Chapter 6 ~ 8
Mechanical Properties

Viscoelasticity
(Chapter 6~7)

Modulus vs. Viscosity

- Mechanical behavior
  - – Hooke's law (ideally time-indep.)
  - – Ideal elastic body

$$\sigma = E\varepsilon, \sigma = \frac{F}{A}, \varepsilon = \frac{\Delta l}{l}$$

- Relaxation behavior
  - \- Newtonian liquid
  - \- ideal viscous body (ideally time-dep.)

$$\sigma = \eta \dot{\varepsilon}, \dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{\Delta l}{l}$$

Young’s modulus as a function of T

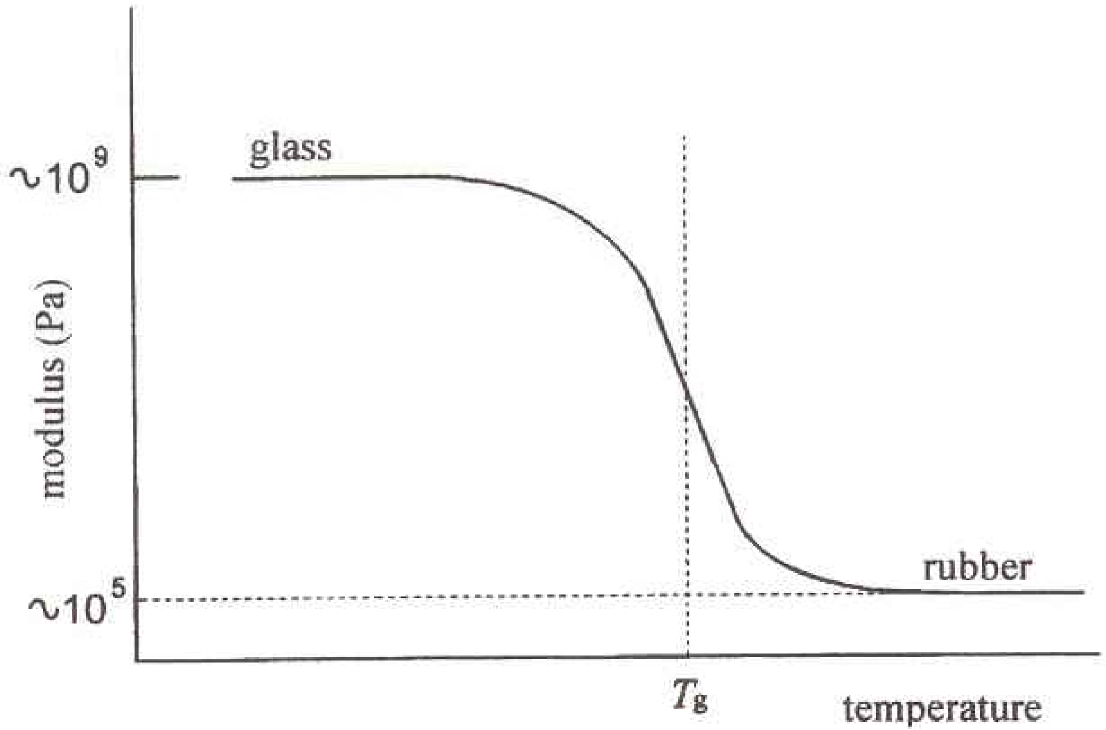


Fig. 6.1 Young’s modulus versus temperature for a model polymer. T_g is the glass-transition temperature.

Uniaxial tension test

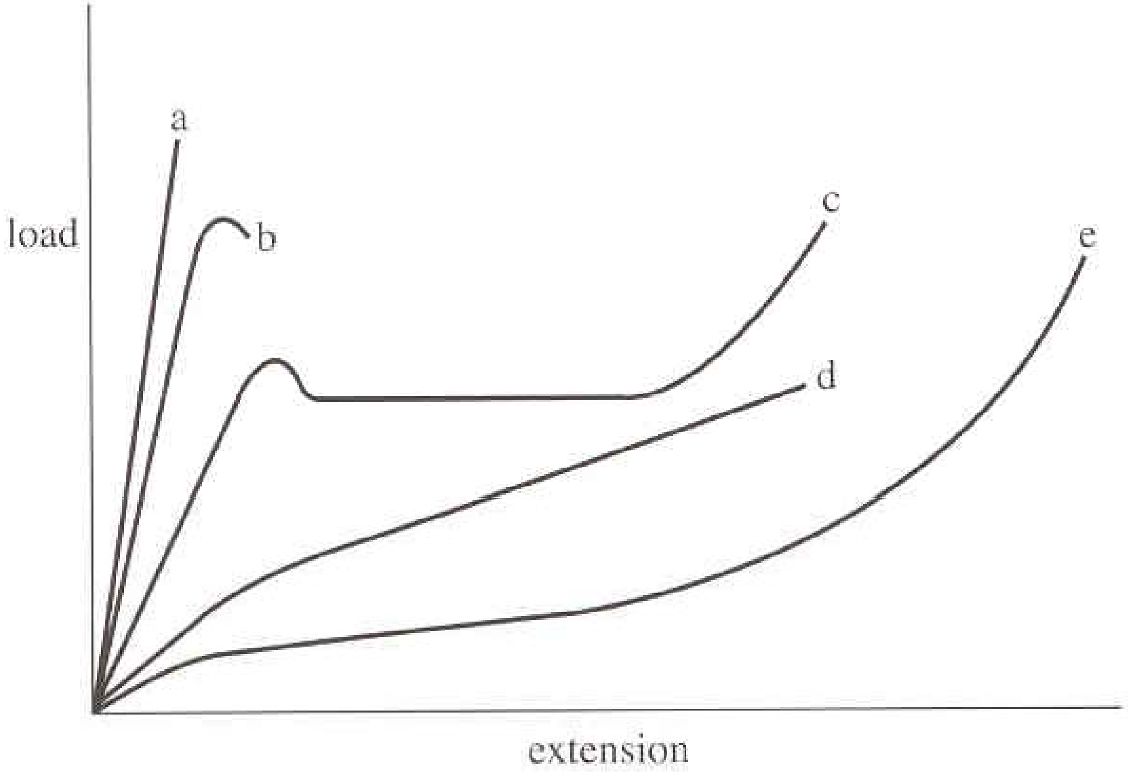


Fig. 6.2 Possible forms of the load–extension curve for a polymer: (a) low extensibility followed by brittle fraction; (b) localised yielding followed by fracture, (c) necking and cold drawing, (d) homogeneous deformation with indistinct yield and (e) rubber-like behaviour.

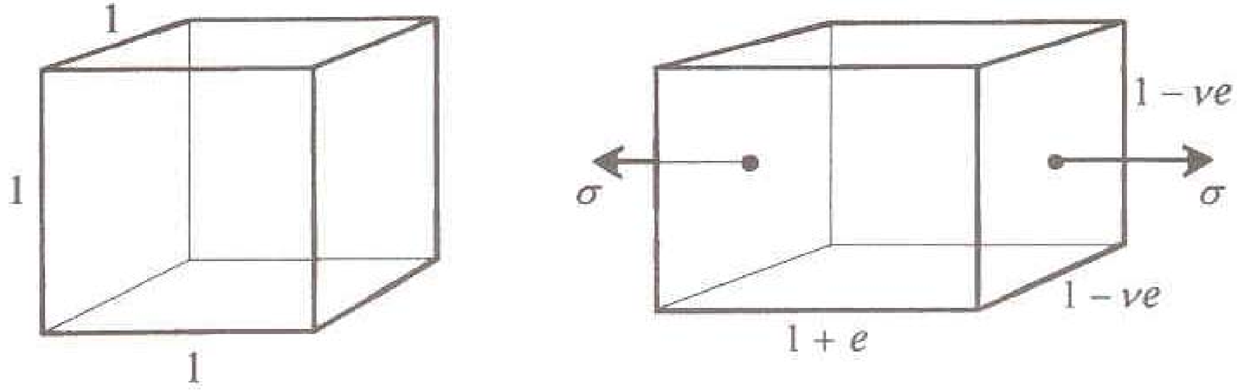
What polymers may exhibit...

- Time-dep. Response
- Non-recovery of strain upon the removal of stress
- Non-linearity of response
- Large strains without fracture
- Anisotropic response

Elastic response of a ideal Hookian body

Under tension or compression

Fig. 6.3 A unit cube before and after applying a tensile stress σ.



$$\sigma = E\varepsilon$$

$$K = \frac{E}{3(1-2\nu)}$$

Poisson's ratio: $\nu = -\frac{\Delta l_{\perp}}{\Delta l_{\parallel}}$

Metal: 0.3~0.4	vol. increase of decrease
rubber: 0.5	No vol. change

Bulk modulus: $\frac{1}{K} = -\frac{1}{V}\frac{dV}{dp}$

Under shear

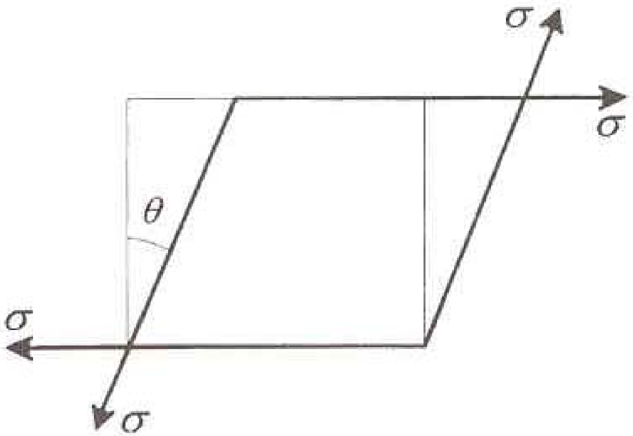


Fig. 6.4 Application of shear stresses σ to the unit cube. The forces σ are applied tangentially to the faces and uniformly spread over them.

