

6

Visco-elasticity

6.1. Models

The expression “*visco-elastic*” signifies the dual nature of a material: on the one hand it behaves in a viscous way, as a liquid, on the other hand elastically, as a solid.

For an *ideal solid*, *Hooke’s law* holds: the stress, σ , applied is proportional to the deformation, ε , and the proportionality constant is the *modulus of elasticity* E , so $\sigma = E \cdot \varepsilon$. Besides E also other quantities play a role, such as the shear modulus, G , in a shearing deformation or torsion, which is related to E . For the sake of simplicity we shall mainly use E as a representative quantity for the elastic stiffness in any geometry of loading.

As a model for E we take a helical spring with stiffness E . The response ε of such a spring to a stress σ is schematically indicated in Figure 6.1; the response is instantaneous, without any time dependency, and the recovery after release of the stress is also instantaneous and complete.

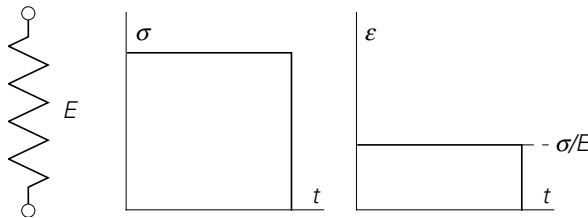


Figure 6.1. Response of an ideal spring.

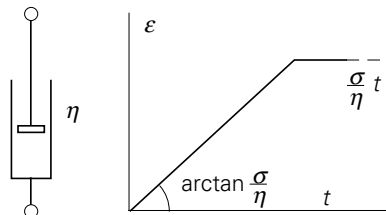


Figure 6.2. Response of an ideal liquid.

For an ideal liquid *Newton’s law* holds: the stress is proportional to the rate of

deformation $d\varepsilon/dt = \dot{\varepsilon}$; the proportionality constant is the *viscosity* η , so $\sigma = \eta \cdot \dot{\varepsilon}$. As a model we choose a *dashpot*; within a cylinder filled with a fluid a piston can move with some clearance. Figure 6.2 shows its behaviour: There is no instantaneous response; the deformation is proportional to time, and no recovery takes place. The dashpot is characterized by η .

For viscoelastic materials combinations of these two models can be used, e.g. a spring and a dashpot in series or parallel. The first combination is called the *Maxwell element*; its response under constant stress is the sum of that of its two components:

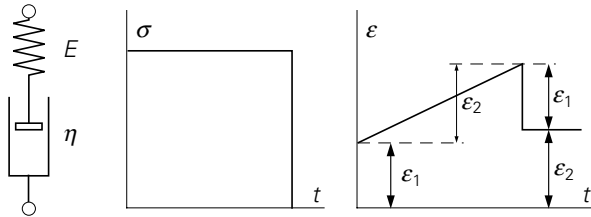


Figure 6.3. Response of a Maxwell element.

$$\varepsilon = \varepsilon_1 + \varepsilon_2 = \frac{\sigma}{E} + \frac{\sigma}{\eta} \cdot t = \sigma \left[\frac{1}{E} + \frac{t}{\eta} \right]$$

i.e. a spontaneous elastic deformation which returns when $\sigma = 0$, plus permanent flow. This element might, very roughly, represent the behaviour of a molten polymer, since we have seen that, besides the normal fluid behaviour, also an elastic component is present, which recovers upon unloading.

Next to this case of *creep* under constant loading, we also consider the *stress relaxation* which occurs when the deformation is kept constant. At $t = 0$ the model is jumpwise deformed to a strain ε . The instantaneous response is a stress $\sigma_0 = E \cdot \varepsilon$; the spring is strained, the dashpot does not yet respond. The dashpot is, at $t = 0$, subjected to the same stress, so it starts flowing, while it takes over an increasing part of the imposed strain so that the strain in the spring, and also the stress, decrease.

At time t the deformation of the spring is ε_1 and that of the dashpot ε_2 , while the stress in both $\sigma_1 = \sigma_2$. Now

$$\sigma_1 = E \cdot \varepsilon_1 = \sigma_2 = \eta \frac{d\varepsilon_2}{dt} = \eta \frac{d(\varepsilon - \varepsilon_1)}{dt} = -\eta \frac{d\varepsilon_1}{dt}$$

since

$$\varepsilon_1 + \varepsilon_2 = \varepsilon$$

$$-\eta \frac{d\varepsilon_1}{dt} = E \cdot \varepsilon_1$$

$$\frac{d\varepsilon_1}{\varepsilon_1} = -\frac{E}{\eta} dt$$

$$\ln \varepsilon_1 = -\frac{E}{\eta} \cdot t + c$$

$$\varepsilon_1 = \exp(-(E/\eta) \cdot t) \cdot c'$$

$$\sigma = E \cdot \varepsilon_1 = E \cdot \exp(-(E/\eta) \cdot t) \cdot c'$$

At $t = 0$ is $\sigma = E \cdot \varepsilon$, so $\sigma(t) = E \cdot \varepsilon \cdot \exp(-(E/\eta) \cdot t) = E \cdot \varepsilon \cdot \exp(-t/\tau)$ in which $\tau = \eta/E$, the *relaxation time*. The relaxation time, as indicated in Figure 6.4, is the time in which the stress is reduced to $1/e$ times its original value (about 37%). (See also Qu. 6.2 and 6.11).

