MTN - 208

Engineering Polymers and Composites

Lecture 5

Prof. Anjan Sil

MMED, IIT Roorkee

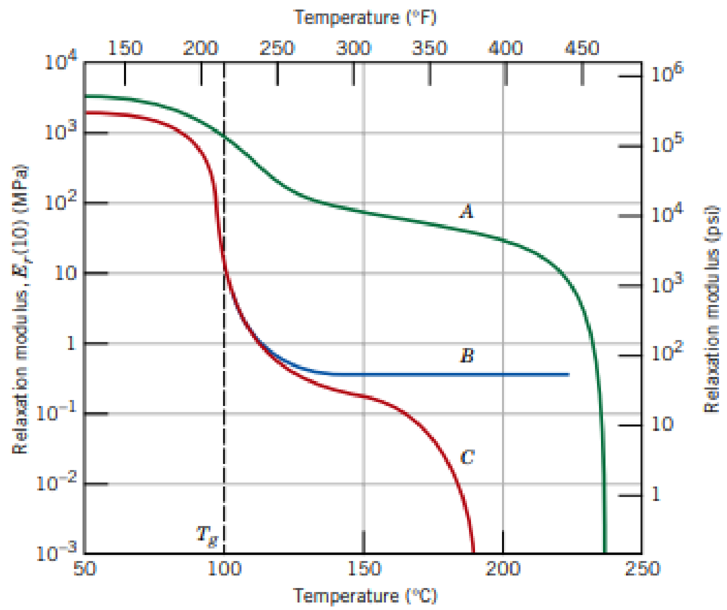


Figure 15.8
Logarithm of the relaxation modulus versus temperature for crystalline isotactic (curve *A*), lightly crosslinked atactic (curve *B*), and amorphous (curve *C*) polystyrene. (From A. V. Tobolsky, *Properties and Structures of Polymers*. Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Viscoelastic Creep Many polymeric materials are susceptible to time-dependent deformation when the stress level is maintained constant; such deformation is termed viscoelastic creep. This type of deformation may be significant even at room temperature and under modest stresses that lie below the yield strength of the material. For example, automobile tires may develop flat spots on their contact surfaces when the automobile is parked for prolonged time periods. Creep tests on polymers are conducted in the same manner as for metals (Chapter 8); that is, a stress (normally tensile) is applied instantaneously and is maintained at a constant level while strain is measured as a function of time. Furthermore, the tests are performed under isothermal conditions. Creep results are represented as a time-dependent creep modulus Ec(t), defined by

$$E_c(t) = \frac{\sigma_0}{\epsilon(t)} \tag{15.2}$$

wherein σ_0 is the constant applied stress and $\epsilon(t)$ is the time-dependent strain. The creep modulus is also temperature sensitive and diminishes with increasing temperature.

With regard to the influence of molecular structure on the creep characteristics, as a general rule the susceptibility to creep decreases [i.e., $E_c(t)$ increases] as the degree of crystallinity increases.

Mechanical properties – linear viscoelasticity

An isotropic perfectly elastic solid obeys equation or $\sigma = G\theta$, if σ is the shearing force and the shearing angle is θ, whereas a perfect Newtonian liquid obeys the equation $\sigma = \eta(d\theta/dt)$, where η is the viscosity of the liquid. The simplest assumption to make about the behaviour of a viscoelastic solid would be that the shear stress depends linearly both on θ and on $(d\theta/dt)$, i.e. that

$$\sigma = G\theta + \eta\,(d\theta/dt)$$

This is essentially the result obtained for one of the simple models for viscoelasticity to be considered below.

The models will assume linearity, as expressed in equations (7.1) and (7.2). These equations apply only at small strains. It should, however, be noted that real polymers are often non-linear even at small strains. The subject of non-linear viscoelasticity lies outside the scope of this study.

Before the models are described, the two simple aspects of viscoelastic behaviour already referred to – creep and stress-relaxation – are considered.

For the full characterisation of the viscoelastic behaviour of an isotropic solid, measurements of at least two moduli are required, e.g. Young's modulus and the rigidity modulus.

A one-dimensional treatment of creep and stress-relaxation that will model the behaviour of measurements of either of these (or of other measurements that might involve combinations of them) is given here. Frequently compliances, rather than moduli, are measured.

This means that a stress is applied and the strain produced per unit stress is measured, whereas for the determination of a modulus the stress required to produce unit strain is measured. When moduli and compliances are time-dependent they are not simply reciprocals of each other.