Shear modulus: $G = \dfrac{\sigma}{\theta}$ $$G = \frac{E}{2\left(1+\nu\right)}$$

$$l_i = \frac{(1+\nu)\sigma_i + 3\nu p}{E} \qquad i = 1,2,3$$

When $\nu = \dfrac{1}{2}, \quad G = \dfrac{E}{3}$

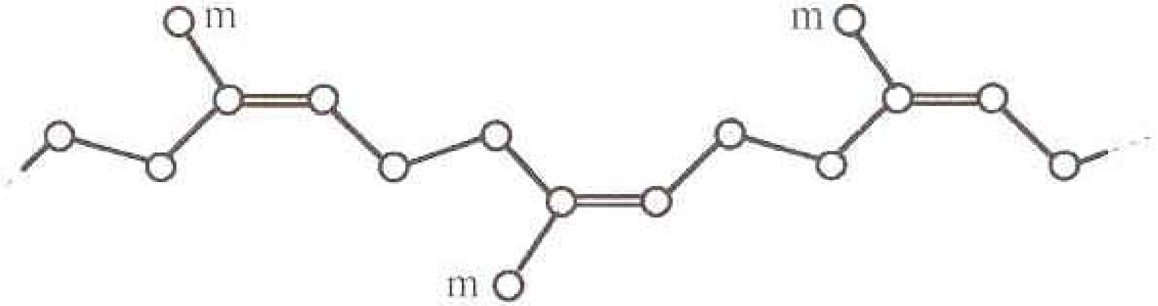
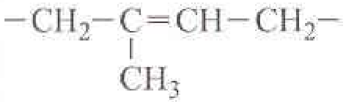


Fig. 6.9 The chemical structure of natural rubber, m = methyl group. (Hydrogen atoms are not shown.)

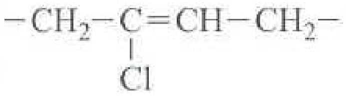


$-CH_2-\underset{CH_3}{C}=CH-CH_2-$

polyisoprene (natural rubber or gutta percha)

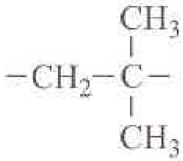
$-CH_2-CH=CH-CH_2-$

polybutadiene (*cis* form)



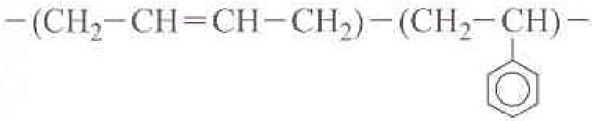
$-CH_2-\underset{Cl}{C}=CH-CH_2-$

polychloroprene (Neoprene)

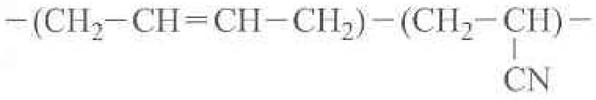


$-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$

polyisobutylene (basis of 'butyl' rubber)

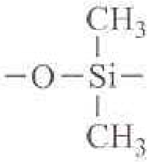


*butadiene-styrene (BSR) rubber



$-(CH_2-CH=CH-CH_2)-(CH_2-\underset{CN}{CH})-$

*butadiene-acrylonitrile ('nitrile') rubber



$-O-\overset{CH_3}{\underset{CH_3}{Si}}-$

poly(dimethyl siloxane) (silicone rubber)

Fig. 6.10 Repeat units of some important natural and synthetic rubbers. In the copolymers marked with an asterisk the respective monomer units occur in a random sequence along the chain (but see also section 12.3.3).

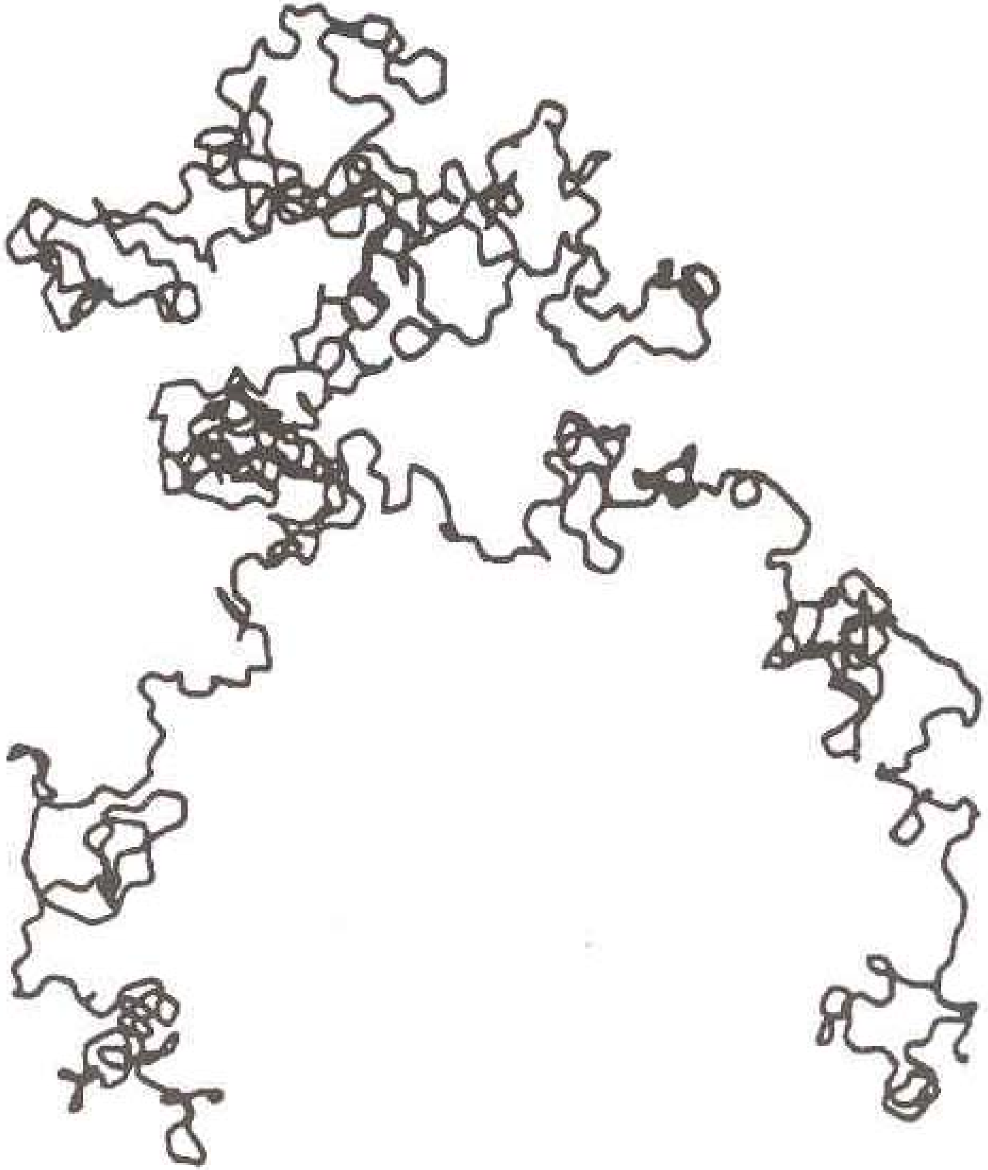


Fig. 6.11 The randomly coiled chain. A photograph of a model of a polymethylene chain containing 1000 links made by setting the links at the correct valence angle and choosing the position of each successive link in the circle of rotation as one of the six equally spaced positions obtained by throwing a die. (Reproduced by permission of Oxford University Press.)

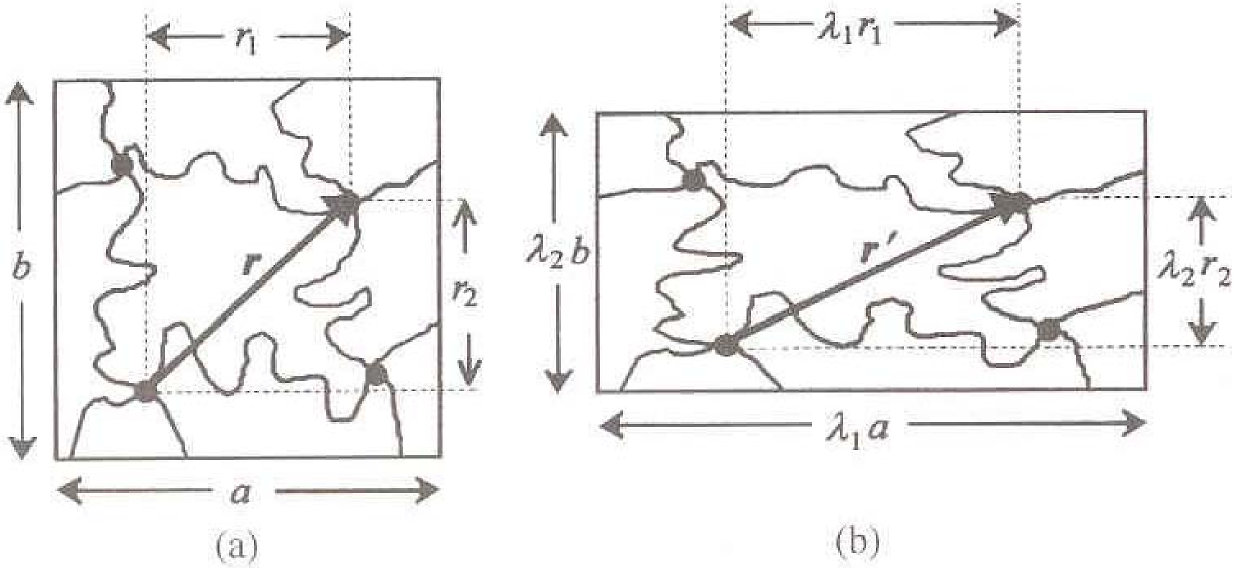


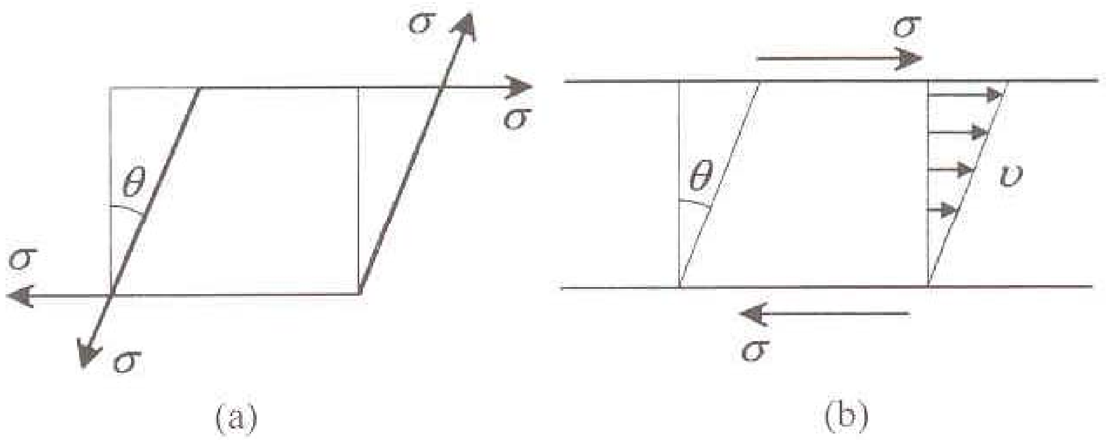
Fig. 6.12 Affine deformation. Projection onto the OX_1X_2 plane of a parallelepiped within the rubber with dimensions a, b and c parallel to the OX_1, OX_2 and OX_3 axes, respectively. (a) Chains before deformation, showing a particular vector $\boldsymbol{r}$ joining two cross-link points, ●, and its components. (b) The same chains and the vector $\boldsymbol{r}'$ joining the same two cross-link points after deformation. The component r_3 is transformed into $\lambda_3 r_3$.

