremely viscous melt, called the *rubber-elastic state*. In this state the elasticity of the material still dominates over its viscosity.

If the temperature is increased even further (◘ Fig. 6.1, temperature range IV), the polymer chains in the material gain molecular mobility. As a result of this, the material can flow more easily and its ability to react elastically decreases. That is, the ability of a sample to take on its original shape after a force has been applied decreases.

If a mechanical stress is applied to the material and then released, part of the resulting deformation is restored, whereas another part of it remains. The latter, at a molecular level, involves the polymer chains reacting to the applied force by taking on a different conformation. Because the newly assumed conformation is not the same as that of the undisturbed state, it is less favorable energetically (▶ Chap. 2). By moving relative to one another, the polymer chains can rearrange in an energetically more favorable conformation if the applied stress acts over a longer period of time or the temperatures are higher.

In temperature range IV shown in ◘ Fig. 6.1, we are dealing with two opposing effects: on the one hand, an elastic component that is dependent upon the entanglements of the polymer chains; on the other, a viscous component that is present if the polymer chains have enough energy to move relative to one another, allowing the sample to flow macroscopically. This intermediate stage is referred to as *rubber-elastic flow*.

Temperature range V describes the gradual transition into a viscous melt that does not possess a significant shape memory. The polymer is in a viscous state in this temperature range.

The boundaries between temperature ranges III and V in ◘ Fig. 6.1 are not clearly defined. The transitions from one stage to another are gradual. Elasticity and shape stability decrease as temperature increases, whereas the ability to flow on a macroscopic level increases.

6.2 Amorphous State

In an amorphous, glass-like solid state, a polymer is similar to a plate of frozen pasta. Considerable force is necessary to deform the material. The chain segments are immobile; in some cases there may be some mobility of the side chains. The latter leads to the material being less brittle (i.e., tougher) than, for example, quartz glass. In this state, even strains of a few percent lead to failure—*brittle fracture*. As already explained in ▶ Chap. 4, at temperatures above T_G the material can yield to an external force without breaking. The energy is dissipated by the molecules rearranging and the material is tough rather than brittle.

As a first approximation, in the frozen state the polymer chains are not arranged in any, sort or long range, regular pattern. At temperatures below T_G, movement of the chain segments is not possible and the molecules cannot change their relative positions. The only movements possible are vibrations at an atomic level. If the temperature rises above T_G, the movement of individual segments becomes possible. A transition to a melt state follows in which the material can flow—even if the viscosity is very high.

A macroscopic flow of the material requires that the polymer chains do not have a high packing density. This is, however, generally the case in the amorphous state. There is a certain amount of *free volume* given by the imperfect packing of the irregularly arranged

chains. This is the case both above and below T_G, and as a consequence the density of the amorphous material is lower than that of the corresponding crystal. An increase in temperature leads to a thermal expansion of the material, the free volume increases, and the polymer chains become more mobile; the viscosity decreases and the melts flows more easily.

6.3 Glass Transition

The changes in the mechanical properties of polymers at the glass transition can be described by a transition from a hard ($T < T_G$) to a soft ($T > T_G$) spring. A polymer chain surrounded by enough free volume with enough thermal energy to allow significant molecular movement is similar to a soft spring. A molecularly frozen polymer chain below T_G can be considered in terms of a hard spring. From physics it is known that both soft and hard springs store elastic energy. The ability to store energy is greatest at the resonance frequency of the spring, whereby the resonance frequency of a hard spring is higher than that of a soft one—hard springs oscillate more rapidly than soft springs.

An amorphous material is, however, not completely homogenous. Generally it is made up of polymer chains of different lengths, and, additionally, the distribution of the free volume is not identical for each chain. Thus, if a polymeric material is heated, as the temperature approaches that of the glass transition, initially only some of the polymer chains transition from a hard to a soft state. This has a strong influence on the ability of the material to store energy. In this temperature range the material is made up of a mixture of 'springs' of different resonance frequencies. Macroscopically, the whole system does not have a homogenous resonance frequency. The result of this is a strong damping of mechanical energy.

Using a material at temperatures close to the glass transition temperature is problematic because of the radical and erratic variation of the mechanical properties (moduli) (Fig. 6.1).

Other properties of the material which change at the glass transition temperature are:

- Specific volume
- Heat capacity
- Refractive index

These changes in properties can be used experimentally to measure the glass transition temperature.

6.4 Factors that Influence the Glass Transition Temperature

The temperature at which the glass transition occurs is essentially determined by the mobility of the polymer chains. In turn the chain mobility is most strongly influenced by the following factors:

- Chain flexibility
- Steric effects
- Tacticity

- Branching and crosslinking
- Molar mass

6.4.1 Chain Flexibility

Fundamentally, flexible chains are more mobile and lead to a lower glass transition temperature. Examples of flexible chain elements are alkyl, ether, or silicone moieties (Fig. 6.2).

In contrast, chain rigidity is increased by the incorporation of rigid segments such as aromatic rings into the polymer backbone.

Table 6.1 shows the influence of chain flexibility on the glass transition temperature of some selected examples.