Creep

Figure shows the effect of applying a stress σ, e.g. a tensile load, to a linear viscoelastic material at time t = 0. The resulting strain e(t) can be divided into three parts: (i) e_1, an essentially instantaneous response, similar to that of an elastic solid; (ii) $e_2(t)$, which tends to a constant value as t tends to 1; and (iii) $e_3(t)$, which is linear in time.

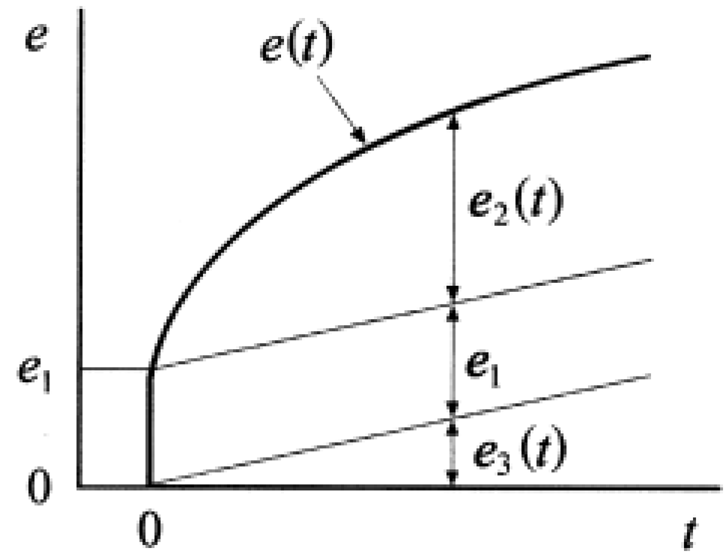


Fig. 7.2 Creep of a viscoelastic solid under a constant stress.

Assuming linearity, i.e. that each part of the strain is proportional to the applied stress, a *time-dependent creep compliance* $J(t)$ can be defined as

$$J(t) = \frac{e(t)}{\sigma} = \frac{e_1}{\sigma} + \frac{e_2(t)}{\sigma} + \frac{e_3(t)}{\sigma} = J_1 + J_2(t) + J_3(t) \tag{7.4}$$

Stress-relaxation

If a sample is subjected to a fixed strain the stress rises ‘immediately’ and then falls with time to a final constant value, assuming that there is no flow, as shown in fig. 7.4.

The stress-relaxation modulus G(t) is defined by $G(t) = \sigma(t)/e$.

A plot of log G(t) against log t is similar to an inverted form of log J(t) against log t. A characteristic relaxation time τ analogous to τ' can be defined.

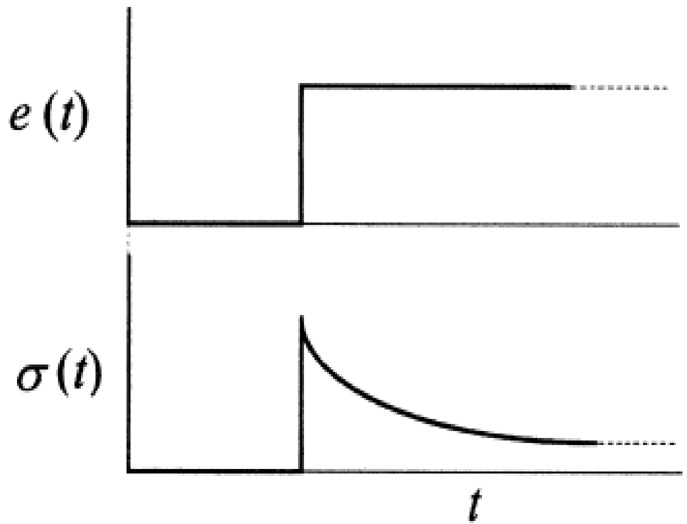


Fig. 7.4 Stress-relaxation. The upper graph shows the applied strain as a function of time and the lower graph the resulting stress.

7.1.4 The Boltzmann superposition principle (BSP)

Boltzmann extended the idea of linearity in viscoelastic behaviour to take account of the time dependence He assumed that, in a creep experiment;

(i) the strain observed at any time depends on the entire stress history up to that time and

(ii) each step change in stress makes an independent contribution to the strain at any time and these contributions add to give the total observed strain.

This leads to the following interpretation of the creep compliance $J(t)$: any incremental stress $\Delta\sigma$ applied at time t' results in an incremental strain $\Delta e(t)$ at a later time t given by $\Delta e(t) = \Delta\sigma\, J(t - t')$, where $t - t'$ is the time that has elapsed since the application of $\Delta\sigma$.