Linear Viscoelasticity

- A perfect Newtonian liq
  - ideal viscous body $\sigma = \eta \dot{\varepsilon}, \dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{\Delta l}{l}$

- A viscoelastic body $\sigma = G\theta + \eta \frac{d\theta}{dt} \varepsilon$

Fig. 7.1 The responses to shear stress of (a) an elastic solid and (b) a Newtonian liquid. The arrows in (b) show the variation of the velocity υ across the sample.



(a)

(b)

- Time-dep. Creep

Creep compliance

Under constant load...

$$J(t) = \frac{l(t)}{\sigma} = \frac{l_1}{\sigma} + \frac{l_2(t)}{\sigma} + \frac{l_3(t)}{\sigma} = J_1 + J_2(t) + J_3(t)$$

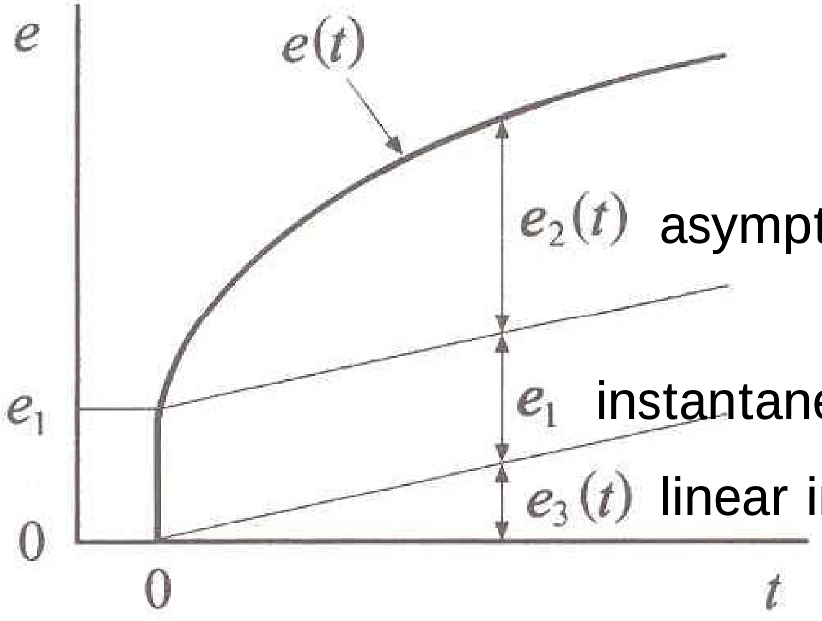


Fig. 7.2 Creep of a viscoelastic solid under a constant stress.

$e_2(t)$ asymptotic as t goes to infinity

e_1 instantaneous

$e_3(t)$ linear in time

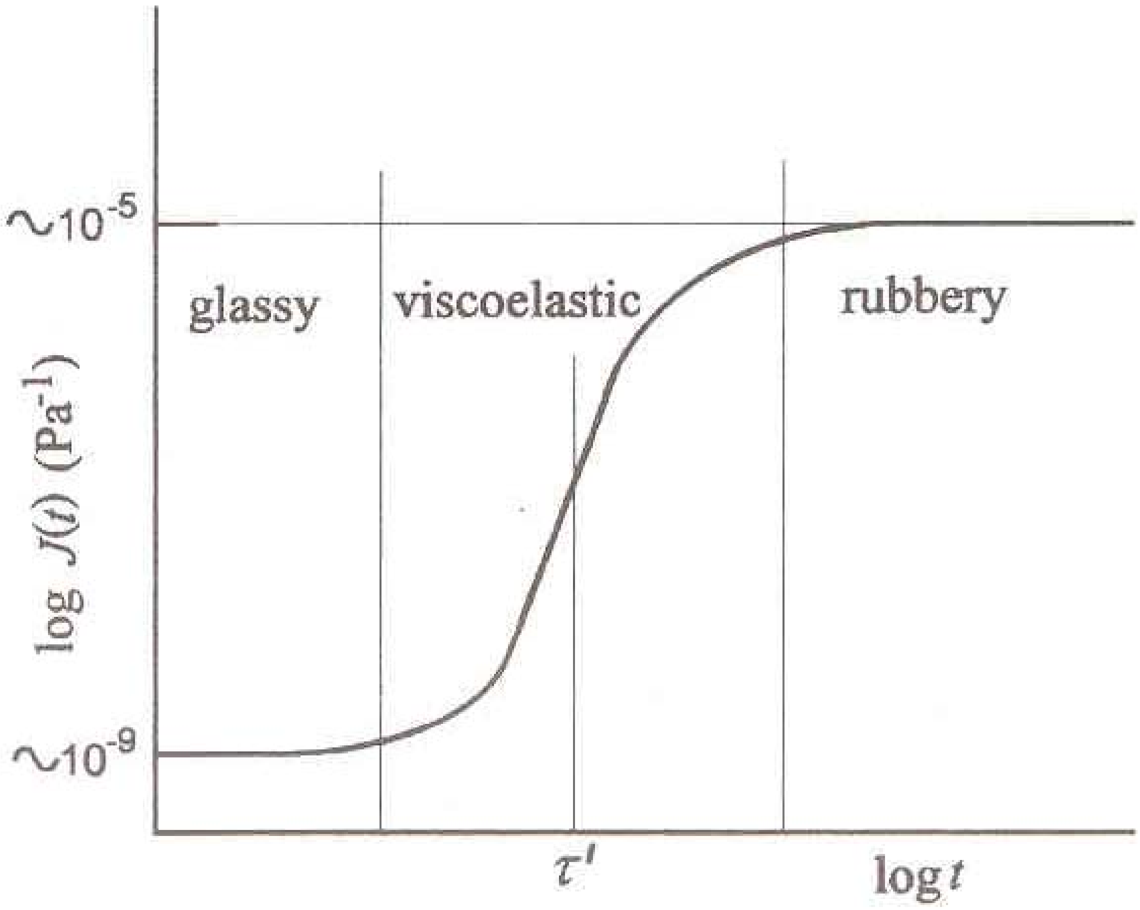


Fig. 7.3 Compliance as a function of time for an idealised amorphous polymer.

- Stress relaxation

Under a fixed strain...

$$\varepsilon(t) = \Delta\sigma_1 J(t - t_1) + \Delta\sigma_2 J(t - t_2) + \Delta\sigma_3 J(t - t_3) + \ldots$$

or

$$\varepsilon(t) = \int_{-\infty}^{t} J(t - t')d\sigma'$$

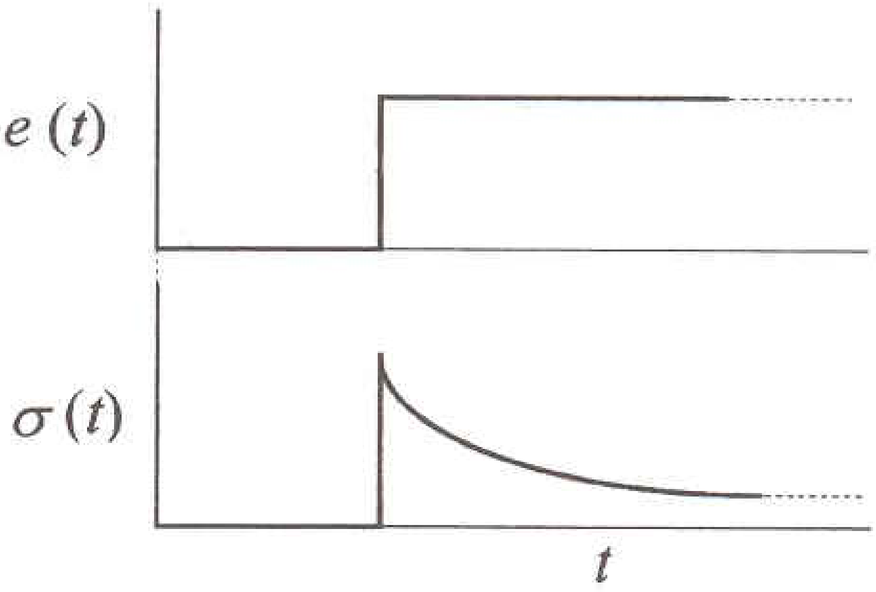


Fig. 7.4 Stress-relaxation. The upper graph shows the applied strain as a function of time and the lower graph the resulting stress.

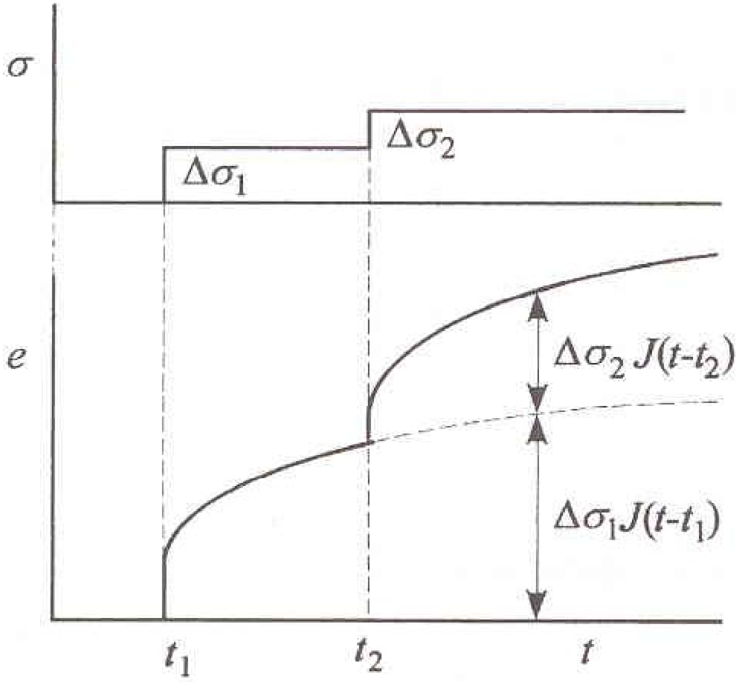


Fig. 7.5 A two-step creep experiment. See the text for explanation and symbols.