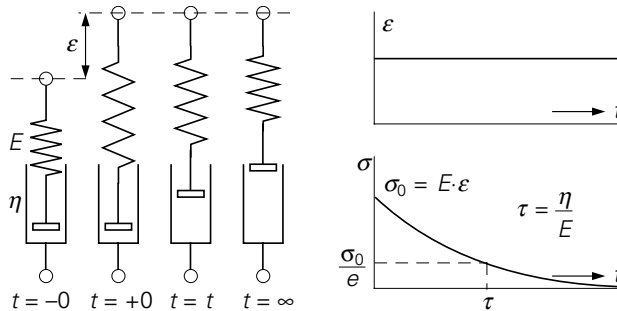


Figure 6.4. Stress relaxation of a Maxwell element.

A parallel array of E and h gives a *Kelvin-Voigt* element. This model does not allow an instantaneous deformation (the stress on the dashpot would be infinite), and it does not show stress relaxation. At a constant stress it exhibits *creep*; at time t its strain is $\varepsilon(t)$; the stress in the spring then is:

$$\sigma_1 = E \cdot \varepsilon(t)$$

in the dashpot

$$\sigma_2 = \eta \cdot \frac{d\varepsilon(t)}{dt}$$

and the total stress, $\sigma_1 + \sigma_2 = \sigma$ is constant.

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

$$\eta \frac{d\varepsilon}{dt} = -E \cdot \varepsilon + \sigma$$

The solution of this differential equation is:

$$\varepsilon(t) = \frac{\sigma}{E} [1 - \exp(-t/\tau)]$$

with $\tau = \eta/E$.

At $t = 0$, $\varepsilon = 0$; at $t = \infty$, $\varepsilon = \sigma/E$; this final deformation is approached asymptotically. After taking away the stress at a new $t = 0$, while $\varepsilon = \varepsilon_1$, it follows from:

$$\sigma = 0 = E \cdot \varepsilon + \eta \frac{d\varepsilon}{dt}$$

and

$$\eta \frac{d\varepsilon}{dt} = -E \cdot \varepsilon:$$

$$\varepsilon = \varepsilon_1 \exp(-t/\tau)$$

in other words: the recovery proceeds asymptotically to $\varepsilon = 0$ with the same relaxation time $\tau = \eta/E$; see Figure 6.5. (see also Qu. 6.5).

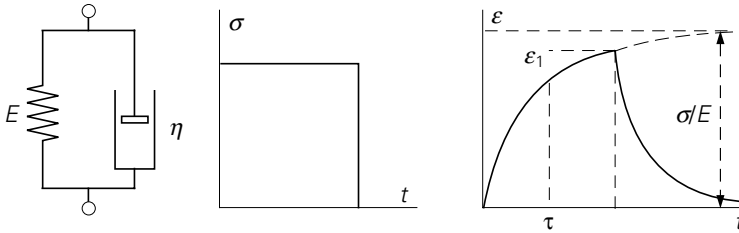


Figure 6.5. Creep of a Kelvin-Voigt element

Both models, the Maxwell element and the Kelvin-Voigt element, are limited in their representation of the actual viscoelastic behaviour; the former is able to describe stress relaxation, but only irreversible flow; the latter can represent creep, but without instantaneous deformation, and it cannot account for stress relaxation. A combination of both elements, the *Burgers* model, offers more possibilities. It is well suited for a qualitative description of creep. We can think it as composed of a spring E_1 , in series with a Kelvin-Voigt element with E_2 and η_2 , and with a dashpot, η_1 (Figure 6.6).

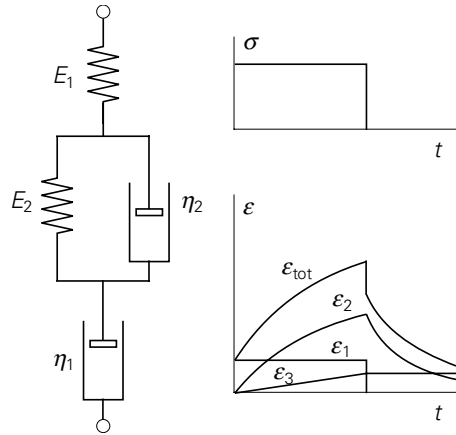


Figure 6.6. Creep of the Burgers model.

Under a constant load σ we can distinguish between three types of deformation:

- the spring: $\varepsilon_1 = \sigma/E_1$
- the Kelvin-Voigt element: $\varepsilon_2 = \sigma/E_2 \cdot [1 - \exp(-E_2 \cdot t/\eta_2)]$
- the dashpot: $\varepsilon_3 = \sigma \cdot (t/\eta_1)$.