As an example, fig. 7.5 illustrates a two-step loading programme. The dashed curve shows the strain $\Delta\sigma_1\, J(t - t_1)$ that would have been present at time $t > t_2$ if the second step in stress $\Delta\sigma_2$ had not been applied at t_2. The actual strain is this strain plus the strain $\Delta\sigma_2\, J(t - t_2)$ produced by the second step in stress applied at t_2.

It is easy to generalise to a *multi-step loading programme*:

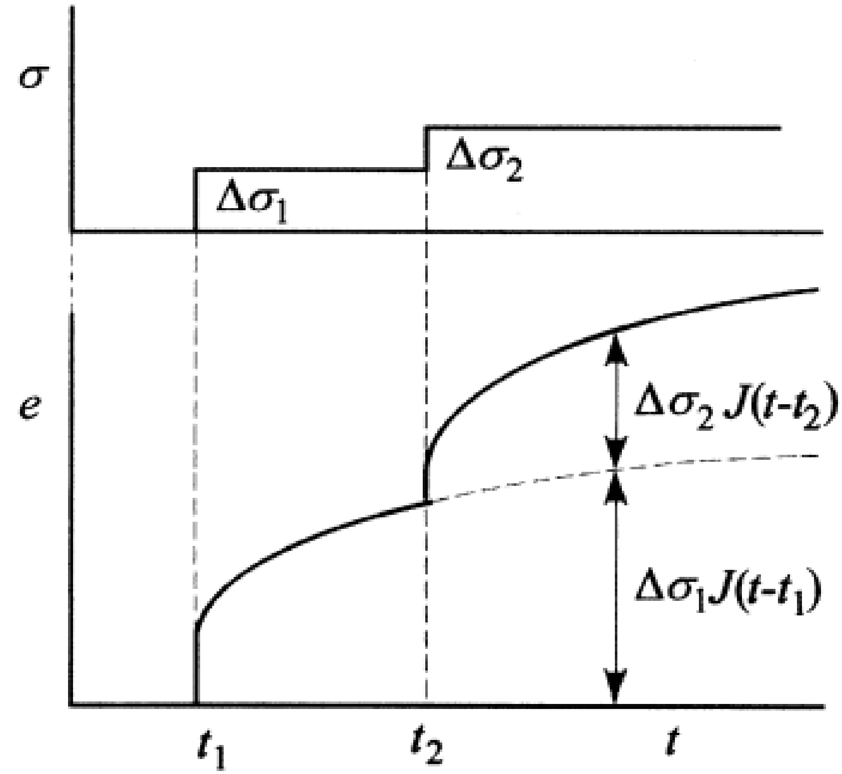
$$e(t) = \Delta\sigma_1\, J(t - t_1) + \Delta\sigma_2\, J(t - t_2) + \Delta\sigma_3\, J(t - t_3) + \cdots \qquad (7.6)$$

or to a *continuously changing stress*:

$$e(t) = \int_{-\infty}^{t} J(t - t')\, \mathrm{d}\sigma(t') = \int_{-\infty}^{t} J(t - t')\, \frac{\mathrm{d}\sigma(t')}{\mathrm{d}t'}\, \mathrm{d}t'$$

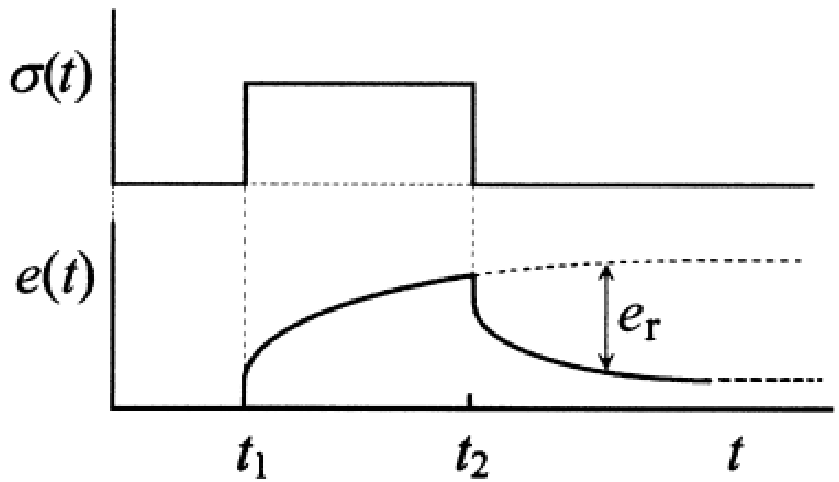
where $\sigma(t)$ is the stress at time t.

Fig. 7.5 A two-step creep experiment. See the text for explanation and symbols.