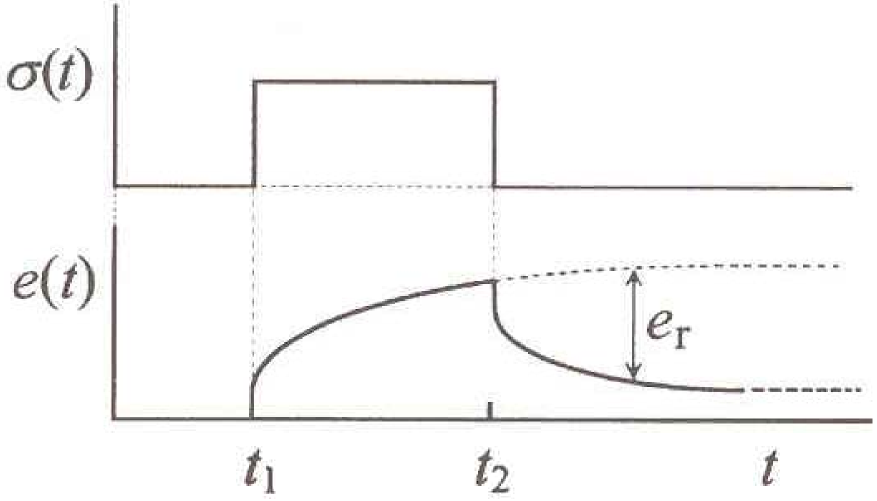
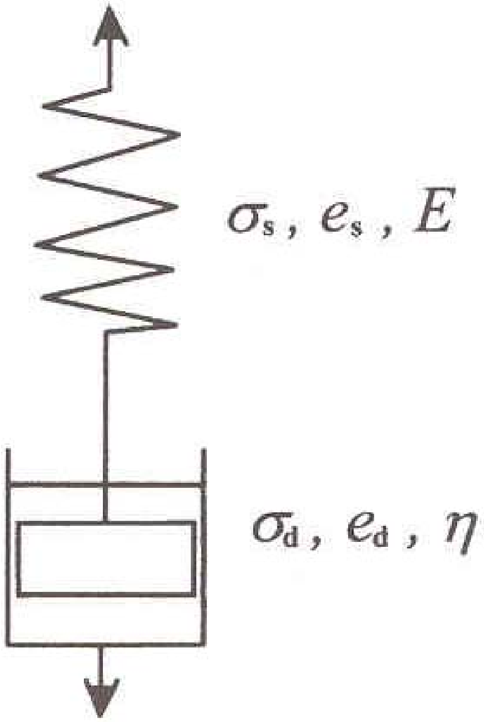


Fig. 7.6 Creep and recovery. The upper graph shows the applied stress as a function of time and the lower graph the resulting strain.

- Maxwell model

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



$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_s}{dt} + \frac{d\varepsilon_d}{dt} = \frac{d\sigma}{Edt} + \frac{\sigma}{\eta},$$

$$\sigma = \sigma_s = \sigma_d \text{ and } \varepsilon = \varepsilon_s + \varepsilon_d$$

At constant strain, $0 = \dfrac{d\sigma}{Edt} + \dfrac{\sigma}{\eta}$

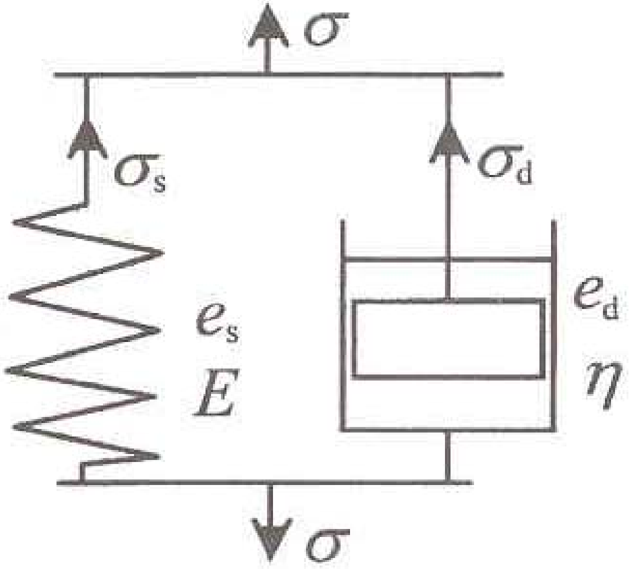
$$\Rightarrow \quad \sigma = \sigma_0 \exp(-\frac{E}{\eta}t)$$

- Voigt-Kelvin model

$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt}, \varepsilon = \varepsilon_s = \varepsilon_d \text{ and } \sigma = \sigma_s + \sigma_d$$

Under constant load, $\sigma = \sigma_0$ $\Rightarrow$ $\varepsilon = \frac{\sigma_0}{E}\left[1 - \exp(-\frac{E}{\eta}t)\right]$

Fig. 7.8 The Kelvin or Voigt model: spring and dashpot in parallel.



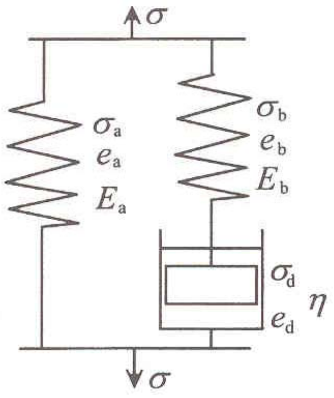


Fig. 7.9 The standard linear solid model.

- Dynamic measurements

  -complex modulus

$$\varepsilon = \varepsilon_0 \exp(iwt) \text{ and } \sigma = \sigma_0 \exp\left[i(wt+\delta)\right]$$

complex modulus

$$G^* = \underset{\nearrow}{G_1} + i\underset{\uparrow}{G_2} = \frac{\sigma}{\varepsilon} = \frac{\sigma_0}{\varepsilon_0}\exp\left[i\delta\right] = \frac{\sigma_0}{\varepsilon_0}\left[\cos\delta + i\sin\delta\right]$$

storage modulus

loss modulus

Energy dissipated per cycle: $\Delta E = \pi G_2 \varepsilon_0^2$

-complex compliance

By definition, complex creep compliance

$$J^* = 1/G^* = J_1 - iJ_2$$

$$J_1 = \frac{G_1}{G_1^2 + G_2^2} \text{ and } J_2 = \frac{G_2}{G_1^2 + G_2^2}$$

Insertion of $\sigma = \sigma_0 \exp(iwt) = (G_1 + iG_2)e$

Following Maxwell model,

$$G_1 = \frac{Ew^2\tau^2}{1+w^2\tau^2} \text{ and } G_2 = \frac{Ew\tau}{1+w^2\tau^2}$$

Calculated results

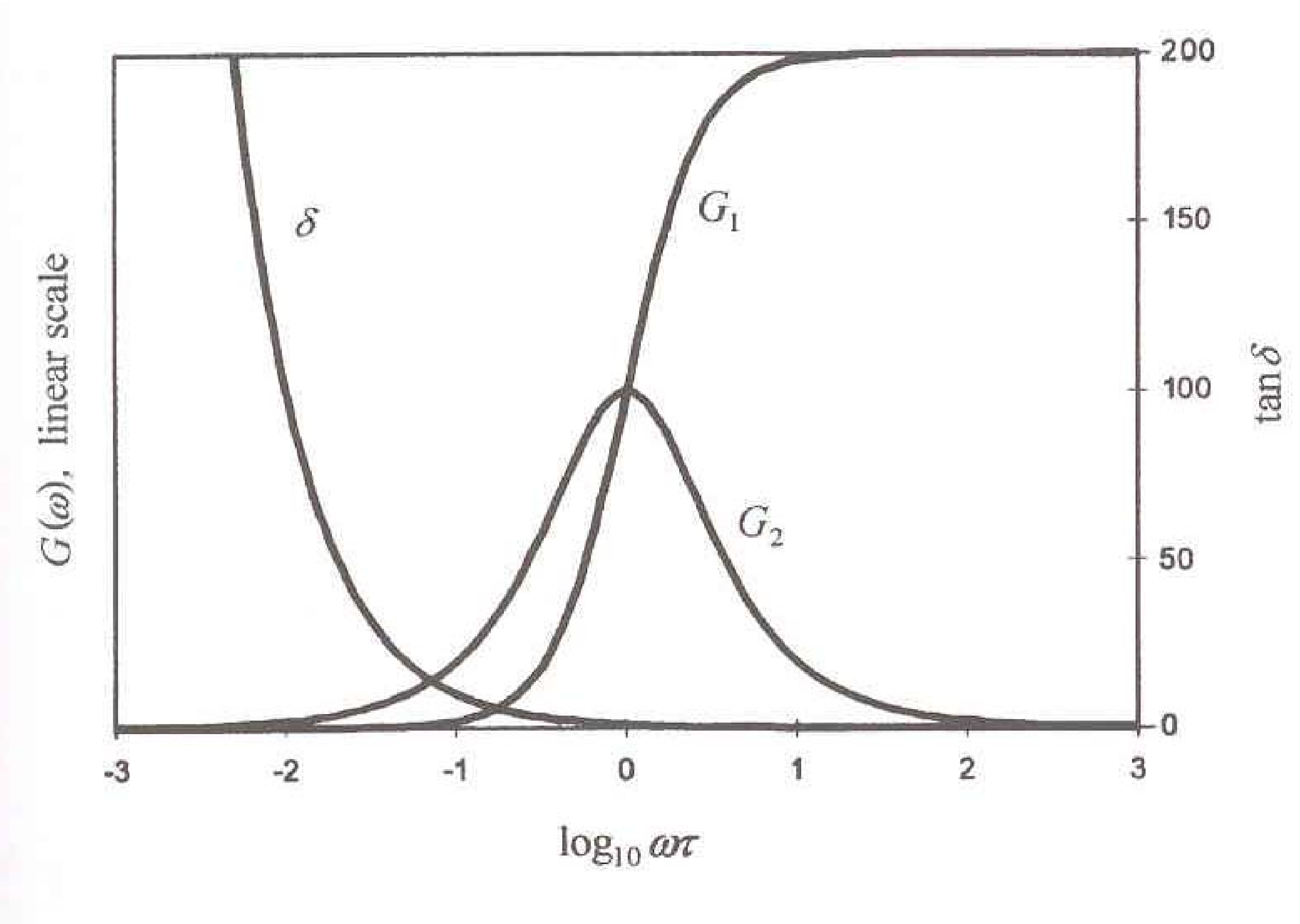


Fig. 7.11 G_1, G_2 and δ as functions of ω for the Maxwell model.