The total deformation is:

$$\varepsilon = \sigma \left[\frac{1}{E_1} + \frac{1}{E_2} \left(1 - \exp(-t/\tau) \right) + \frac{t}{\eta_1} \right]$$

$$\tau = \frac{\eta_2}{E_2}$$

which means

- spontaneous elastic deformation,
- delayed elastic deformation, or reversible creep,
- irreversible creep (flow) (see also Qu. 6.7 en 6.8).

The models described so far provide a *qualitative illustration* of the viscoelastic behaviour of polymers. In that respect the Maxwell element is the most suited to represent fluid polymers: the permanent flow predominates on the longer term, while the short-term response is elastic. The Kelvin-Voigt element, with an added spring and, if necessary, a dashpot, is better suited to describe the nature of a solid polymer. With later analysis of the creep of polymers, we shall, therefore, meet the Kelvin-Voigt model again; in more detailed descriptions of the fluid state the Maxwell model is being used.

In a quantitative way, these simple models are not powerful enough to account for

the behaviour of a real polymer. One of their prime shortcomings is, that they describe processes with a *single relaxation time* only. To illustrate this, we consider the stress relaxation of a Maxwell model. In a σ - $\log t$ plot (Figure 6.7) the stress relaxation curves for three different values of the relaxation time have been indicated; with this way of plotting the three curves have the same shape and are shifted with respect to the $\log t$ axis. Also a more realistic relaxation curve is drawn, which extends over a much broader region of the $\log t$ scale than a single element.

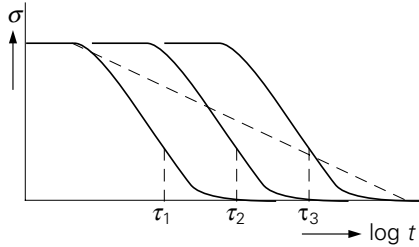


Figure 6.7. Relaxation of three single Maxwell elements compared with actual behaviour.

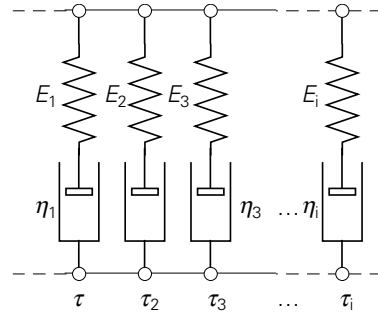


Figure 6.8 Generalized Maxwell model.

The reality is better approximated by a “generalized Maxwell model” (Figure 6.8), consisting of a large number of Maxwell elements in parallel, each with its own relaxation time, τ_i , and its own contribution, E_i , to the total stiffness. This system can be described by:

$$\sigma(t) = \varepsilon E_1 \cdot \exp(-t/\tau_1) + \varepsilon E_2 \cdot \exp(-t/\tau_2) + \dots + \varepsilon E_i \cdot \exp(-t/\tau_i)$$

or:

$$\sigma(t) = \varepsilon \sum_1^n E_i \cdot \exp(-t/\tau_i)$$

A relaxation function is now defined as

$$E(t) = \sum_1^n E_i \cdot \exp(-t/\tau_i)$$

We prefer to use a *continuous spectrum* $H(t)$, the *relaxation spectrum*:

$$E(t) = \int_0^\infty H(\tau) \cdot \exp(-t/\tau) \cdot d\tau$$

in which $H(\tau)d\tau$ is the contribution to the stiffness in the interval between τ and

$\tau + d\tau$.

In a similar way the creep can be represented by a number of Kelvin-Voigt elements in series:

$$\varepsilon(t) = \frac{\sigma}{E_1} \cdot [1 - \exp(-t/\tau_1)] + \dots + \frac{\sigma}{E_i} \cdot [1 - \exp(-t/\tau_i)] + \dots$$

of

$$\frac{\varepsilon(t)}{\sigma} = \sum_1^n i \left[\frac{1}{E_i} \cdot (1 - \exp(-t/\tau_i)) \right]$$

To express creep, use of the reciprocal modulus, the *compliance*, $D = 1/E$, is to be preferred; the creep function then reads:

$$D(t) = \frac{\varepsilon(t)}{\sigma} = \sum_1^n i D_i \cdot [1 - \exp(-t/\tau_i)]$$

or, as a continuous spectrum:

$$D(t) = \int_0^{\infty} L(\tau) \cdot [1 - \exp(-t/\tau)] \cdot d\tau$$

The spectrum $L(\tau)$ is called the *retardation spectrum*. With the integration from $\tau = 0$ to $\tau = \infty$ the immediate elastic response and the irreversible flow are, respectively, automatically taken into account.

With all these models, the simple ones as well as the spectra, it has to be supposed that stress and strain are, at any time, proportional, so that the relaxation function $E(t)$ and the creep function $D(t)$ are independent of the levels of deformation and stress, respectively. When this is the case, we have *linear viscoelastic behaviour*. Then the so-called *superposition principle* holds, as formulated by Boltzmann. This describes the effect of changes in external conditions of a viscoelastic system at different points in time. Such a change may be the application of a stress or also an imposed deformation.

The superposition principle states that each change gives its own contribution to a (later) effect, independent of the other changes. This is important, since not only the magnitude of the change, but also the time elapsed to the observation of its effect, influence the magnitude of the effect.