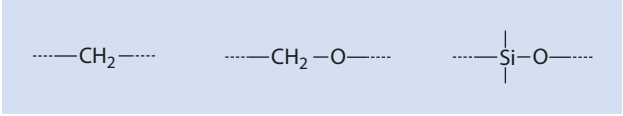
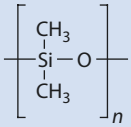
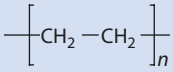
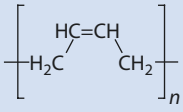
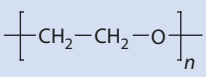
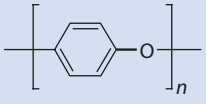


Fig. 6.2 Examples of flexible chain elements

Table 6.1 Glass transition temperature (T_G) of selected polymers having chains of varying flexibility (decreasing from top to bottom)

	T_G (°C)
	−123
	−93
	−85
	−67
	+83

Sterically demanding, stiff segments in the main polymer chain lead to a less mobile polymer chain and the glass transition temperature increases. Thus, polyphenyl ether has a glass transition temperature of +83 °C (bottom line of Table 6.1).

6.4.2 Steric Effects/Substituents

Flexible side chains increase the available free volume and thus the mobility of the polymer chain. As a result of this the glass transition temperature is lowered (Table 6.2).

Polar substituents can form hydrogen bonds or dipole–dipole interactions which fix the position of the polymer chains and decrease their mobility; the glass transition temperature is increased (Table 6.3).

Additional methyl groups in an α-position relative to the substituent result in a substantial stiffening of the polymer chain and so to an increase in the glass transition temperature of 70–100 °C. A classic example of this is polymethacrylates, which have higher glass transition temperatures than the corresponding polyacrylates.

6.4.3 Tacticity, Branching/Cross-Linking, and Molar Mass

The influence of the configuration or tacticity of polymers from vinyl monomers is only pronounced if there is more than one substituent, such as an additional methyl group, adjacent to the double bond—as is the case for the polymethacrylates mentioned above. Such monomers are, however, usually radically polymerized, whereby the tacticity of the polymer formed cannot be, or is only marginally, controlled. The glass transition

Table 6.2 Influence of linear alkyl substituents on the glass transition temperature (T_G) of polymers with the structure $(CH_2–CHX)_n$

–X	T_G (°C)
–H	–93
$–CH_3$	–20
$–C_2H_5$	–24
$–C_3H_7$	–40
$–C_4H_9$	–50

Table 6.3 Influence of polar substituents on the glass transition temperature (T_G) of $(CH_2–CHX)_n$

–X	T_G (°C)
$–CH_3$	–20
–Cl	+81
–CN	+105

temperature of typical polyolefins such as polypropylene is, in contrast, not (or only marginally) dependent on the tacticity because of the missing second substituent.

If the material is cross-linked, the cross-links function as permanent entanglements and chain movement is restricted. At low cross-link densities the glass transition temperature increases almost linearly with the number of cross-links. Materials with a high cross-link density tend to exhibit a broad, ill-defined glass transition.

The polymer chain ends are, in contrast to the other segments along the chain, relatively mobile. Because of this they are able to 'create' comparatively more free volume around themselves. By the same argument as that used above, polymers with lower molar mass have lower glass transition temperatures. This effect can be described by Bueche's empirical equation:

$$T_G = T_G^{\infty} - \frac{const.}{M_n} \tag{6.1}$$

T_G^{∞} Glass transition temperature for $M_n \rightarrow \infty$

The equation can be applied to molar masses M_n of above ~5000 g/mol. Thus, the glass transition temperature asymptotically increases to a limiting temperature valid for very high (infinite) molar mass.

Theories Describing Free Volume

The term 'free volume' has already been used several times when describing the glass transition temperature. It is assumed that the volume V of a polymer sample is made up of a volume V_0 that is occupied by the polymer molecules and an additional free volume V_f that is available for the rotational and translational movement of the molecules:

$$V = V_0 + V_f \tag{6.2}$$

V Total volume
V_0 Volume of the chains
V_f Free volume

Both V and V_0, as well as V_f, are dependent on the temperature. For a polymer in its fluid or a rubber-elastic state, the free volume increases with temperature. Visually, the mobility of the molecules increases. However, if the temperature decreases, the free volume shrinks and below a critical temperature—the glass transition temperature—it doesn't change any more; the molecules are immobile.

The main difficulty of theoretically describing the glass state using free volume is that free volume is not an equilibrium state. Basic approaches to a theoretical description of the glass state that should be mentioned are:

- Williams, Landel, and Ferry's kinetic approach (WLF equation)
- Gibbs and DiMarzio's thermodynamic approach
- Gibbs and Adam's combination approach

For more details the interested reader is referred to the corresponding literature (Adam and Gibbs 1965; DiMarzio et al. 1976; Eisele 1990; Williams et al. 1955). Estimating what proportion of the material is free volume is both theoretically and experimentally difficult, and estimates vary according to parameters such as polymer and temperature between 2.5 % and 12 % of the total volume.

6.4.4 Plasticizers

Plasticizers are low molar mass, non-volatile compounds added to a polymer to change its properties. Generally these compounds have a 'lubricating effect' on the polymer chains. The molecules can move more easily when surrounded by low molar mass material. The addition of a plasticizer thus results in an increase in the mobility of the chains and consequently to a lowering of the glass transition temperature. Plasticizers are therefore used so that soft, flexible materials can be obtained from stiff, brittle base polymers.

A technically important material, which often has large quantities of plasticizers added to it, is polyvinyl chloride (PVC). PVC without plasticizer has a glass transition temperature of 81 °C. If 30–40 % plasticizer is added, so-called soft-PVC is obtained, which has a glass transition temperature of <0 °C. Important uses of this material are for the manufacture of raincoats, curtains, and cable sheathing.