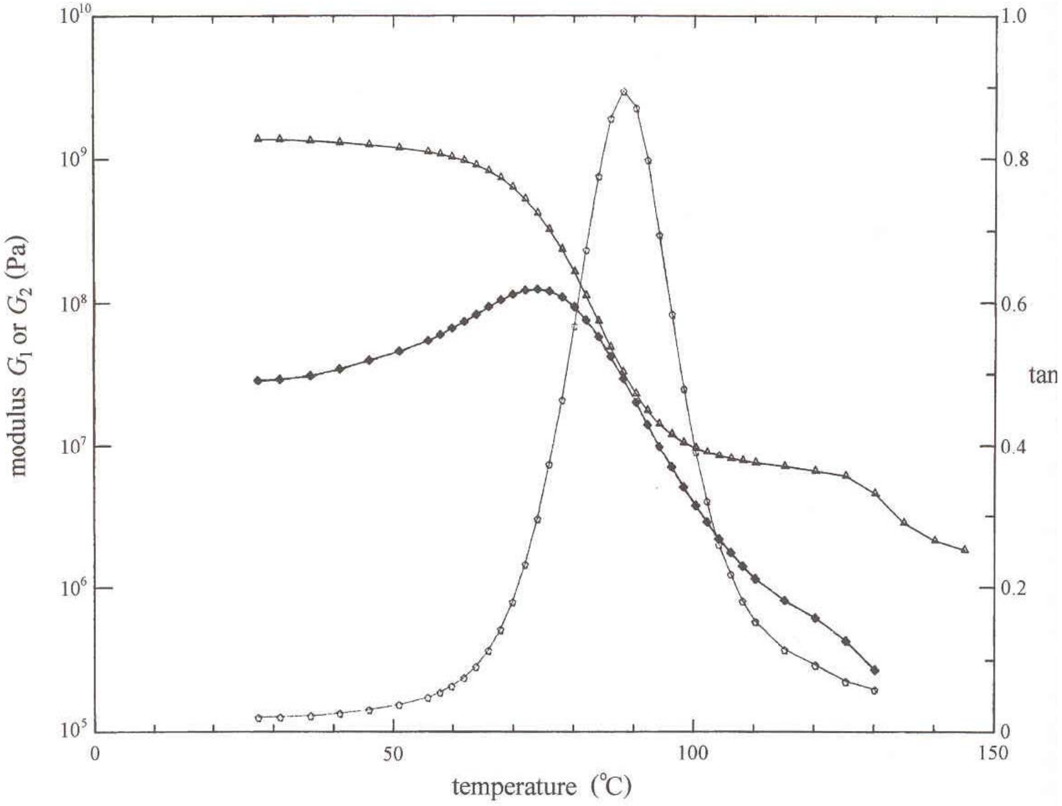
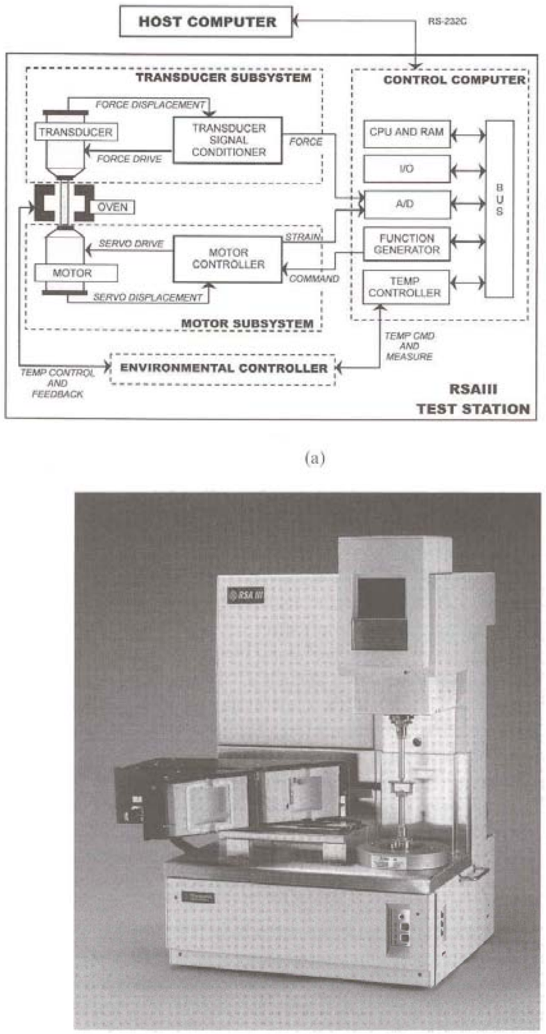


Fig. 7.15 A temperature sweep of modulus and tan δ for a PVC sample: △, G_1; ◆,
and ○, tan δ. (Courtesy of Dr I. Karaçan.)



(a)

(b)

Fig. 7.13 The Rheometrics Solids Analyser RSA III. (a) A schematic diagram of the control system. (b) The oven doors are shown open with the oven drawn aside and a sample is shown ready for a bending test. (Courtesy of Rheometric Scientific GmbH.)

- Time-temperature superposition

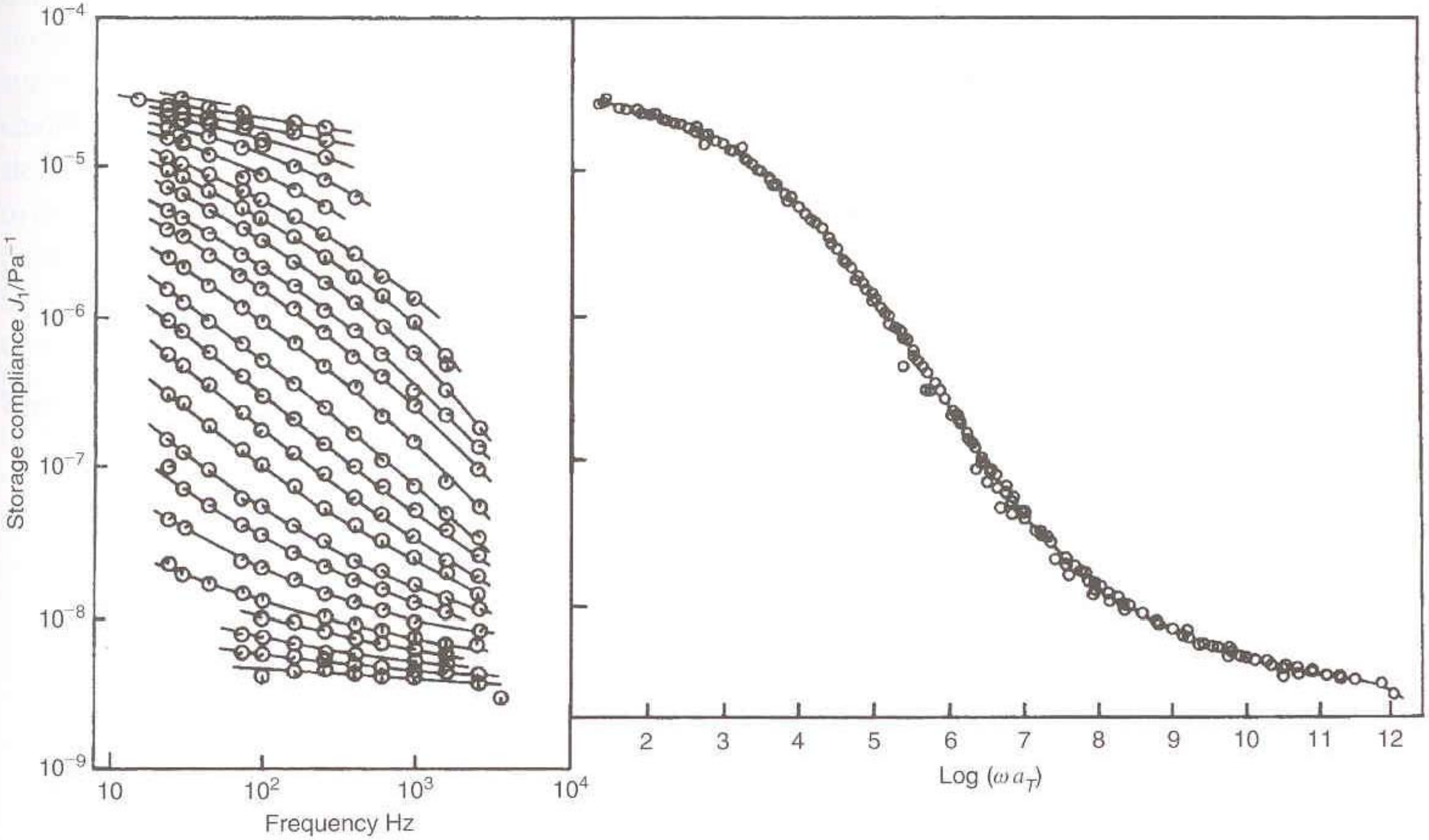


Fig. 7.14 The storage compliance of poly(n-octyl methacrylate) in the glass-transition region plotted against frequency on a logarithmic scale. Left-hand side: values obtained at 24 temperatures, ranging from −14.3 °C (bottom curve) to 129.5 °C (top curve); right-hand side: the master curve obtained by using appropriate shifts log a_T. Note that the horizontal scales differ by a factor of two for the two parts of the figure. (Adapted by permission of Academic Press.)