A simple example of the superposition principle is given in Figure 6.9. At $t = t_1$ a stress σ_1 is applied, which is increased to σ_2 at $t = t_2$. The response of the system is such that the strain from $t = t_2$ is a superposition of the strain as a result of a

continuation of σ_1 and the one resulting from a stress $\sigma_2 - \sigma_1$, applied at $t = t_2$.

Expressed in a formula:

$$\varepsilon(t) = \sigma_1 \cdot D(t - t_1) + (\sigma_2 - \sigma_1) \cdot D(t - t_2)$$

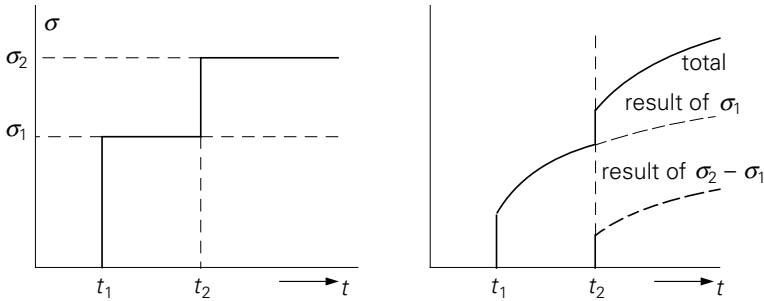


Figure 6.9. Superposition principle.

With an arbitrary, continuously changing stress $\sigma(t)$, this can be written as:

$$\varepsilon(t) = \int_{-\infty}^t D(t-t') \frac{d\sigma}{dt'} \cdot dt'$$

For each small variation in stress $(d\sigma/dt') \cdot dt'$ at $t = t'$, its contribution to the deformation is determined by the pertinent compliance $D(t - t')$.

Later on we shall see that the superposition principle is, for polymers, only seldomly obeyed; linear viscoelasticity is only met at *very small stresses and deformations*; at loading levels occurring in practice the behaviour may strongly deviate from linearity. However, the superposition principle provides a useful first-order approximation.

The functions $E(t)$ and $D(t)$ are of importance for two reasons. First, they provide a first impression of the response of a polymer under stress or strain as a function of time; they are, therefore, of interest when plastics are used in load-bearing constructions.

On the other hand knowledge of these functions and of the spectra of relaxation (or retardation) times derived from them, is very helpful for obtaining insight into the *molecular mechanisms* by which they are originated. Analysis of the time dependency of mechanical properties thus provides a powerful tool to investigate the relations between structure and properties.

Creep and relaxation experiments are carried out on time scales ranging from several seconds up to several years. When knowledge of the viscoelastic behaviour on

shorter time scales is also required, then vibration experiments (dynamic mechanical experiments) have to be carried out.

6.2. Dynamic mechanical behaviour

When a periodic deformation, $\varepsilon = \varepsilon_0 \cdot \sin \omega t$, is imposed upon a purely elastic material, the stress will also be periodic according to $\sigma = \sigma_0 \cdot \sin \omega t$ (the use of a cosine function gives the same results). With viscoelastic materials, however, a *phase shift* δ occurs:

$$\sigma = \sigma_0 \cdot \sin(\omega t + \delta)$$

This can be understood as follows: For an ideal spring $\delta = 0$; for a pure liquid:

$$\sigma = \eta \cdot (d\varepsilon/dt) = \eta \cdot \varepsilon_0 \cdot \omega \cdot \cos \omega t = \sigma_0 \cdot \sin(\omega t + \frac{\pi}{2})$$

then $\delta = \frac{\pi}{2}$ (90°); the stress proceeds in advance of the strain over a quarter of a period. For a viscoelastic material δ is in between these extremes: $0 < \delta < \frac{\pi}{2}$. The equation for σ can be worked out further:

$$\begin{aligned} \sigma &= \sigma_0 \cdot \sin(\omega t + \delta) = \sigma_0 \cdot [\sin \omega t \cdot \cos \delta + \cos \omega t \cdot \sin \delta] = \\ &= (\sigma_0 \cdot \cos \delta) \cdot \sin \omega t + (\sigma_0 \cdot \sin \delta) \cdot \cos \omega t \end{aligned}$$

This equation shows the existence of *two components of the stress*: the first one is in-phase with the deformation, with an amplitude $\sigma_0 \cdot \cos \delta$, the second one has a phase difference of 90° , with an amplitude $\sigma_0 \cdot \sin \delta$.

We can also define two moduli of elasticity σ/ε :

$$E_1 \text{ (in-phase)} = (\sigma_0/\varepsilon_0) \cdot \cos \delta$$

$$E_2 \text{ (90° out-phase)} = (\sigma_0/\varepsilon_0) \cdot \sin \delta$$

and the stress can be written as:

$$\sigma = \varepsilon_0 \cdot (E_1 \cdot \sin \omega t + E_2 \cdot \cos \omega t)$$

while

$$\tan \delta = E_2/E_1$$

Since E_1 is the elastic part of the modulus, it is called the “*storage modulus*”. It is, namely, a measure for the energy stored in a reversible way. E_2 denotes the viscous part, and is thus a measure for the energy dissipated into heat per period of vibration; it is called “*loss modulus*”.

