

Deformation and flow of amorphous materials.

Polymers are sufficiently different structurally to as compared to metals & ceramics.

First, polymeric solids are commonly amorphous.

This precludes plastic deformation by slip.

Further, a lot of 'free space' is introduced into the material.

Second = many of our polymers are linear with

strong, covalent intra molecular bonds & weak secondary inter molecular bonds.

Third = if single bond can be rotated $c \rightarrow c$

Elastic strain.

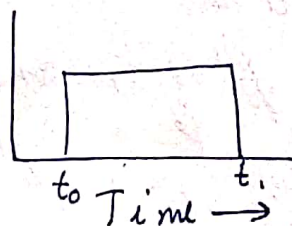
Stresses introduce elastic strains.

Elastic strain develops when the stress is applied, remains constant at constant stress, and disappears when the stress is removed.

① strain develops when the stress is applied, remains constant at constant stress, and disappears when the stress is removed.

elastic strain γ_e

①



G
modulus

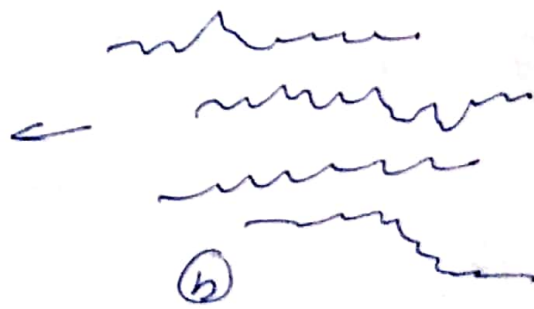


② Spring model or Hooke model

Typically the initial elastic modulus for most polymers is low when compared with those of other materials.

Reasons for this low value \rightarrow

① The presence of free space that is commonly present in amorphous materials. Dimensional changes are made without straining the atom to atom bonds. More important for linear molecules, however, is the straightening of kinked & coiled molecules & the unfolding of molecular crystals. This extension can occur with little stretching of the atom-to-atom bonds.

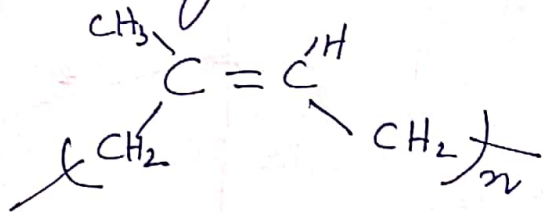


folding of chains

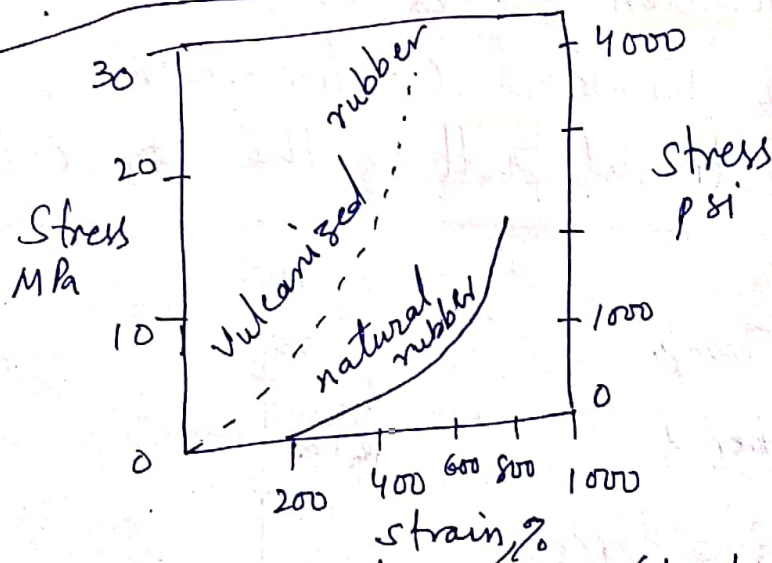
straightening of kinked &/or folded molecules (linear polymers) (a) without tension (b) pulled.

③ With additional strain, the covalent bonds come into play, and the s/c ratio increases; the elastic modulus increases.