• Glass transition in amorphous polymers

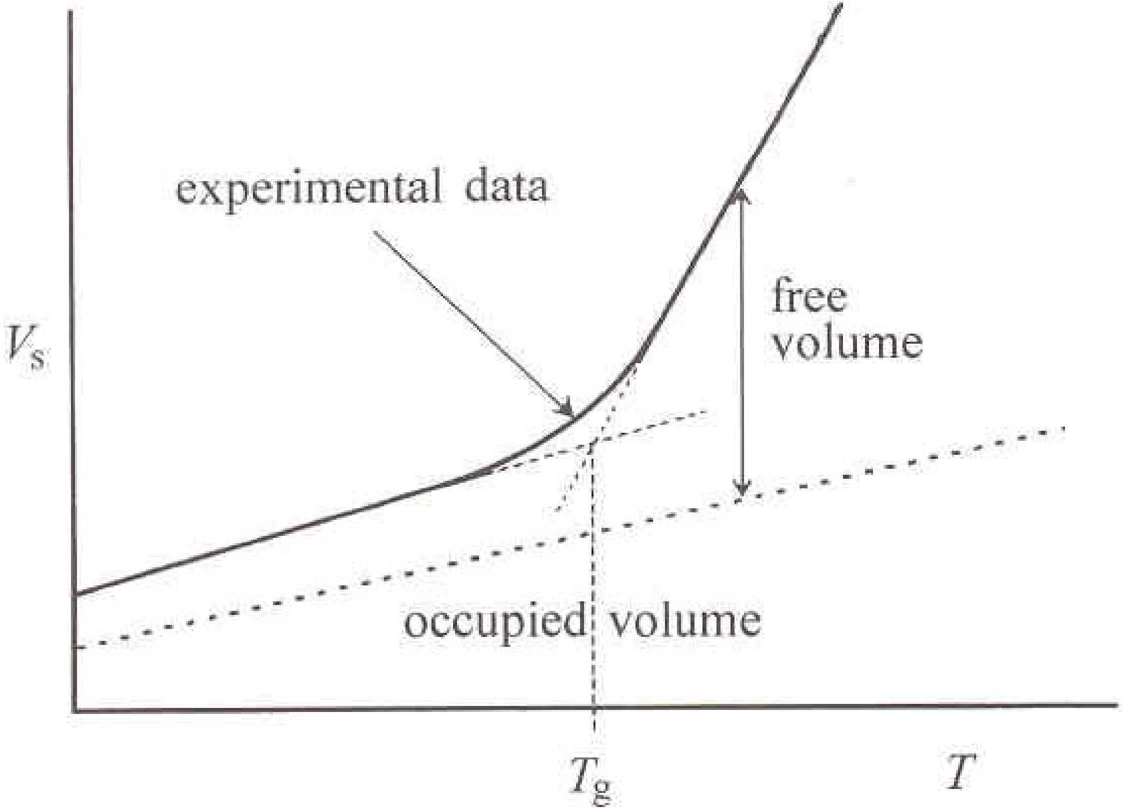


Fig. 7.16 A schematic diagram showing the determination of T_g from a plot of specific volume against temperature and the definition of the free volume.

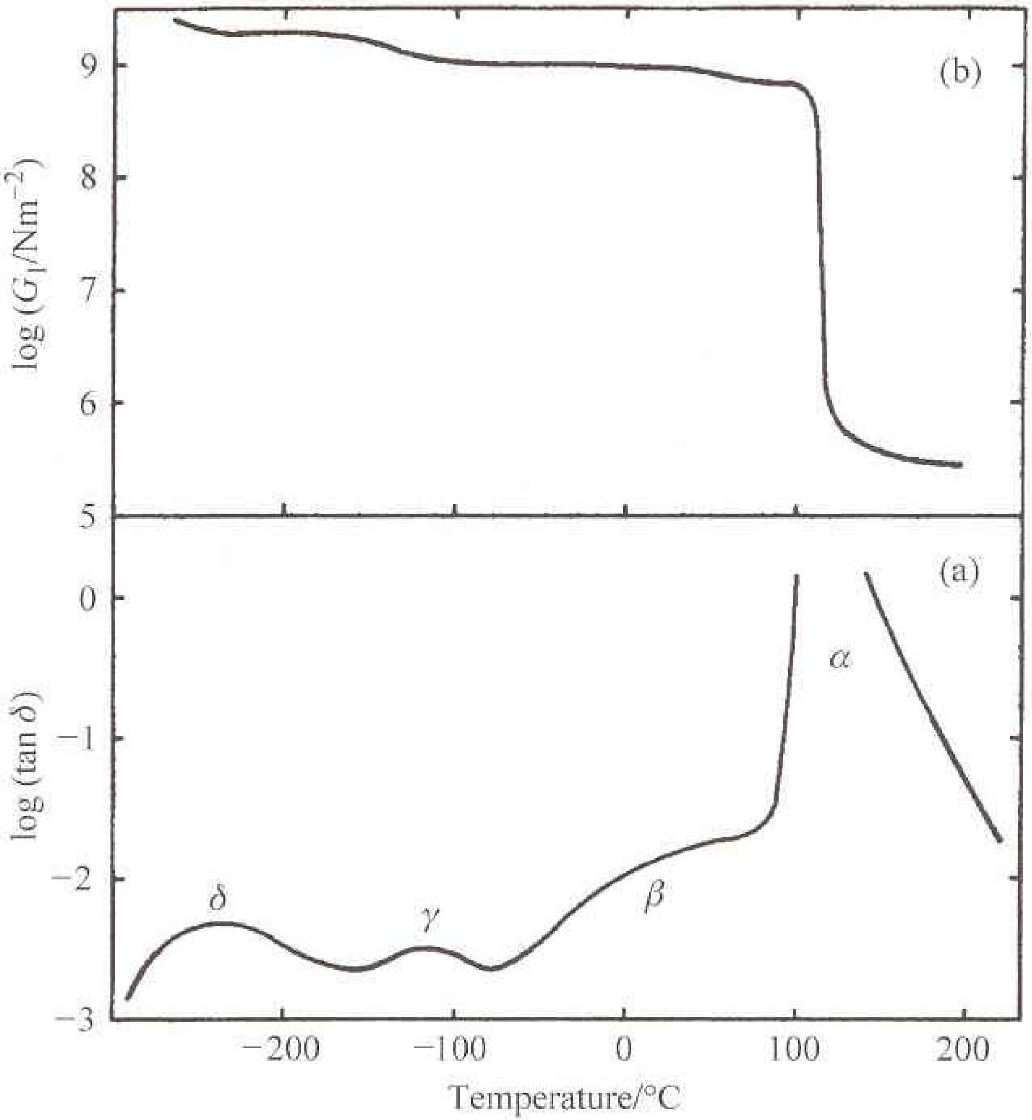
- Factors affecting Tg

  -Main chain flexibility

  -Side group

  -Plasticizers etc...

Fig. 7.17 Variations of shear modulus G_1 and $\tan\delta$ with temperature for polystyrene. (Reproduced by permission of Oxford University Press.)



Yield and Fracture of Polymers
(Chapter 8)

Importance of Yield or Fracture

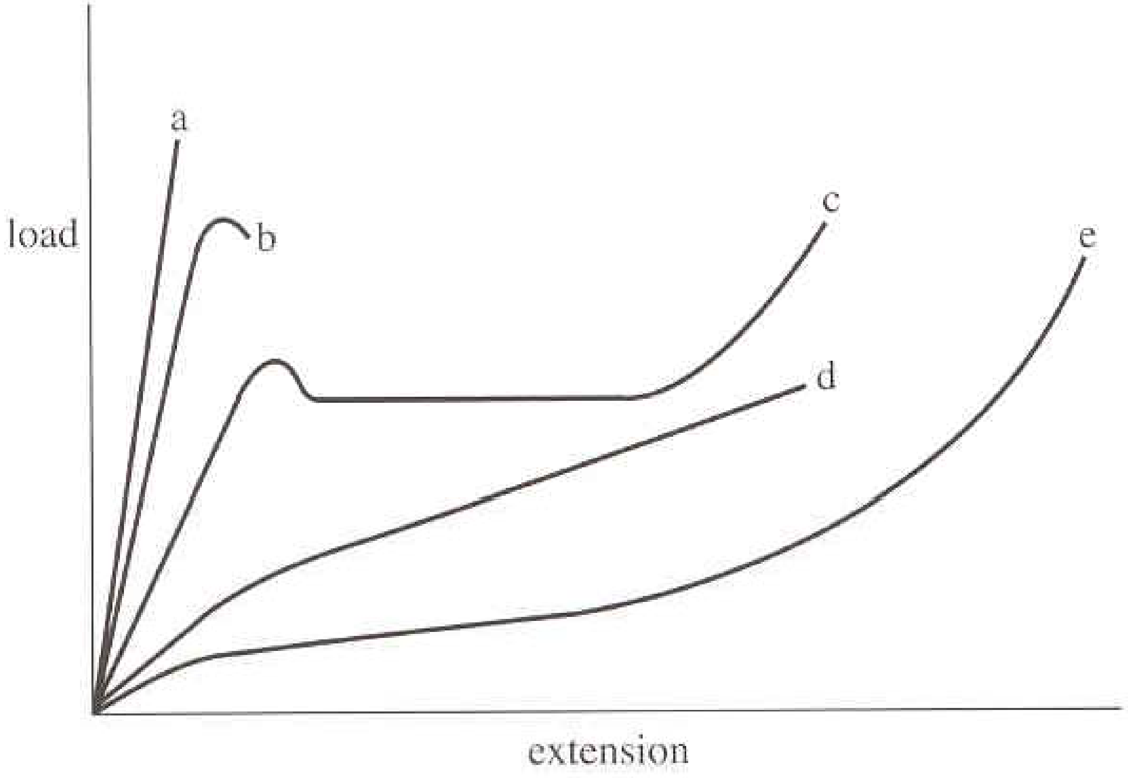


Fig. 6.2 Possible forms of the load–extension curve for a polymer: (a) low extensibility followed by brittle fraction; (b) localised yielding followed by fracture, (c) necking and cold drawing, (d) homogeneous deformation with indistinct yield and (e) rubber-like behaviour.

Yield

Ideal yield behavior

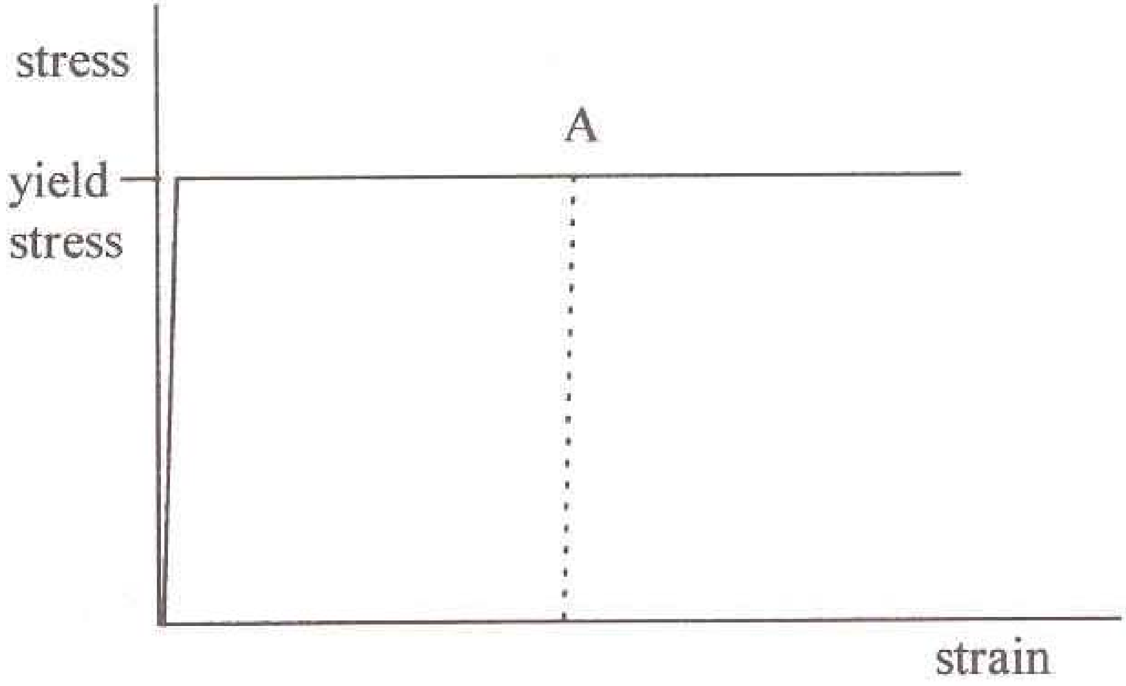


Fig. 8.1 Ideal yield behaviour. The full lines represent the stress–strain relationship on loading and the dotted line represents the relationship when unloading takes place starting at the point A.