Periodic vibrations, mechanical as well as electrical, are often represented as a uniform motion along a circle with angular velocity ω . The projection on a horizontal axis carries out a harmonic vibration $r \cdot \cos \omega t$ (Figure 6.10). This can, mathematically, be expressed in a very elegant way by considering the rotating point as a *complex number*:

$$r^* = x + iy \quad (i = \sqrt{-1})$$

x is then the projection on the horizontal axis, varying according to $x = r \cdot \cos \omega t$, and is the real part of the complex number r^* ; iy is the imaginary part. This way of representation is based on the well-known formula:

$$e^{ix} = \cos x + i \cdot \sin x$$

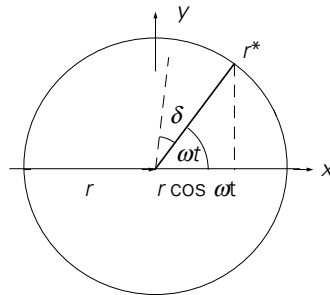


Figure 6.10. Complex representation of a harmonic vibration.

A periodic deformation with amplitude ε_0 is then given by:

$$\varepsilon = \varepsilon_0 \cdot \exp(i\omega t)$$

while we tacitly assume that we consider the real part, $\varepsilon = \varepsilon_0 \cdot \cos \omega t$, only. The expression for the stress then becomes:

$$\sigma = \sigma_0 \cdot \exp i(\omega t + \delta)$$

(by which we mean its real part:

$$\sigma = \sigma_0 \cdot \cos(\omega t + \delta))$$

The phase difference δ is, in the complex plane, the angle between the radius vectors of σ and ε . The E modulus can now easily be written as a *complex quantity*, E^* (Figure 6.11):

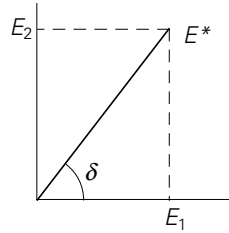


Figure 6.11. Complex modulus of elasticity.

$$E^* = \frac{\sigma}{\varepsilon} = \frac{\sigma_0 \cdot \exp i(\omega t + \delta)}{\varepsilon_0 \cdot \exp i \omega t} = \frac{\sigma_0}{\varepsilon_0} \cdot \exp(i\delta) = \frac{\sigma_0}{\varepsilon_0} \cdot (\cos \delta + i \cdot \sin \delta) =$$

$$= \frac{\sigma_0}{\varepsilon_0} \cos \delta + i \frac{\sigma_0}{\varepsilon_0} \sin \delta = E_1 + i \cdot E_2$$

In contrast to σ and ε , E^* retains its nature as a complex quantity, composed of a *storage modulus* (the real part) and a *loss modulus* (the imaginary part).

The use of complex numbers appears to offer considerable advantages in simplifying calculations on vibrating systems. A *damped vibration*, for instance, is represented by:

$$\varepsilon = \varepsilon_0 \cdot \exp(i\omega t) \cdot \exp(-\alpha t) = \varepsilon_0 \cdot \exp(i\omega - \alpha)t$$

This expression is much easier to handle in differentiation etc., since the periodic part, $\exp(i\omega t)$ (which means: $\cos \omega t$) and the damping part $\exp(-\alpha t)$ are combined into a single exponential function.

Various types of vibration experiments can be carried out to measure E_1 and E_2 at a certain frequency. An example is the *torsion pendulum*, in which the sample, connected to an auxiliary mass, is brought into a free torsional oscillation. From the frequency of the pendulum (around 1 to 10 sec) E_1 is calculated, from the rate of damping $\tan \delta$ and E_2 . Other types of dynamic mechanical measurements can be carried out at higher frequencies, such as *bending vibrations* with or without extra mass, wave propagation, etc. By combining a number of these different techniques, a time scale ranging from 10 to 10^{-8} sec can be covered.

6.3. Integration

In combination with creep and relaxation measurements a total time span of $\approx 10^{-8}$ sec to 10^8 sec (3 years) can be covered. The usual techniques to measure the response of a polymer over this time span are schematically represented in Figure 6.12.

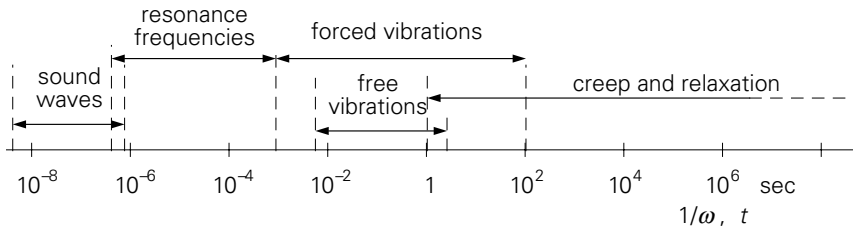


Figure 6.12. Time and frequency span for various methods.