The effect of the addition of a plasticizer on the glass transition temperature can be estimated using

$$\frac{1}{T_G} = \frac{w_{Pol}}{T_{G,\,Pol}} + \frac{w_W}{T_{G,W}} \tag{6.3}$$

w_{Pol}	Mass fraction of the polymer
w_W	Mass fraction of the plasticizer
$T_{G,\,Pol}$	Glass transition temperature of the polymer
$T_{G,W}$	Freezing point or glass transition temperature of the plasticizer
T_G	Glass transition temperature of the plasticized polymer

Water can have a strong plasticizing effect on hydrophilic polymers. In these cases, the properties of the material are very dependent on the surrounding conditions, especially the humidity of the surroundings. This effect, which, for example, can be observed with the biopolymer starch, means that using such materials is a challenge.

6.5 Rheological Behavior of Polymer Melts

The rheological behavior of polymer melts is complex but relevant for understanding amorphous materials at temperatures above T_G as well as for understanding the processing of polymers (▶ Chap. 17), as processing usually involves polymer melts. For this reason, the next part of this chapter deals with *rheology*, the science of flow behavior, and its relevance to polymers.

6.5.1 Newtonian Fluid

According to Newton, the rheological behavior of a simple fluid can be described by

$$\sigma = \eta\left(\frac{dv}{dx}\right) \tag{6.4}$$

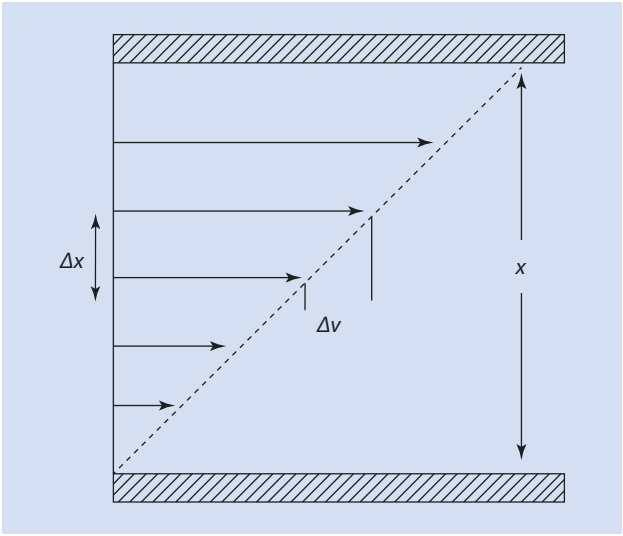


Fig. 6.3 Rheological properties of a Newtonian fluid. The bottom plate remains static and the top plate moves with a velocity *v* and a separation *x* relative to the bottom plate

Equation (6.4) establishes a correlation between the shear rate (dv/dx) and the shear stress σ. For the simplest case, a Newtonian fluid, the shear rate is linearly proportional to the shear stress. The proportionality constant η is the viscosity.

The flow properties of a Newtonian liquid between a static and moving plate are shown schematically in Fig. 6.3.

Two smooth sheets, between which there is a layer of fluid of thickness **x**, are moved relative to one another with a tangential velocity v. The top layer of fluid adheres to the sheet above it and pulls a layer of fluid with it. The friction between the fluid layers leads to a further layer of fluid following the one above it, albeit with a slower speed. The layer of fluid next to the bottom sheet is at rest ($v = 0$). The friction F_R which opposes the movement is proportional to the shear rate dv/dx and the area A (▶ see (6.5)). The proportionality constant η in this equation is also called the *dynamic viscosity* for this reason.

$$F_R = A \cdot \eta \left(\frac{dv}{dx} \right) \tag{6.5}$$

With the definition of shear stress

$$\sigma = \frac{F_R}{A} \tag{6.6}$$

(6.5) can be transformed into Newton's law of friction (6.4).

6.5.2 Non-Newtonian Fluids

By introducing a coefficient of viscosity n it is possible to take nonlinear relationships between shear stress and shear rate into account:

$$\sigma^n = B\frac{dv}{dx} \tag{6.7}$$

Substituting $n=1$ and $B=\eta$ gives (6.4). Using $n>1$ the rheology of polymers can be described. The coefficient B decreases with an increasing shear rate. The gradient of the curve decreases (upper curve in Fig. 6.4). The fluid (polymer melt) initially behaves as an elastic body and then begins to flow. This behavior can be explained by considering that, at rest, the polymer chains are looped and entangled so that they resist displacement. As the velocity gradient increases, the polymer chains become disentangled and aligned parallel to the applied stress; flow becomes increasingly easy. This effect is known as structural viscosity or shear thinning.

The entanglement of the polymer chains are the main reason for the high viscosity of polymer melts. However, they are effective when the chains are longer than a certain length. Short chains are unable to form effective entanglements. The minimal chain length needed for entanglements to form and viscosity to be affected is called the critical chain length ζ_c. As a rule of thumb, ζ_c corresponds to main chains consisting of about 100 units. The critical chain length is generally longer for non-polar polymers than for polar polymers. Because of the stronger interactions between the chains, polar polymers tend to be more able to form effective entanglements.

With a plot of log η against log M_n (Fig. 6.5) it is often possible to observe that, below a critical chain length, the logarithm of the viscosity varies with the logarithm of the molar mass with a gradient of 1 (n *in* (6.7) = 1). Above the critical chain length, the viscosity increases roughly with the cube of the molar mass in a way that is roughly proportional to the cube of the molar mass (n *in* (6.7) ≈ 3).