Table 8.1. *Idealised creep and yield behaviours*

Behaviour	Creep	Yield
Is a threshold stress required?	No	Yes
Does stress increase with strain?	Yes	No
Is strain recoverable on removal of stress?	Yes	No

Fig. 8.2 'Competition' between yield and brittle fracture. The curves show schematically the dependences of brittle-fracture stress and yield stress on temperature. The dashed lines correspond to higher strain-rates than do the full lines. See the text for discussion. (Adapted by permission of I. M. Ward.)

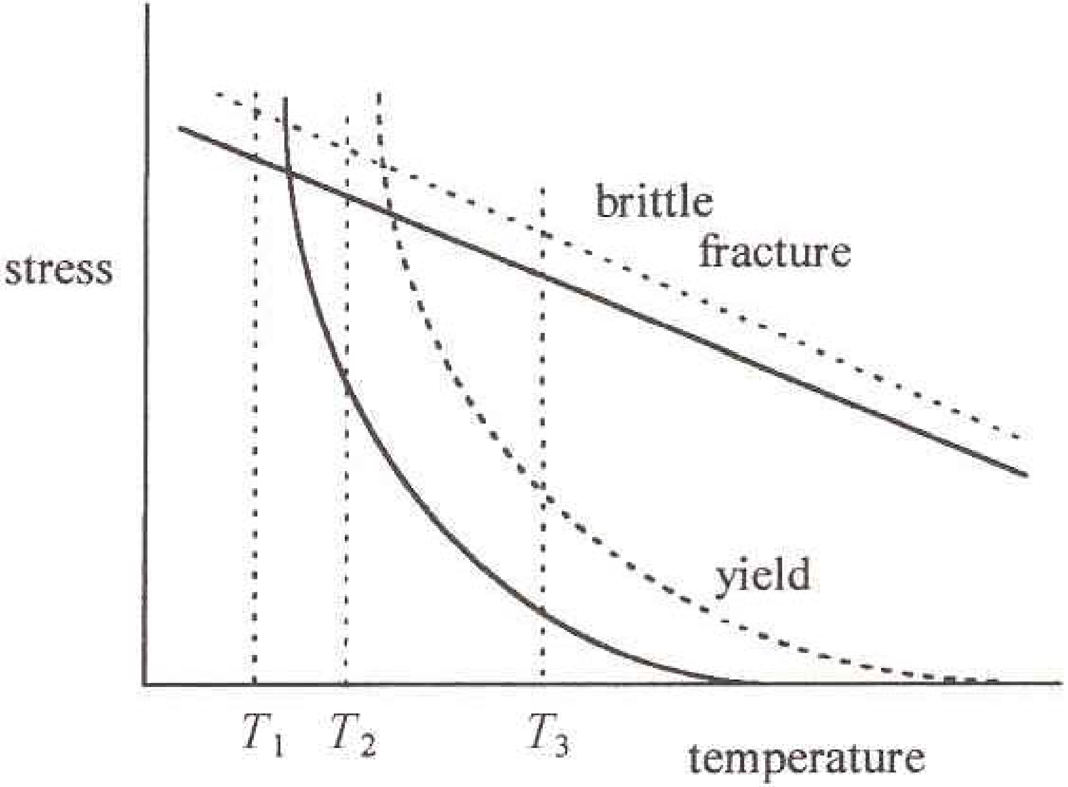
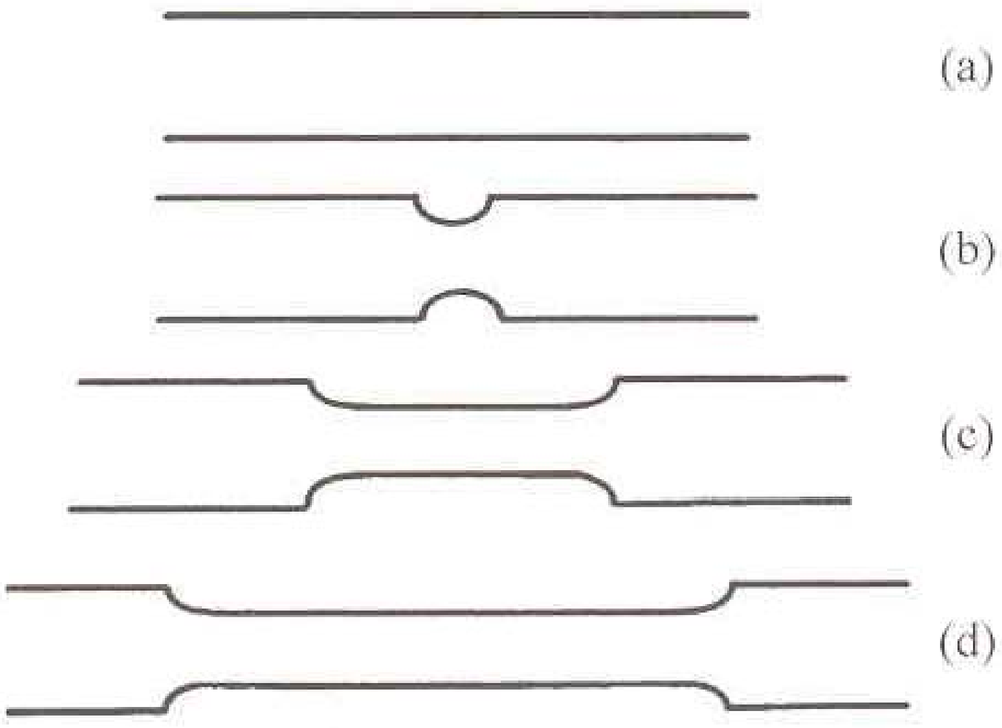
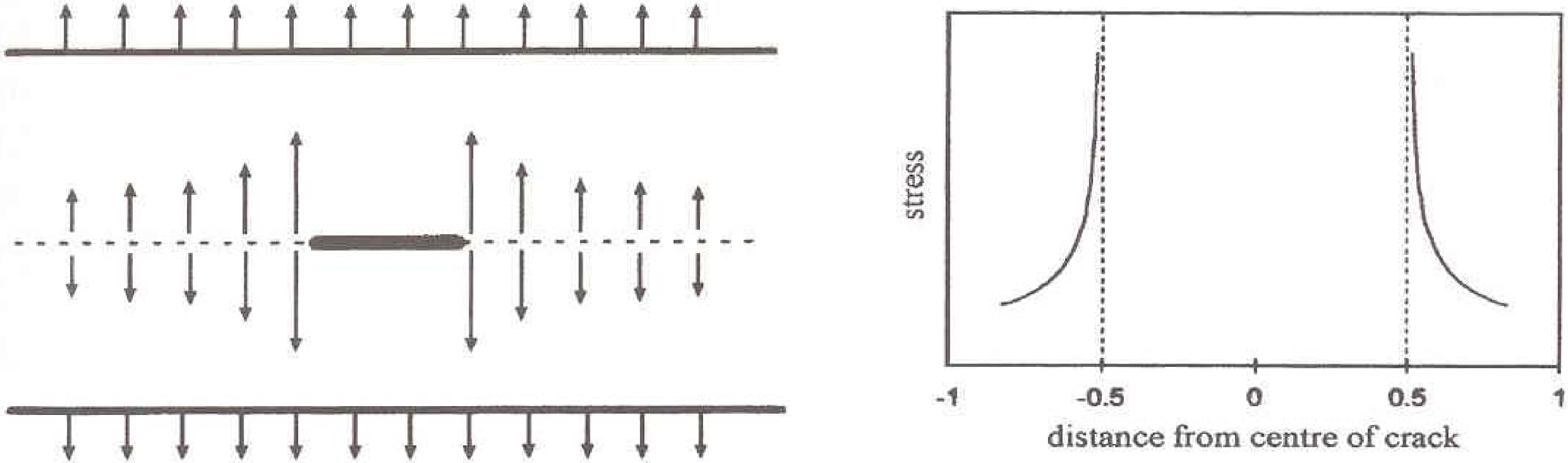


Fig. 8.3 Necking and cold drawing (schematic): (a) represents a length of undrawn sample; (b) shows the start of neck formation at a point of slight weakness; (c) and (d) show progressive elongation of the neck, which eventually spreads through the whole sample.



Fracture



(a) (b)

Fig. 8.7 The tensile stress near a crack in a sheet of polymer in tension. (a) A schematic representation of the stress. The arrows at the top and bottom of the diagram represent a uniform tensile stress applied to the polymer sheet in a direction normal to the crack, represented by the short thick line at the centre. The arrows pointing upwards from the dotted centre line represent the forces exerted by the upper half of the sheet on the lower half, whereas the arrows pointing downwards represent the forces exerted by the lower half of the sheet on the upper half. (b) The form of the tensile stress given by Irwin's equations for a crack of length one unit. See also section 8.3.4.