When we try to combine the results of these various methods into a single integrated picture, we have to take into account three points:

- With some experiments a *stress is imposed*, such as with creep tests and with vibrations in which the sample is subjected to a periodic stress. With other experiments the *deformation* is given and the resulting stress is being measured, such as with stress relaxation and with vibration tests with an imposed periodic strain. The results of these two different types of methods cannot directly be translated into each other but only by complex transformations, in other words:

$$D(t) \neq \frac{1}{E(t)}$$

- In various experiments *different elastic constants* are being determined; with a torsion pendulum, for instance, the shear modulus, G , is measured, with creep or vibrations in elongation or in bending the Young's modulus, (tensile modulus), E . For an isotropic material the relation between E and G is as follows:

$$E = 2 \cdot G \cdot (1 + \nu)$$

in which ν is the Poisson ratio, or the ratio between transverse contraction and elongation in uniaxial strain. For ideal rubbers (no volume change upon elongation), $\nu = 0.5$; for glassy polymers and polymer crystals $\nu \approx 0.33$, so that E/G is in between 3 and 2.7. Complications arise when the transverse contraction in one direction is hindered, for instance with forced vibrations of a sheet; in such a case not E is measured but $E/(1 - \nu^2)$. Moreover, the Poisson ratio also depends on time or frequency.

- In the third place the question arises how the *time and frequency scales* have to be joined together to connect results of creep or relaxation to those of vibration experiments. It will be clear that here the superposition principle can be applied, since with vibrations the imposed stress (or the strain) varies continuously. Using this principle and using the complex E modulus (or the complex compliance D), it can be shown that, with a few simplifications, t and $1/\omega$ can be considered as the same parameter, while $\omega = 2\pi\nu$ (ν is the frequency in cycles/sec). It has been

shown that in this way static and dynamic experimental results can be joined together satisfactorily.

Many measurements have been carried out with a large number of, sometimes very complicated, techniques. A shorter route towards a global knowledge over such a broad range of time and frequency, is supplied by the overall *equivalence of time and temperature*. In its simplest form, this equivalence can be expressed via the assumption that the effect of temperature on a molecular process often follows Arrhenius' law:

$$\tau = c \cdot \exp(A/RT)$$

in which τ is the relaxation time of such a process. Also the frequently used model representations with springs and dashpots lead to this equation: If we suppose the spring constants, E , to be independent of temperature, and the viscosities η as $\eta = c' \exp(U/kT)$ (which is the usual behaviour of a viscosity), then the relaxation time is

$$\tau = \frac{\eta}{E} = \frac{c'}{E} \exp(U/kT) \quad (= c \cdot \exp(A/RT))$$

With an increase in temperature from T_0 to T the modulus curve will then be *shifted* along the $\log t$ axis over a distance:

$$\ln a_T = \frac{A}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

in which the quantity a_T is defined as:

$$a_T = \frac{t_{\text{rel}}(T)}{t_{\text{rel}}(T_0)} \quad (\text{Figure 6.13}).$$

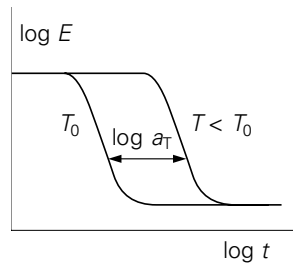


Figure 6.13. Time-temperature shift.

This offers the possibility to carry out measurements in a limited interval of $\log t$ (of $\log \omega$) at several levels of temperature, to derive the shift factor $a_T(T)$ from the results, and to construct a *master curve* over a broad range of $\log \omega$. This is illustrated in Figure 6.14.

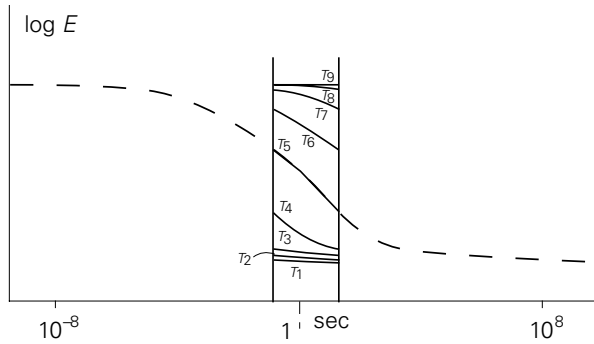


Figure 6.14. 'Mastercurve'.

Along the routes described thus far, it is possible to characterize E and its both components E_1 and E_2 , either in the complete, elaborate way or via the short-cut using the t - T relation, over a broad region of $\log t$ ($\log \omega$). A general schematic picture of E_1 and E_2 as functions of frequency or time is given in Figure 6.15. Generally speaking, *two maxima* in E_2 occur, corresponding to two transitions in E_1 . Next to these main transitions, a number of secondary transitions may be present. These are, however, not adequately represented in the resulting curve from a $\log t - T$ shift, which provides, therefore, despite of its simplicity, a very limited overall view only.