Thus the $s-e$ relationship becomes significantly non-linear. This increase is very marked for rubbers (elastomers), since their conformation is particularly tortuous.



This non-linearity is less for cross-linked polymers, and for those with 3-D network structures.

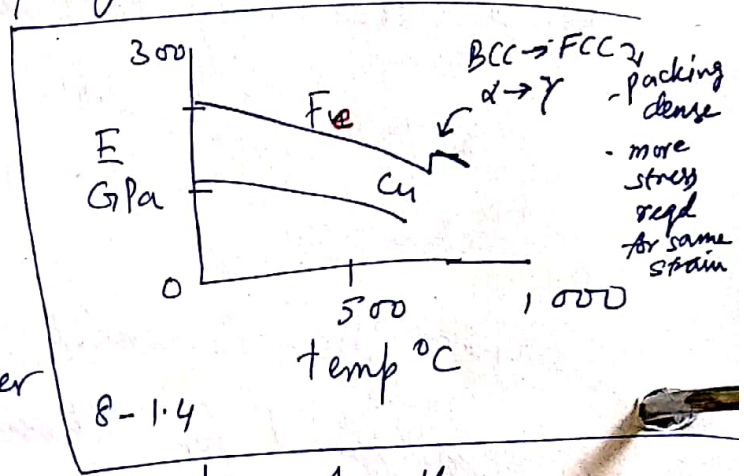


Stress-strain curves for rubber (isoprene). The elastic modulus, ds/de , is low in natural rubber (unvulcanized) until the molecules become aligned with the direction of stress. The vulcanized rubber is cross-linked with less opportunity for extending the molecules. Therefore, it has a higher modulus.

Typically the elastic modulus decreases with increasing temperature. This is true for metals, ceramics and polymers other than elastomers.

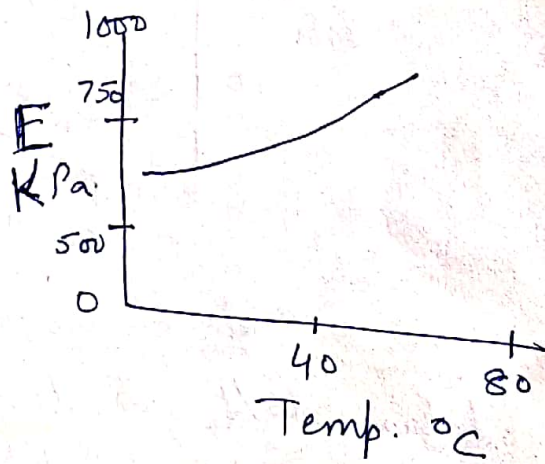
In elastomers, the elastic modulus increases as the temperature rises because the greater

thermal agitation favours a return to the more stable kinked conformation, in opposition to the directional pull on the stretched chains



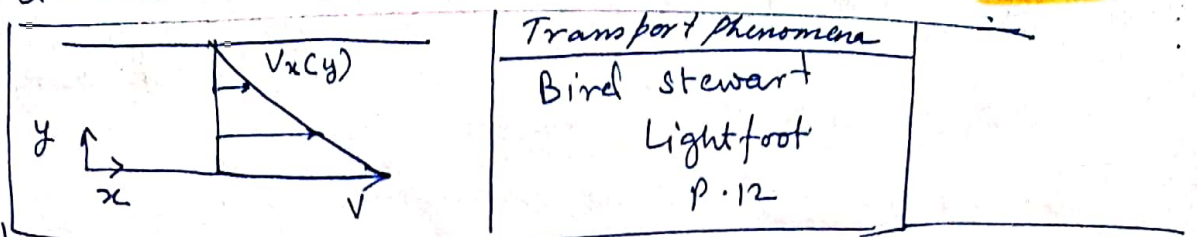
Young's modulus vs Temp.
(stretched rubber)

The retractive forces of kinking are greater ~~than~~ with more thermal agitation. Therefore $E \uparrow$ with Temp. \uparrow



Viscous flow. Fluids & amorphous solids are subject to viscous flow independent of any crystal structure. In simple Newtonian fluids, the velocity ~~is~~ is gradient of flow $\frac{dv}{dy}$ is

proportional to the applied shear stress τ .