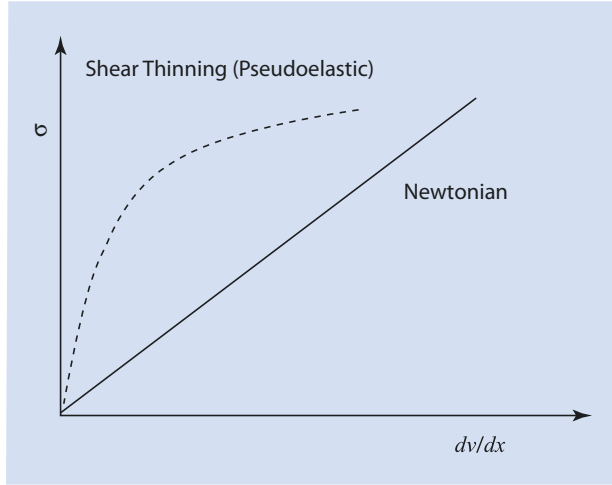


Fig. 6.4 Comparison of a Newtonian and a structurally viscous fluid

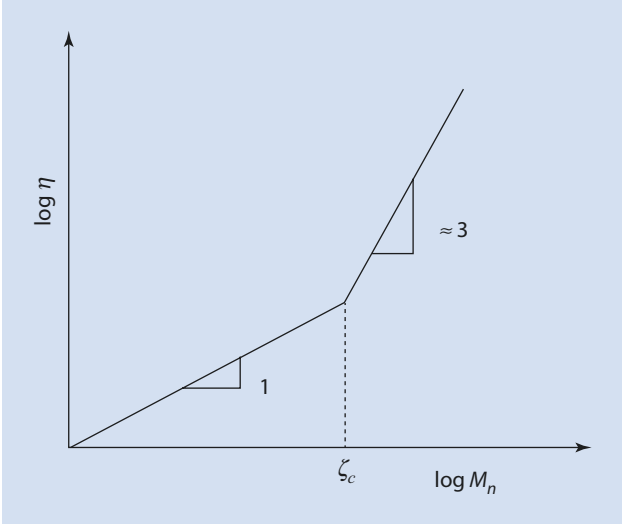


Fig. 6.5 Determining the critical chain length ζ_c above which entanglements of the polymer chains affect the viscosity of a polymer melt

6.5.3 Process of Reptation

Being entangled with other chains, the movement of intact polymer coils through the melt does not take place. Instead, the individual chains have to 'wriggle' around the entanglements. This is effected by the movement of individual chain segments and allows the polymer to be divided into independent kinetic units for a theoretical treatment. The polymer melt flows when these units change their position. They can, for example, move in a crankshaft-like movement in the melt (Fig. 6.6).

This process is called *reptation*. In the reptation model the entanglements are considered as fixed sites in the network which define the shape of a tube through which the polymer chain moves (Fig. 6.7a).

The change in position in the tube takes place by a meandering of a few chain segments. The movement can be visualized by thinking of the way a snake moves, or the way a carpet slides over a smooth surface (Fig. 6.7b).

Rate of the Reptation Process

The time that the polymer chain takes before it leaves the tube created by the entanglements is defined as the relaxation time τ_P and, without proof:

$$\tau_P = \frac{(n \cdot l_0)^2}{2D_t} \tag{6.8}$$

τ_P	Time the polymer requires to leave the 'tube'
n	Number of reptation units in the polymer chain
l_o	Length of a segment (under ϴ-conditions, ▶ Chap. 2)
D_t	Diffusion coefficient within the reptation tube

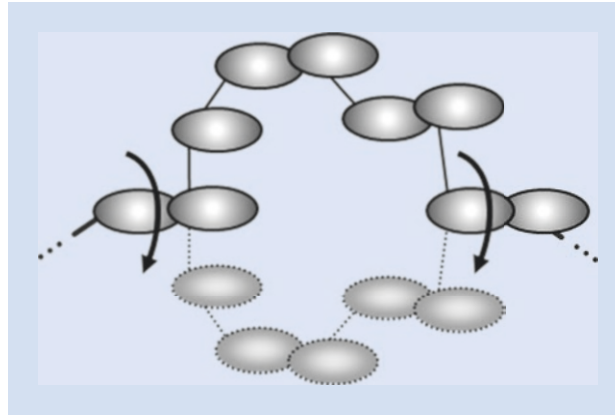


Fig. 6.6 Crankshaft-like movement of the segments of a polymer chain in the melt

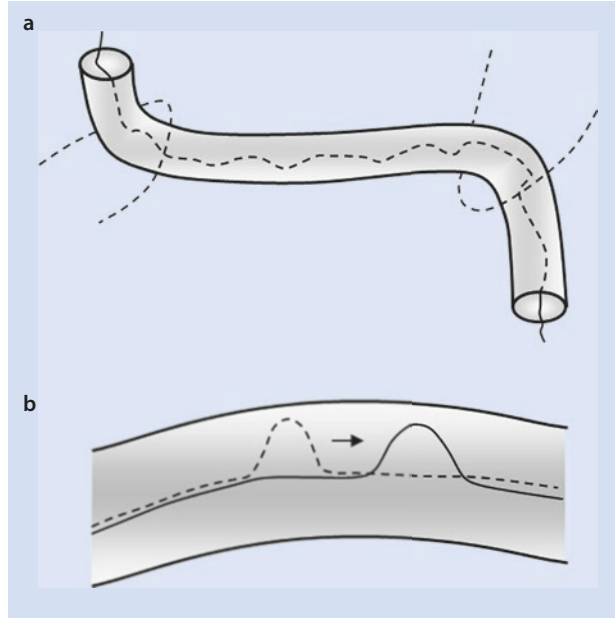


Fig. 6.7 Illustration of the reptation process. (**a**) Definition of the reptation pathway by the entanglements with neighboring chains. (**b**) Meandering movement of a macromolecule

The relaxation time is thus proportional to the square of the chain length and indirectly proportional to the diffusion coefficient D_t of the polymer chain within the tube.