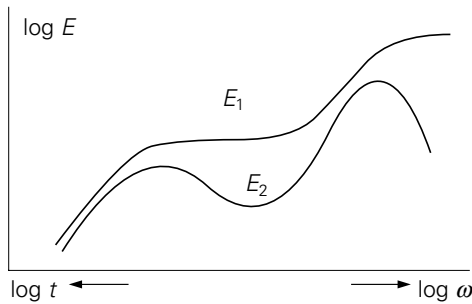


Figure 6.15. Two relaxation mechanisms.

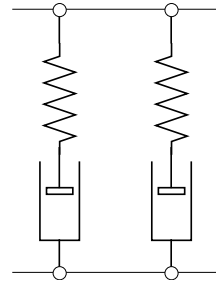


Figure 6.16. Two (broad) Maxwell elements.'

The pattern in Figure 6.15, read from the right to the left on the $\log t$ scale, resembles the relaxation behaviour, the decrease of E with increasing time under a constant strain, for two Maxwell elements in parallel (Figure 6.16), though over a much broader interval of $\log t$. It could, therefore, be considered as the behaviour of *two broad clusters of Maxwell elements*. The $\log E$ - $\log \omega$ curve thus indicates the existence of two broad relaxation mechanisms, each with a spectrum of relaxation times. This general picture is shown by all polymers, except by *permanent networks*, where the left-hand (low ω , long t) mechanism is not present.

After what has been said about the T - t equivalence, it is not surprising that the time dependency of E_1 resembles the T -dependency, which we have considered in detail before. In $E(\log t)$ we see, indeed, the same phases and transitions as in $E(T)$ (Figure 6.17). It should be remarked that this *time-temperature equivalence* only holds for *amorphous polymers* or for the amorphous part in semi-crystalline polymers.

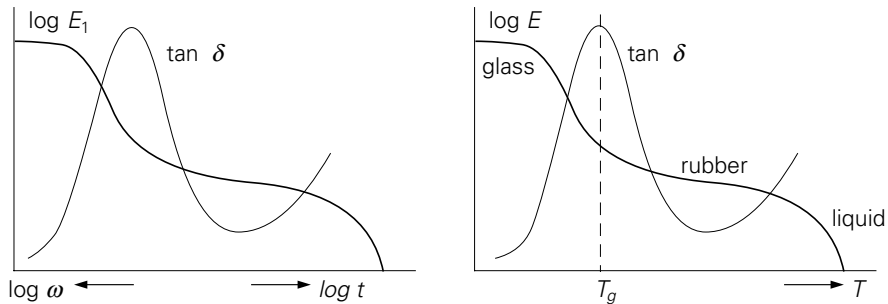


Figure 6.17. Comparison of time- and temperature scale.

In practice, $E(T)$ can be determined in a much easier way than $E(t)$; it can be done with a single device, e.g. a torsional pendulum, or its modern equivalent, DMTA, at an about constant frequency. The glass-rubber transition covers some tens of degrees on the T -scale; on the time scale it extends over many decades.

Both E_2 and $\tan \delta$ show *maxima* in the regions where E_1 strongly changes. This can be understood as follows: At very high frequencies, thus in the glassy region, the chain motions are so small that they hardly give rise to energy losses (in spring-dashpot models: the dashpot hardly moves and the whole deformation is taken up by the spring). At very low frequencies, e.g. in the rubbery region, losses also hardly occur; though the viscosity plays a role, the rates of deformation are so small that the energy dissipation is low. In between, in the transition region, these extreme situations do not exist, and the damping, the energy dissipated per cycle, shows a maximum.

6.4 Problems

6.1. To what extent can a Maxwell-element (spring and dashpot in series) be used as a model for the real behaviour of a polymer?

6.2. A fluid polymer behaves like a Maxwell-element: a spring with $E = 10^5$ Pa in series with a viscosity $\eta = 10^7$ Pa·s. At $t = 0$ a constant stress of 10^4 Pa is applied to the material during a period of 500 s. From $t = 500$ s the deformation is kept

constant, while the stress relaxation is recorded as a function of time.

- What is the value of the deformation ε immediately after applying the stress at $t = 0$?
- What is the value of the deformation ε at $t = 500$ s?
- What is the value of the stress σ at $t = 800$ s?
- Draw the curves of σ and ε as a function of time between $t = 0$ and $t = 800$ s.
- To what extent will a real polymer deviate from this behaviour?

6.3. To what extent can a Kelvin-Voigt element (spring and dashpot parallel) be used as a model for the real behaviour of a polymer?

6.4. A force of 600 N is applied in the length direction of a small plastic bar with a length of 10 cm, a width of 1 cm and a thickness of 1 mm. Under the influence of this force the bar shows an elongation as a function of time as given in figure 6.18.