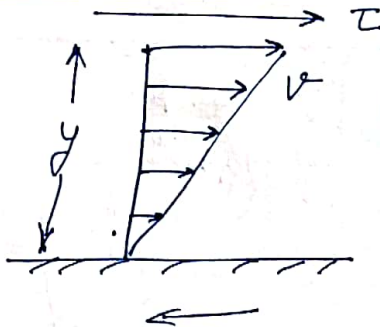
Force in x direction on a unit area \perp to the y dirn. (fluid of lesser y on fluid of greater y)

$$\tau_{yx} = -\mu \frac{dv_x}{dy} \quad \left\{ \begin{array}{l} \frac{F}{A} = \tau \\ F \propto A \\ \propto \frac{1}{y} \text{ distance between plates} \end{array} \right. \quad \mu = \text{viscosity}$$

$$\frac{dv}{dy} = f \tau \quad f = \text{fluidity}$$

$$\text{viscosity } \eta = \frac{1}{f} = \tau / (dv/dy)$$

Viscosity η , is the ratio of shear stress τ to velocity gradient v/y



viscosity decreases with increased temperature

$$\text{SI units} = \frac{\text{N}}{\text{m}^2} / (\text{m/s/m}) = \frac{\text{N}}{\text{m}^2} \cdot \text{s} = \text{Pa} \cdot \text{s}$$

$$1 \text{ Poise} = 1 \text{ Pa} \cdot \text{s} \quad \{ \text{Handbook data is in poise.} \}$$

Fluidity and viscosity are temperature sensitive since they require the movement (by shear) of atoms and molecules with respect to their neighbours.

$$f = f_0 e^{-E/kT}$$

for a Newtonian fluid
(obeys Newton's law of viscosity)

E = activation energy
for the flow of atoms or molecules.

More commonly ~~ln~~ $\eta = \eta_0 e^{E/kT}$

or

$$\ln \eta = \ln \eta_0 + E/kT$$

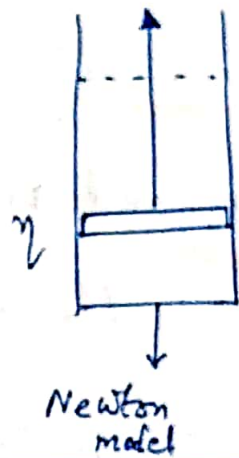
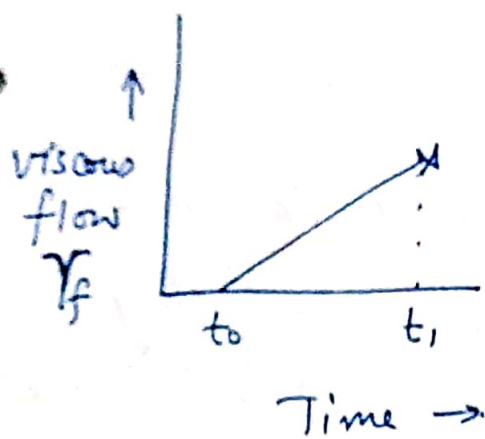
T is in K and k is the Boltzmann's constant,
($1.38 \times 10^{-23} \text{ J/K}$)

Viscosities of non crystalline materials (20°C)

Material	Viscosity η Pa·s
Air	0.000018
Pentane C_5H_{12}	0.00025
Water	0.001
Phenol C_6H_5OH	0.01
Syrup 60% sugar	0.055
machine oil	0.1 to 0.6
Glycerin	0.9
Sulfur (120°C)	10^2
Window glass 800°C	10^4
Window glass 515°C	10^{12}
Polymer T_g	$\sim 10^2$
Polymer $T_g + 15^\circ C$	$\sim 10^8$
Polymer $T_g + 35^\circ C$	$\sim 10^5$

Materials with $> 10^4$ Pa.s are semisolids that can maintain self support for limited periods.

Flow starts when the shear stress is applied, continues at a constant rate under a constant stress, and has no recovery after the stress is removed.



Ideal (Newtonian) fluid :-

- Ⓐ Displacement
- Ⓑ Dashpot model

The flow is proportional to time. The flow

is not reversible when the shear stress is removed at t .