An interesting and important application of the BSP is creep followed by recovery. Consider the loading programme shown in fig. 7.6: apply stress σ at time t_1; hold the stress constant until time t_2 and then reduce the stress to zero. This last step is equivalent to applying an *additional stress* $-\sigma$ at t_2. Thus, according to the BSP, at $t > t_2$, $e(t) = \sigma J(t - t_1) - \sigma J(t - t_2)$. Note that recovery e_r is not defined as one might expect; it is defined as the difference between the existing strain at t and the strain that would have been observed at t if the stress had not been removed

Fig. 7.6 Creep and recovery. The upper graph shows the applied stress as a function of time and the lower graph the resulting strain.



Viscoelastic behaviour is often represented by mechanical models consisting of elastic springs that obey Hooke’s law and dashpots containing viscous liquids that obey Newton’s law, equation (7.2).

The two simplest models each use one spring and one dashpot and lead to simple exponential relaxation: (a) the Maxwell model – spring and dashpot in series; and (b) the Kelvin or Voigt model – spring and dashpot in parallel.

These models have relaxation and retardation behaviour of the simplest kind described by equation (7.10) and its equivalent for stress-relaxation and it can be shown (see problem 7.2) that both models obey the BSP.

In discussing the models, which are really one-dimensional, no distinction is made between load and stress, which is equivalent to considering unit cross-section.

The Maxwell model

This model consists of a spring and dashpot in series, as shown schematically in fig. 7.7. If a fixed strain is suddenly applied, the spring responds immediately by extending and a stress is produced in it, which is therefore also applied to the dashpot.

The dashpot cannot be displaced instantaneously but begins to be displaced at a rate proportional to the stress.

The strain and stress in the spring thus decay to zero as the dashpot is displaced at a decreasing rate and is eventually displaced by the same amount as the spring was originally displaced.

This is therefore a model for stress-relaxation, but the stress relaxes to zero, which is not always the case for real polymers. Under constant stress, the spring remains at constant length, but the dashpot is displaced at a constant rate, so that the model cannot describe creep.

For the spring

$$\sigma_s = Ee_s$$

and for the dashpot

$$\sigma_d = \eta \frac{de_d}{dt}$$

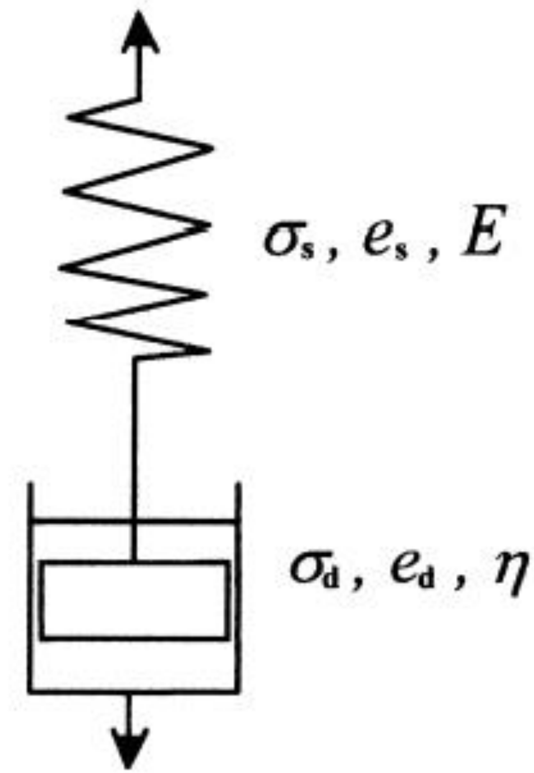
For a series system

$$\sigma = \sigma_s = \sigma_d \qquad \text{and} \qquad e = e_s + e_d$$

Thus

$$\frac{de}{dt} = \frac{de_s}{dt} + \frac{de_d}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

Fig. 7.7 The Maxwell model: spring and dashpot in series.



For stress-relaxation at constant strain e is independent of t, so that

$$\frac{\mathrm{d}e}{\mathrm{d}t} = 0 \qquad \text{and} \qquad \frac{1}{E}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \frac{\sigma}{\eta} = 0 \tag{7.15}$$

Integration leads to

$$\sigma = \sigma_o \exp(-Et/\eta) = \sigma_o \exp(-t/\tau) \tag{7.16}$$

with $\sigma_o = eE$. The stress decays exponentially to zero with a *relaxation time* $\tau = \eta/E$. It follows from equation (7.14) that, if σ is constant, $\mathrm{d}e/\mathrm{d}t = \sigma/\eta$ and is constant. This is the formal expression of the fact that this model cannot describe creep, as has already been indicated.