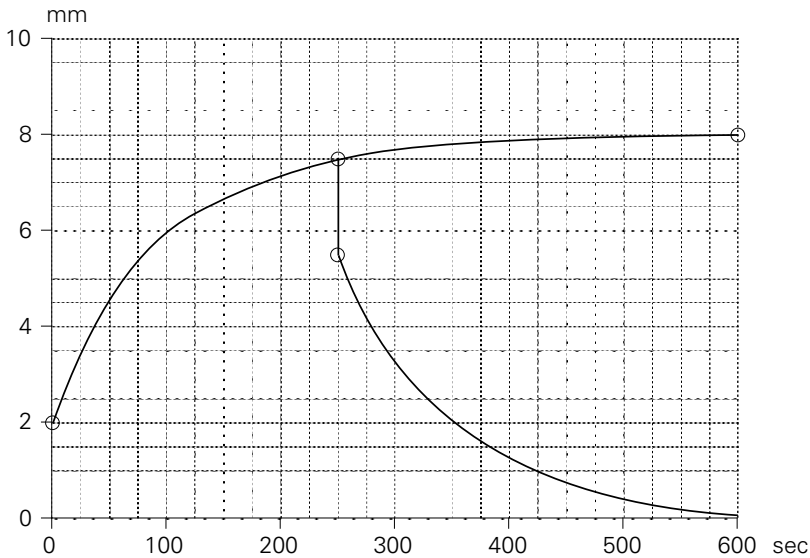


Figure 6.18. Figure for problem 6.4.

- Which spring-dashpot model should be able to describe this behaviour?
- Determine or estimate the values of parameters for this particular model (E moduli and viscosity).
- Draw the elongation as a function of time when the force is withdrawn after 250 seconds.
- Give a number of reasons why a polymer in reality will not behave like this pattern.

6.5. A polymer behaves like a Kelvin-Voigt element (spring $E_1 = 3 \cdot 10^8$ Pa parallel to viscosity $\eta = 3 \cdot 10^{14}$ Pa·s) connected in serie with a spring $E_2 = 3 \cdot 10^9$ Pa. At $t = 0$ a

stress $\sigma = 6 \cdot 10^6$ Pa is applied to the system; After $3 \cdot 10^6$ seconds the stress is removed.

Draw the curve of the deformation as a function of time and calculate the deformation (%)

- Just after applying the stress.
- Just before the removal of the stress.
- Just after the removal of the stress.
- $3 \cdot 10^6$ seconds after the removal of the stress.

6.6. In problem 6.5 it was presumed that after the removal of the stress the strain as a function of time could be described with the formula $\varepsilon = \varepsilon_0 \exp(-t/\tau)$. Prove that this is true based on the superposition principle.

6.7. A force of 10,000 N is applied to a polymer bar with a length of 20 cm and a cross section of 1 cm^2 . After 1.5 hour the length has increased to 25 cm. From the moment the force has been removed the strain can be described by $\Delta l = 4 \cdot \exp(-2t)$ cm, with t expressed in hours from the moment of the withdrawal of the force. Develop a spring-dashpot model that will represent this behaviour.

6.8. The same problem as given in 6.7, but now the strain is described by $\Delta l = 4 \cdot \exp(-2t) + 0.5$ cm.

6.9. A stretching experiment with constant rate of strain is applied to a Maxwell-element (spring E with dashpot η in series). What will be the shape of the stress - strain diagram?

6.10. The same question as posed in 6.9, but now for a Kelvin-Voigt element (spring E with dashpot η parallel).

6.11. A visco-elastic system is subjected to an instantaneous deformation of 100 %. The stress, necessary for this deformation, is 2 MPa. After the deformation the stress decreases as a function of time as displayed in the table below.

t (sec)	0.01	0.10	0.20	0.50	1	2	5	10	20	50	100
σ (MPa)	1.99	1.90	1.82	1.61	1.37	1.14	1.01	1.00	1.00	1.00	0.99

t (sec)	200	500	1,000	2,000	5,000	10,000	20,000	50,000
σ (MPa)	0.98	0.95	0.90	0.82	0.61	0.37	0.14	0.00

Give a model for this behaviour.

6.12. The modulus of elasticity of a polymer is often represented by a complex quantity: $E^* = E_1 + i \cdot E_2$.

- What is the meaning of E_1 and E_2 in this formula?

- b. In what way can these quantities be measured, e.g. around 1 Hz?
- c. In what way does the damping factor, $\tan \delta$, depend on these quantities?
- d. Give a number of cases in which $\tan \delta$ has a practical technological meaning.

6.13. In figure 6.19 the damping factor is plotted against the temperature for two situations (p and q).

- a. p and q are valid for which two types of polymers?
- b. Where is the first maximum for both of these two curves situated?
- c. Which value will the curve of p reach with a further increase of temperature?.
- b. Explain why the curve of situation q does not approach to zero, but to a finite value.

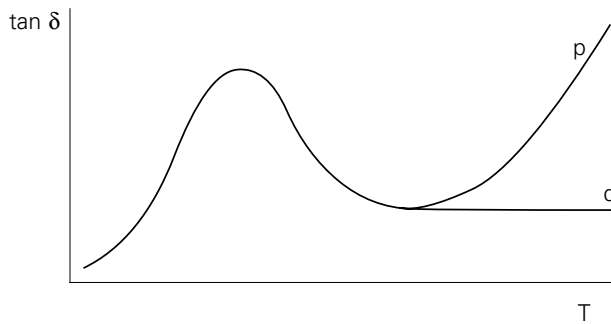


Figure 6.19. Figure for problem 6.4.