Dashpot = loose fitting piston (down down)

Polymer viscosity :- Lab. experience shows that

T_g coincides with viscosity of approximately 10^{12} Pa.s.

At lower temp.s molecular rearrangements do not occur.

Polymers do not display strict Newtonian behaviour.

The following empirical relationship holds for a no. of linear

polymers :- $\log_{10} \eta = 12 - (17.5 \times \Delta T) / (52 + \Delta T)$

ΔT is the added temperature above T_g , i.e. $(T - T_g)$

rearrange $\log_{10} \eta = A + B / (52 + \Delta T)$ $A = -55$ $B = 910$

As the temperature is raised, the value of $\log_{10} \eta$ drops below the value of 12, as

\Rightarrow Polymers should be molded into plastic products above their T_g . The specific processing temperature depends on the pressures to be used. ~~an eqn can be~~

Viscoelastic deformation

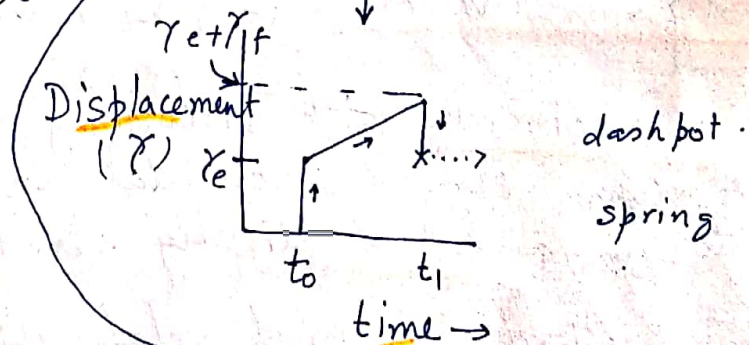
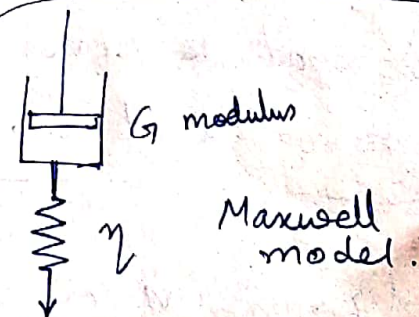
Elastic strain γ_e , and viscous flow, γ_f occur simultaneously. In the simplest case, they are additive

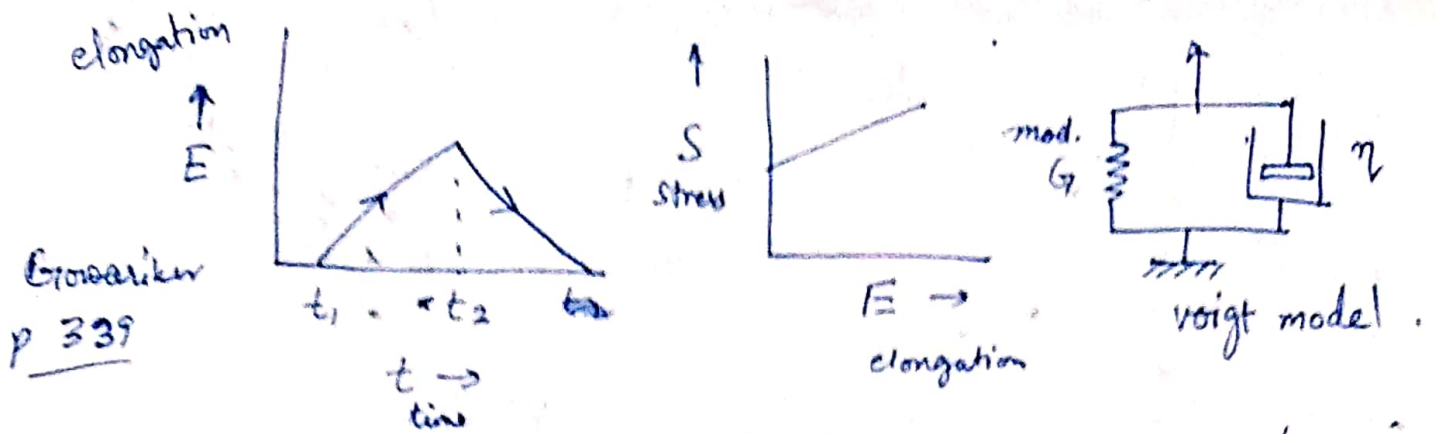
$$\gamma = \gamma_e + \gamma_f$$

Viscoelasticity (series model)

The total displacement is the sum of the elastic strain, γ_e and viscous flow, γ_f .