This diffusion coefficient is given by (also without proof)

$$D_t = \frac{k_B T}{f_t} = \frac{k_B T}{n\zeta} \tag{6.9}$$

f_t Friction factor of the chain

ζ Friction factor of a segment

By introducing a theoretical relaxation time for the single segments τ_{P0}:

$$\tau_P = \frac{l_0^2}{2D_t} n^2 = \frac{l_0^2}{2D_t n} n^3 = \frac{{l_0}^2 \cdot \zeta}{2k_B T} \cdot n^3 \cong \tau_{P0} \cdot n^3 \tag{6.10}$$

On account of the dependence of the diffusion coefficient on the chain length, if effective entanglements exist, the relaxation time of the polymer chain is proportional to the chain length cubed, consistent with the gradient of the line in Fig. 6.5 above the critical chain length.

The relaxation time τ_{P0} defined in (6.10) is the hypothetical relaxation time of a polymer chain with only one chain segment and is of the order of 10^{-10} s. Thus the relaxation time for a polymer with 10,000 bonds is of the order of 100 s.

The reptation process can describe the diffusion of a polymer molecule under different conditions. As well as describing the viscous flow process, it can also be used to describe the solution of a polymer molecule at the surface between a solid polymer and a solvent. This model can also be used to describe the welding of polymeric materials (▶ Chap. 17). In both latter cases the polymer diffuses over a boundary layer made up of either a solvent or another polymer.

The viscosity of a polymer chain is temperature dependent and can be described by a simple Arrhenius equation:

$$\eta \propto \exp^{\frac{-E_A}{k_B T}} \tag{6.11}$$

E_A	Activation energy
k_B	Boltzmann constant
T	Absolute temperature

This relationship is valid at temperatures that are at least 100 °C above the glass transition temperature. At lower temperatures the velocity of the reptation process and thus the melt viscosity is not determined by the thermal energy available for movement but rather by the shrinking of the free volume at low temperatures.

6.6 Viscoelasticity

6.6.1 Influence of Time on the Mechanical Behavior

As has already been discussed in ▶ Sect. 6.1, amorphous polymers of large molar mass do not suddenly transition into a low viscosity melt at their glass transition temperature but pass through a range of states in which the material still exhibits a degree of elasticity, i.e., shape memory. The requirement for this is that the molar mass is not too small. A rotation of the individual chain segments around single bonds in the polymer chain is possible at temperatures above the glass transition temperature, as has already been set out in ▶ Sect. 6.1. Thus, if a stress acts on the entangled polymer coil the individual segments can assume an alternative conformation without any bonds being broken. If the length of the macromolecule is longer than the critical chain length introduced in ▶ Sect. 6.5 then effective entanglements

exist that counteract the deformation of the sample. Only at temperatures that are considerably above the glass transition temperature do the polymer chains disentangle so fast that no elastic behavior is observed; at such high temperatures the polymer melt behaves almost as a 'normal' low viscosity fluid.

Deformation of a polymer sample at temperatures that are not much higher than the glass transition temperature leads to the polymer chains assuming an energetically less favourable conformation. As a result, as has already been mentioned above, elastic energy is stored in the material. What then happens is largely dependent on the duration of the stress.

Short Term Exertion of Force

If the externally applied force is only applied for a short period of time, then the polymer chain takes on its original energetically favorable conformation again. The material springs back completely and returns to its original shape; the deformation process is totally reversible.

Prolonged Exertion of Force

Alternatively, during a prolonged exertion of force, a reorientation (or at least a partial one) of the polymer chains relative to one another occurs. Because of the externally applied forces, the polymer chains are unable to take on their original entangled conformation. This leads to a movement of the polymer chains relative to one another—the material starts to flow.

The same considerations apply to the temperature at which the exertion of force takes place. The mobility of the polymer chains increases at a higher temperature so that the polymer flows after shorter times under stress than at lower temperatures.

When considering polymers under these conditions, we are dealing with materials that behave, depending on the duration of the force exerted upon them and the temperature, either as viscous fluids or as elastic materials. This characteristic is known as *viscoelasticity*. The range of viscoelasticity is marked by two cases at the extremes of the viscoelastic spectrum: a 'free flowing (and elastic) fluid' and an 'elastic (non-flowing) material.' According to Hooke, for an elastic material follows:

$$\sigma = E \cdot \varepsilon \tag{6.12}$$

σ Stress
E Elastic modulus
ε Elastic extension of the length *l* by the factor *x*

From Newton for viscous, free flowing liquids follows:

$$\sigma = \eta \frac{d\varepsilon}{dt} \tag{6.13}$$

η Viscosity

Thus, the resulting stress is proportional to the rate of extension but independent of the extension itself.