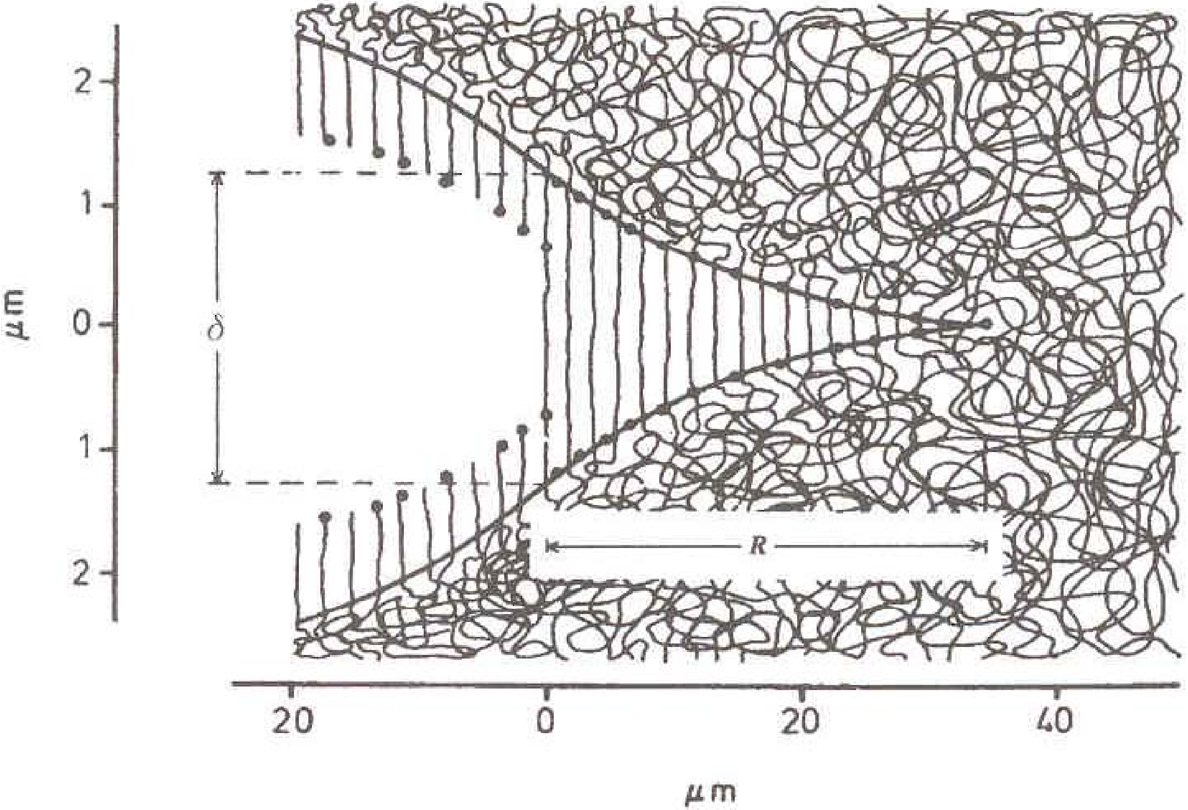
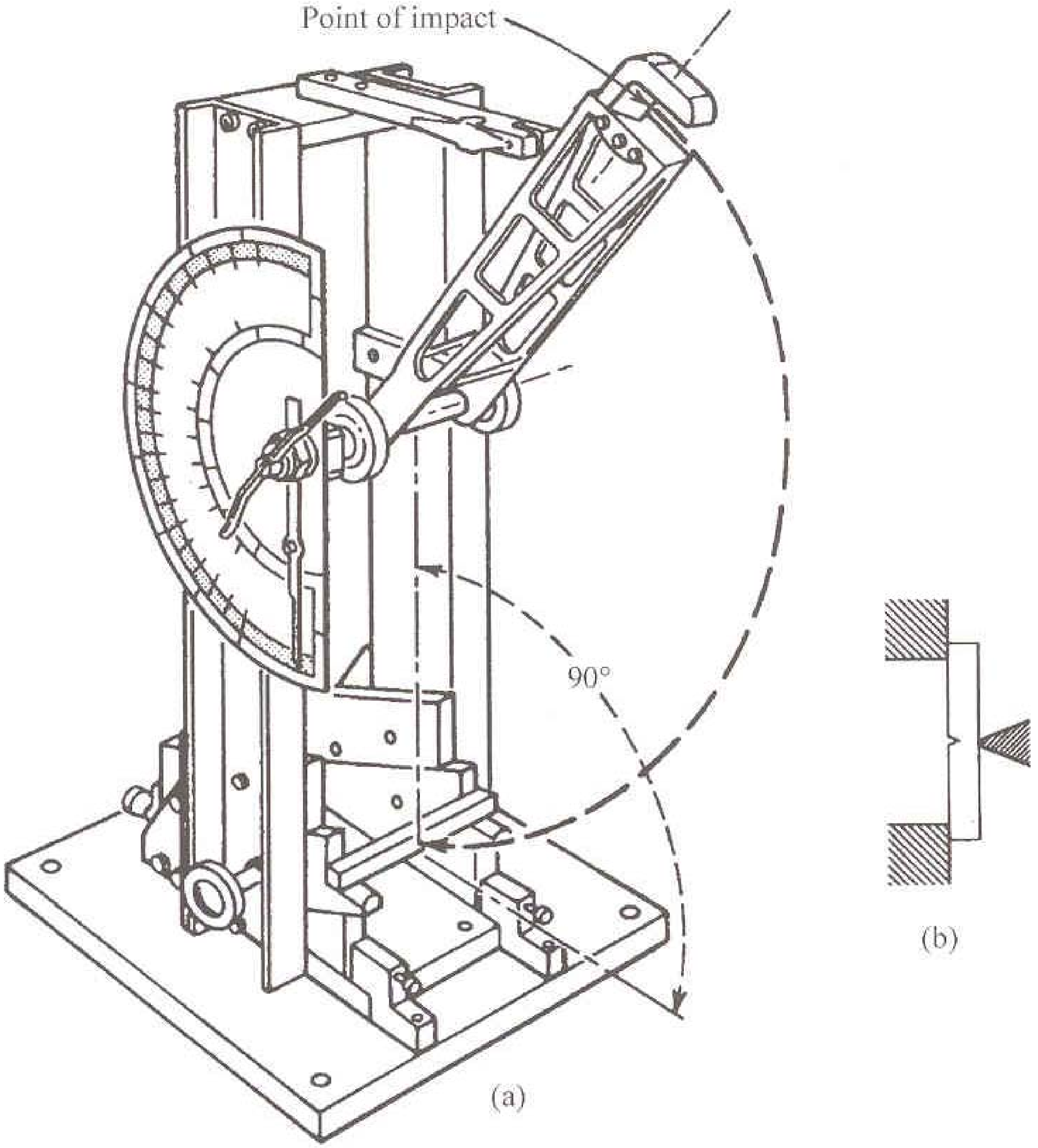


Fig. 8.9 The shape of a craze profile. The thickness of the craze at the crack tip is $\delta = 8\sigma_{\mathrm{cr}}R/(\pi E^*)$. The deformation behaviour of the molecules is indicated schematically, but see also the text and fig. 8.10. The dimensions are those of a particular craze observed in poly(methyl methacrylate). Note the different vertical and horizontal scales. (Adapted with permission of IOP Publishing Limited.)

Fig. 8.13 The Charpy impact test: (a) the pendulum tester, ASTM 256; and (b) the sample and striking hammer tip. ((a) Reprinted and (b) adapted, with permission from the American Society for Testing and Materials.)



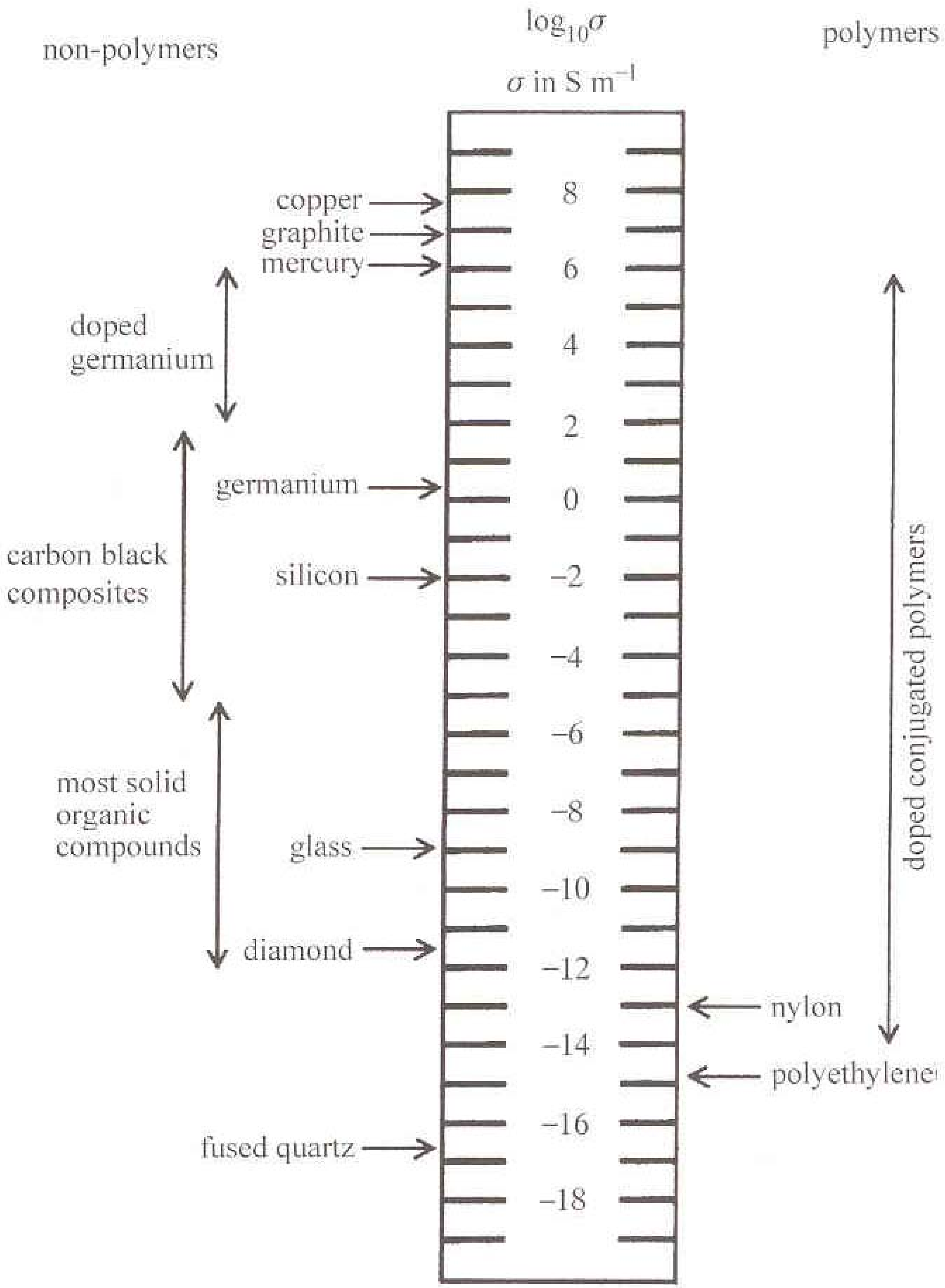


Fig. 9.1 Electrical conductivities of polymers compared with those of other materials. All values are approximate.