Another common model places the two displacements in parallel. It ^{considers} says that elastic strain cannot occur without viscous movements, eg. for the straightening of kinked elastomeric chains requires a relative





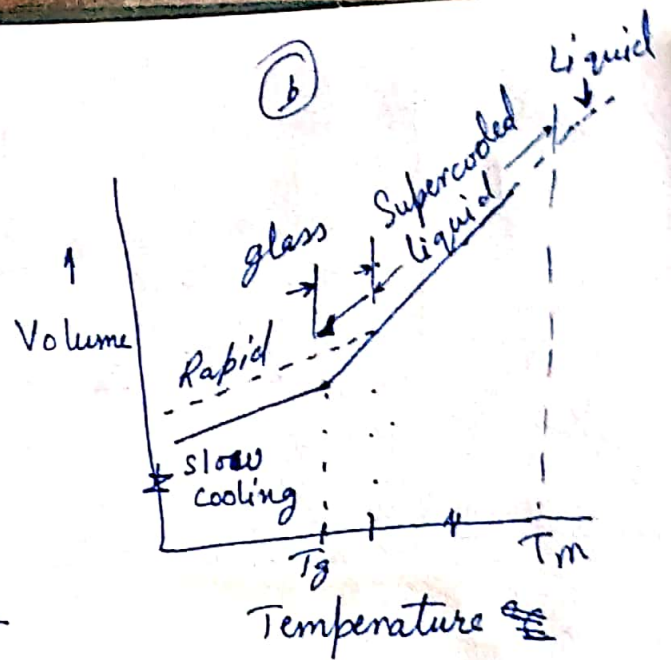
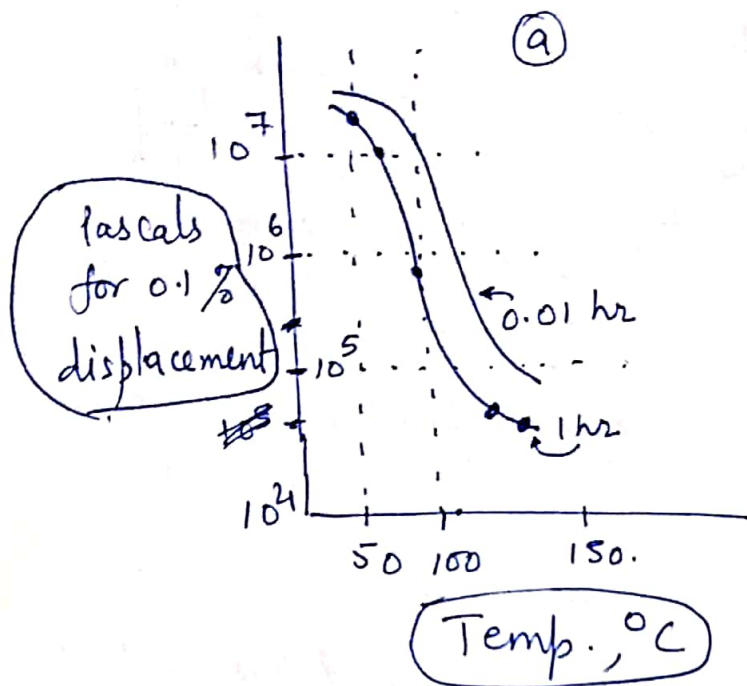
Elongation-time behaviour & stress-strain
behaviour.

flow within the material. γ_c & γ_f proceed in ||.

Fig.

Shear stress required to produce 1% strain in polymethyl methacrylate (PMMA) as a function of temperature. ~~A marked~~ A marked change occurs above T_g .