These laws can either be visualized in terms of a damper (Newton) or a spring (Hooke). In the case of a Hookean spring, the applied stress σ is proportional to the expansion ε and the elastic energy can be stored in the spring. A damper can be envisaged as the mechanical equivalent of a plate that carries out work in a fluid with viscosity η. In this case the applied stress is independent of the expansion; energy is dissipated (Fig. 6.8).

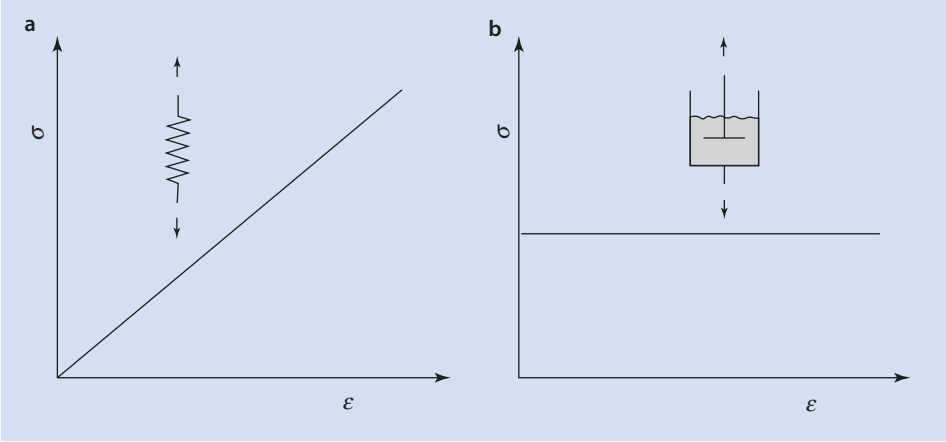


Fig. 6.8 $\sigma = f(\varepsilon)$: (**a**) for an elastic material (storage of energy); (**b**) for a viscous fluid (dissipation of energy)

Neither of these models describes viscoelastic polymers correctly. To describe such systems, combination models are necessary.

6.6.2 The Maxwell Approach

The Maxwell model is a serial arrangement of a spring and a damper (Fig. 6.9).

The total elongation is composed of an elastic (ε_{elast}) and a viscous (ε_{visc}) component in viscoelastic systems:

$$\varepsilon = \varepsilon_{elast} + \varepsilon_{visc} \tag{6.14}$$

Equations (6.12) and (6.13) (Hooke and Newton) can now be transformed as follows:

$$\text{Hooke}: \frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} \quad \text{Newton}: \frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} \tag{6.15}$$

and with (6.14) it follows:

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \cdot \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \tag{6.16}$$

For a constant extension ε, i.e., for $\frac{d\varepsilon}{dt} = 0$ it results (6.17):

$$\sigma = \sigma_0 \exp\left(-\frac{E}{\eta}t\right) \tag{6.17}$$

σ_0 Stress at the time $t = 0$

E Module of elasticity

η Viscosity (Fig. 6.11)

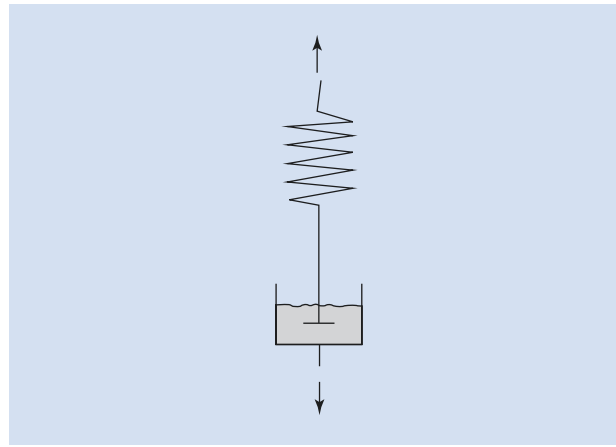


Fig. 6.9 Maxwell model consisting of a spring and a damper

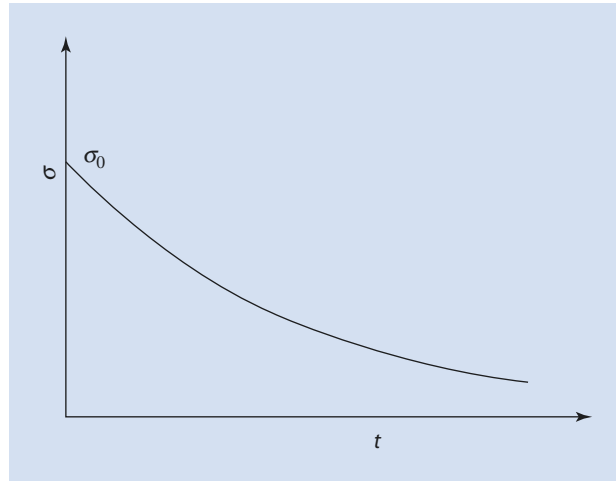


Fig. 6.10 $\sigma = f(t)$ according to the Maxwell model

This means that the stress σ, the force necessary to stretch a particular object, decreases exponentially with time (Fig. 6.10). The model describes the *stress relaxation* of a viscoelastic system that has suddenly been stretched to a given length and is then fixed. This can easily be demonstrated using a serial arrangement of spring and damper: if the model is stretched quickly, in the first instance, the damper element is not stretched, only the spring, because of the inertia of the damper element. If, at this moment, the applied force is removed just as quickly as it was applied, the spring springs back completely. If the force is applied over a longer period of time—as is the case in the Maxwell model—then the damper is irreversibly stretched, whereas the spring contracts back into its original shape. As a result, over time, the applied tension decreases exponentially to zero.

This simple model describes the behavior of a viscoelastic polymer under constant elongation. If the elongation is maintained over a longer period of time, then the polymer chains have enough time (by moving relative to one another) to rearrange themselves into an energetically more favourable conformation.

The quotient of viscosity η and module of elasticity E is defined as the relaxation time τ in (6.18):

$$\tau = \frac{\eta}{E} \tag{6.18}$$

If $t = \tau$ then the applied stress has decreased to $1/e$ of the initial value.

The Maxwell model therefore describes the time dependency of stress at constant elongation and the relaxation of stress that follows an elongation. From Fig. 6.10 it can be derived that for extremely short periods of elongation the system exhibits an (extremely short) phase of elastic behavior followed by creep or flow. In contrast to what is actually observed for viscoelastic systems, the model does not predict elastic behavior for an extended, observable period. The model also does not predict that elongation under constant stress is time dependent because it assumes that the constant elongation is independent of time.

6.6.3 Voigt–Kelvin Model

Unlike the Maxwell model, the Voigt–Kelvin model defines elongation under constant stress as a function of time. This model can be described mechanically by the parallel arrangement of spring and damper (Fig. 6.11).

In analogy with (6.16), the stress is the sum of the elastic and the viscous components:

$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt} \tag{6.19}$$

When applying a constant tension σ_0 that has an immediate effect, for example by attaching a weight, integration of (6.19) gives

$$\varepsilon = \frac{\sigma_0}{E}\left(1 - \exp\left(-\frac{E}{\eta}t\right)\right) \tag{6.20}$$

The change in elongation as a function of time according to (6.20) is shown in Fig. 6.12.

The form of the curve in Fig. 6.12 can also easily be explained using the mechanical model from Fig. 6.11. If a parallel arrangement of a damper and a spring is stretched by a constant force, initially, the damper prevents an elongation of the system because of its inertia. After an elapse of time an elongation does occur but it is increasingly attenuated by the resilience of the spring and eventually plateaus. Thus, this simple mechanical model describes the delayed reaction of a viscoelastic polymer to an external force caused by the polymer chains taking a certain length of time to rearrange.

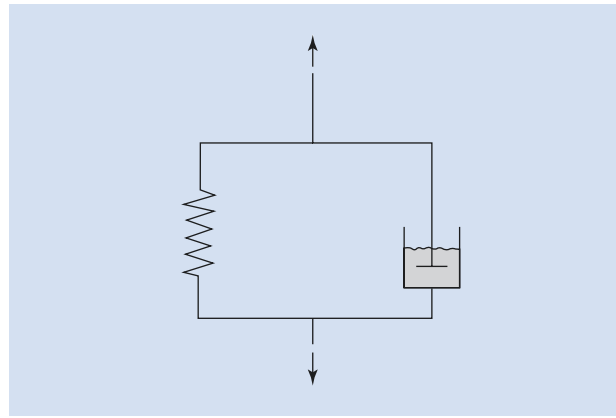


Fig. 6.11 The Voigt–Kelvin model for a spring and a damper

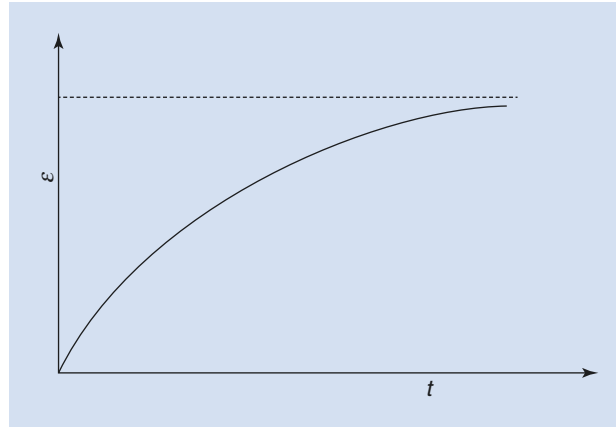


Fig. 6.12 Elongation ε as a function of time t according to the Voigt–Kelvin model

Here too, in analogy with the treatment above, the retardation time τ_R of the Kelvin–Voigt model can be defined by the quotient of η and E:

$$\tau_R = \eta / E \tag{6.21}$$

If $t = \tau_R$ then the elongation ε has increased to 63% $(1 - 1/e)$ of its equilibrium value.

As with the Maxwell model, the Voigt–Kelvin model does not offer a complete description of viscoelastic behavior. It allows for delayed elongation, the delayed response of a viscoelastic polymer to a constant applied force. It does not, however, describe the irreversible flow that occurs in a viscoelastic system.