The molecules have the freedom to kink and turn by thermal agitation above the glass temperature. Below that temperature, there is insufficient thermal agitation to permit rearrangements of molecules. Thus this point represents a discontinuity in the thermal behaviour of the material. The stress required for a deformation changes by more than two orders of magnitude at the glass temperature.



Viscoelastic deformation (ordinate) vs Temperature
(Polymethyl methacrylate PMMA)

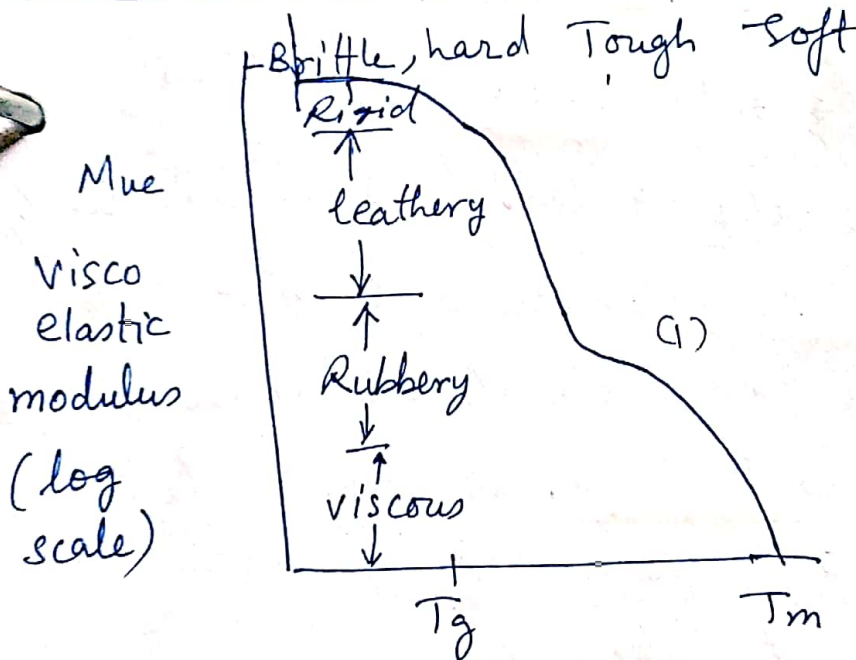
(a) With more time at a given temperature, less stress is required for unit deformation. There is a major decrease in the modulus, M_{ve} , at the glass temperature.

(b) The glass temperature is lower with slower cooling, because more time permits molecular adjustments to the stress.

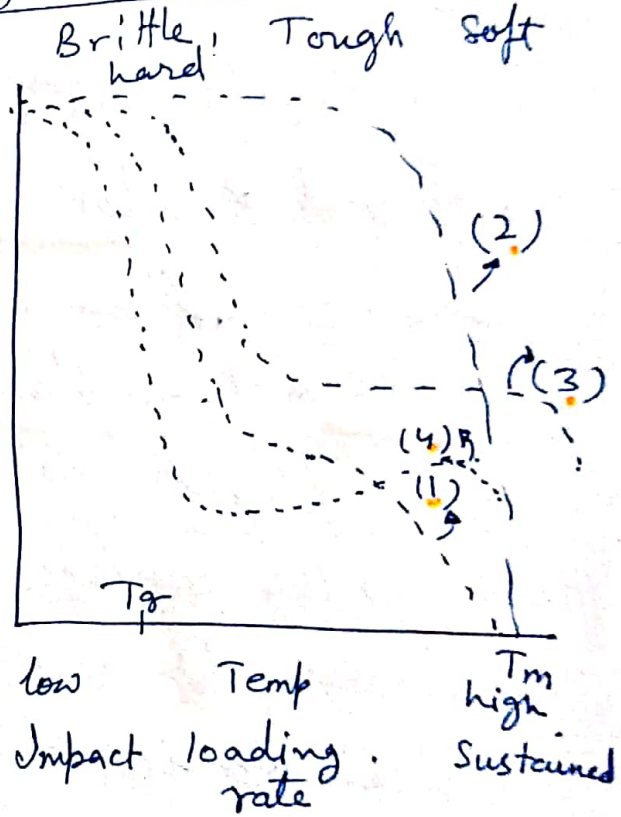
The two curves (a) indicate that less stress is required when the time of stressing is increased from 36 sec to 1 hr. The two curves also indicate that the glass temp. drops $\sim 10^\circ\text{C}$ as the time is increased from 0.01 to 1 hr.

(b) → This change is reflected as a drop in the T_g with slower cooling. With slower cooling rates, or with longer times, the molecules can be rearranged at somewhat lower temperatures

One can compare different molecular structures and their effect on deformation in fig. where $M_{ve} = \tau / (\gamma_e + \gamma_f)$



low ← Temperature → High
Impact ← loading rate → sustained



Viscoelastic modulus vs structure (schematic)

- (1) Amorphous linear polymer. (2) Crystalline (100%) polymer. (3) Cross-linked polymer. (4) Elastomer (rubber)

As in τ is shear stress and γ is shear deformation, γ_e being elastic deformation and γ_f being displacement by viscous flow. The abscissa has been generalized.

- (a) The right end includes higher temperatures and/or longer times, both of which introduce more deformation (and therefore lower values for M_{ve}). At the left end \leq below T_g , only elastic deformation can occur. ~~the~~ Here the material is comparatively rigid, a clear plastic tumbler used for soft drinks on air flights is an example. In the range of the T_g , the material is leathery; it can be deformed and even folded, but it does not spring back quickly to its original shape. In the rubbery plateau, polymers deform readily but quickly regain their previous shape if the stress is removed. A rubber ball & a polyethylene "squeeze" bottle ~~are~~ are examples of this behaviour because they are soft and quickly elastic. At still higher temperatures, or under sustained loads, the polymer deforms extensively by viscous flow.

(b) Fig compares the deformation behaviour for the different structural variants with the amorphous polymer in (a). Curve ② is a highly (100%) crystalline polymeric material does not have a glass temperature. Therefore, it softens more gradually as the temperature increases, until the melting temp. is approached, at which point fluid flow becomes significant. The higher HDPEs lie between curves ① & ② because they possess 50% crystallinity.

(3) → The behaviour of cross linked polymers such as vulcanized rubber which is harder than non vulcanized ones. If a larger fraction of the possible cross-links are connected curve ③ is raised more & more. ~~Eff~~ Effects of cross linking carry beyond the melting point into ~~a~~ the true liquid. A network polymer such as phenol formaldehyde may be considered as an extreme example of cross-linking. It gains its thermoset characteristics from the fact that the 3D amorphous structure carries well beyond an imaginable melting temp.

Once the glass temperature is exceeded, elastomeric materials can ~~be~~ be rotated and unkinked to produce considerable strain. If the stress is

removed, the molecules quickly snap back to their kinked conformations. This reinking tendency increases with the greater thermal agitation at higher temperatures. Therefore the behaviour curve ⁽⁴⁾ increases slightly to the right across the rubbery plateau. Of course, the elastomer finally reaches the temperature at which it becomes a true liquid, and flow proceeds rapidly.

Example 10-11

The glass transition temperature of a thermoplastic polymer is 95°C . The viscosity at 110°C is four times too great for a particular molding process. (a) What temperature is required?

Assume that the temperature can ^{not} be controlled to closer than $\pm 1^{\circ}\text{C}$.

(b) What viscosity variation might be expected?

Procedure :- $M_{ve} = \tau / (\gamma_e + \gamma_f)$

The viscosity drops sharply as the glass T_g is exceeded. We shall solve the viscosity at 110°C . Then we shall determine the temperature at which the viscosity is reduced by a factor of 4. Finally, we shall determine the viscosity variation as the temperature is ~~re~~ raised or

lowered 1°C .