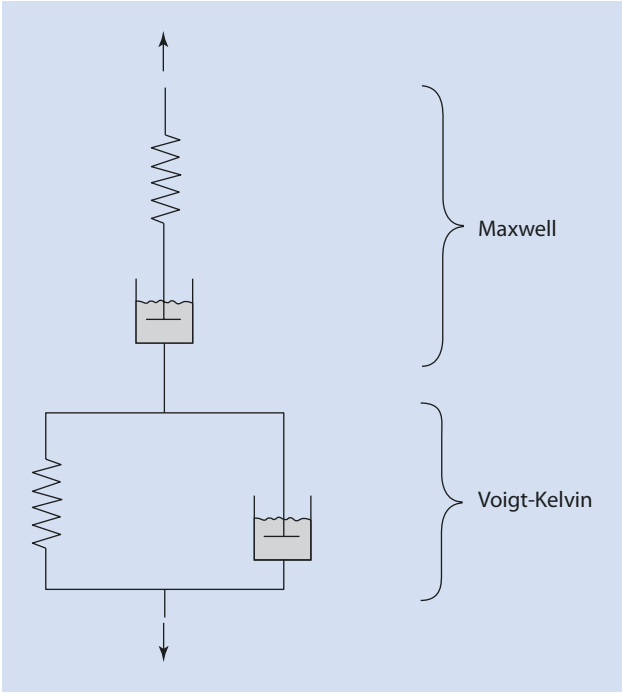


Fig. 6.13 Set-up of springs and dampers in the Burgers model

6.6.4 The Burgers Model

The Burgers model is a combination of the Maxwell model with the Voigt–Kelvin model. Thus, it can be described by the arrangement of two springs and two dampers shown in Fig. 6.13.

To understand the model better, the following describes the reaction of the system if it is suddenly stretched by a certain amount at a certain time t_0, this applied force then being maintained for a given time and then removed. The dependence of the elongation on time is shown in Fig. 6.14. This process can be divided into five phases:

a. From 0 to A no force is being applied to the sample and it is not stretched. This conforms to the arrangement shown in Fig. 6.14a.
b. From A to B the force is suddenly applied to the sample at t_0. In the mechanical model the upper Hookean spring reacts to this force instantaneously. If the applied force is removed just as quickly, then the system springs back completely to point A. The bottom spring cannot follow this quick movement as it is linked to the damper.
c. From B to C the two dampers in the mechanical model only move if the stress is maintained for a finite period of time. The second spring is then stretched. In this case the bottom damper describes the irreversible flow of the model, and the energy that is needed to stretch the upper damper is stored in the spring connected in parallel to it.

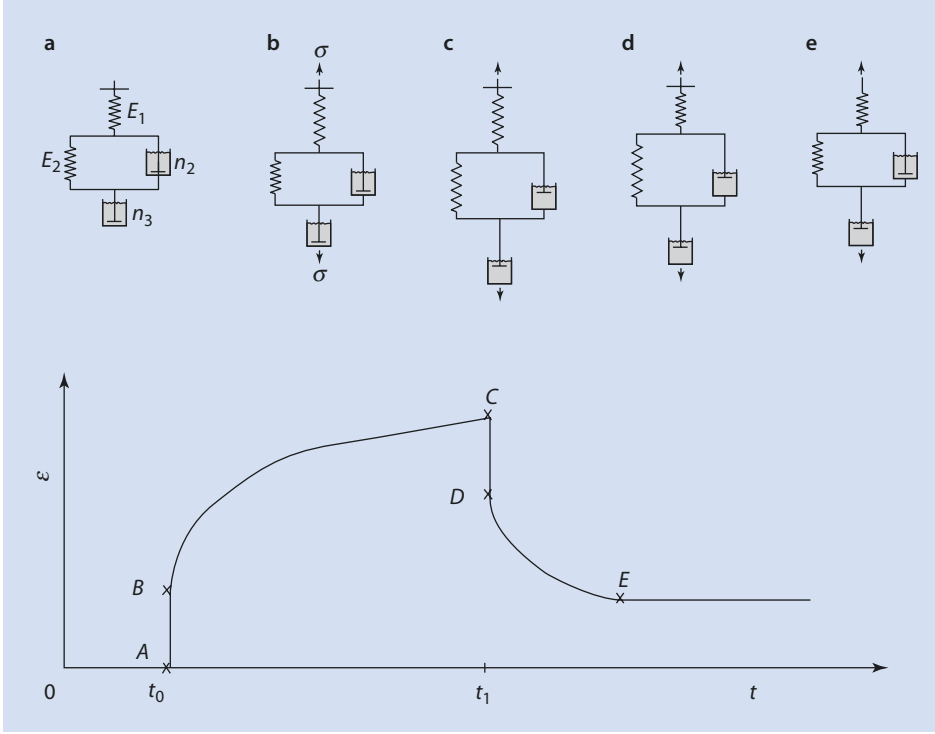


Fig. 6.14 Elongation ε as a function of time t according to Burgers' model

d. From C to D, if the applied force is removed then the upper spring instantaneously springs back to its original position but the lower spring cannot follow this movement.
e. From D to E the second spring also springs back to its original position but with a time delay determined by the relaxation of the damper coupled with it. The bottom damper remains elongated.

The Burgers model describes the behavior of a viscoelastic system relatively well. When a force is applied for a short period of time, for example by a short impact, the entangled polymer chains are unable to rearrange relative to one another. Elastic behavior is observed and a complete return to the original shape takes place. If the force is applied over a longer period of time the polymer chains can detach themselves from one another and can change their relative position, and the material starts to flow. If the applied force is removed a partial return to the original shape takes place but a permanent deformation remains.

To summarize the above, viscoelasticity is characterized by the following phenomena:

1. A time and frequency of the material properties—either elastic or viscous behavior is observed depending on the duration of the applied force
2. Hysteresis, i.e., irreversible processes resulting in the system not returning to its initial state

Important hysteresis effects are:

- Creep or viscous flow
- Stress relaxation
- Time delayed reaction of the material (phase shift) if an oscillating force is applied

The latter is the basis for the dynamic-mechanical-thermal analysis (DMTA) discussed in ▶ Chap. 4.

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