$$\log_{10} \eta = 12 - (17.5 \times \Delta T) / (52 + \Delta T)$$

Calculation

(a) At 110°C , $\Delta T = 15^{\circ}$;

$$\log_{10} \eta = 12 - (17.5 \times 15) / (52 + 15)$$

$$\log_{10} \eta = 8.1 \quad \eta = 120 \text{ MPa}\cdot\text{s}$$

$$\text{one fourth} = 120/4 = 30$$

Since $30 \text{ MPa}\cdot\text{s}$ is desired,

$$\log_{10} 30 = 12 - (17.5 \times \Delta T) / (52 + \Delta T)$$

$$\Delta T = 18^{\circ}, \quad T = 113^{\circ}\text{C}$$

(b) At 114°C , where $\Delta T = 19^{\circ}\text{C}$,

$$\log_{10} \eta = 7.3 \quad \eta = 20 \text{ MPa}\cdot\text{s}$$

~~log~~ At 112°C , where $\Delta T = 17^{\circ}\text{C}$

$$\log_{10} \eta = 7.7 \quad \eta = 50 \text{ MPa}\cdot\text{s}$$

Comments = Eqn is an approximation.

Therefore, the relationship may vary, depending ~~up~~ on the nature of the polymer. However this calculation ~~it~~ does illustrate the sensitivity of the viscosity ~~of~~ the temp.

10-P11
p 388

Estimate the viscosity of PVC at
 105°C

Polymer $T_g \sim 10^{12} \eta$ Pa.s

$T_{gPVC} = 85^{\circ}\text{C}$

$$\log_{10} \eta = 12 - (17.5 \times \Delta T) / (52 + \Delta T)$$
$$= 12 - (17.5 \times 20^{\circ}\text{C}) / (52 + 20^{\circ}\text{C})$$

$$\Delta T = 105 - 85 = 20^{\circ}\text{C}$$

$$= 12 - 4.86 = 7.14$$

$$\eta = 13,768,571.65 = 13.7 \times 10^6 \text{ Pa.s}$$

$$\text{or } 14 \times 10^6 \text{ Pa.s}$$

10-P12

The viscosity of water is 0.001 Pa.s at 20°C ,
and 0.00028 Pa.s at 100°C .

- (a) What is the activation energy for flow?
(b) What is the viscosity at 0°C ?

~~$\log_{10} \eta = 12 - (17.5 \times \dots$~~

(a) $\ln \eta = \ln \eta_0 + E/kT$

~~$\eta_0 = 0.001 \text{ Pa.s}$~~

$$k = 13.8 \times 10^{-24} \text{ J/K}$$

$$\ln \eta_{20} = \ln \eta_0 + E/kT \rightarrow 293 \text{ K}$$

$$\ln \eta_{100} = \ln \eta_0 + E/k \cdot 373$$

$$\ln \eta_{100} - \ln \eta_{20} = \frac{E}{k} \left[-\frac{1}{293} + \frac{1}{373} \right]$$

$$= \frac{E}{13.8 \times 10^{-24}} (-7.32 \times 10^{-4})$$

$$\# E \left(\frac{-7.32}{13.8} \times 10^{20} \right) = \left(\begin{array}{l} \ln \\ 0.00028 \\ \ln \\ -0.001 \end{array} \right)$$

$5.3 \times 10^{19} E = \frac{1.36 \times 10^{-23}}{0.00072}$	0.00100
	0.00028
	0.00072
$E = 1.36 \times 10^{-23} \text{ J}$	$24 \times 10^{-21} \text{ J/Ans}$

$$\frac{13.8 \times 10^{-24} (\ln 0.001 - \ln 0.00028)}{\left[\frac{1}{293} - \frac{1}{373} \right]} = E = \frac{1.36 \times 10^{-23}}{2.4 \times 10^{-20}}$$

or $24 \times 10^{-21} \text{ J}$
Ans ✓

(b) $\ln \eta_{100} - \ln \eta_{20} = \frac{E}{k} \left[\frac{1}{373} - \frac{1}{273} \right]$

$$\ln \eta_{20} = \ln \eta_{100} - \left(\frac{24 \times 10^{-21}}{13.8 \times 10^{-24}} \right) \left[\frac{1}{373} - \frac{1}{273} \right]$$

$$\ln \eta_{20} = -6.473$$

$$\eta_{20} = 1.54 \times 10^{-3}$$

or $0.0016 \text{ Pa}\cdot\text{s}$
Ans ✓