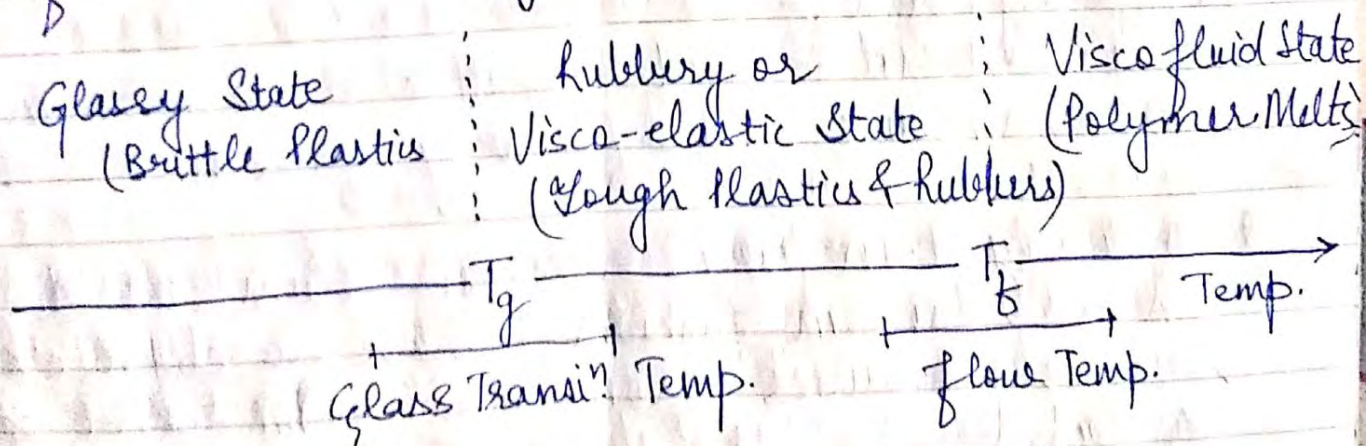


UNIT - 7

- # GLASS TRANSITION TEMPERATURE, T_g & its determining?
- free Vol. Theory
 - WLF Eq?
 - factors affecting T_g .

I. Glass Transition Temp., T_g .

- There is a "temp. boundary" for almost all amorphous polymers (and many crystalline polymers) only above which the substance remains soft, flexible & rubbery and below which it becomes hard, brittle & glassy. The temp. at this boundary is called as "Glass Transition Temp., T_g ."
- Hard State = Glassy State
- Soft State = Rubbery or viscoelastic state.



- States of Aggregation.
 - Small molecules may exist as s, l or g.
 - But polymers exist only as s or l & never as gas \therefore they decompose before reaching their b-pt.

The Amorphous & the Glassy States:-

The distribution of polymer chains in amorphous polymers is completely random. There is no ordered arrangement as in case of crystallites of partially crystalline polymers. Therefore, the molecular motion in such amorphous polymers ~~is~~ takes place ~~at~~ at temp's. much below the melting pt. of ~~the~~ such crystallites. As this molecular motion increases the amorphous (so called) polymer passes through a glass like to rubber-like state and finally becomes molten. This leads to many physical ~~and~~ properties and material applications of polymer to change.

Q. Why does an "amorphous polymer glass" is prone to brittle fracture?

Follow. are the properties of a amorphous polymer in its glassy state:-

- 1) The material is rigid & brittle because chain units are immobile and effectively frozen.
- 2) Optically transparent because chains are distributed in a random fashion & have no definite boundaries or discontinuities from which ~~the~~ light could be reflected.

To such an arrangement, now, if a small stress is applied, it exhibits a rapid elastic response resulting from purely local, bond angle deformation. Although modulus is high, the deformation is limited to $\approx 1\%$ (dx)

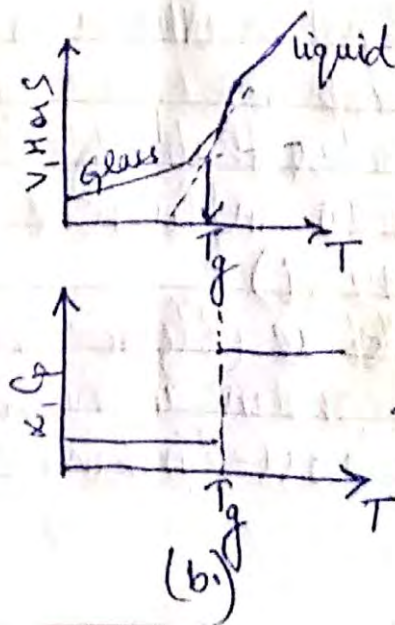
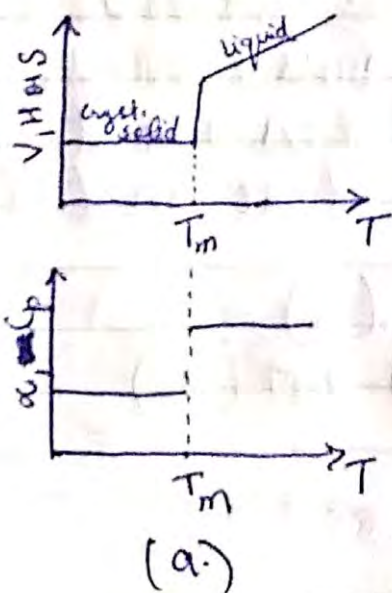
to the lack of glide planes in the disordered mass.

This also means that the applied stress σ cannot be dissipated into the whole polymer but can cause bond rupture at the point where stress is high. This makes the glassy polymer prone to brittle fracture.

- The glass transition is not specific to long chain polymers. Any substance that can be cooled to a sufficient degree below its melting temp. w/o crystallizing will form a glass.
- The transition from a glass to a rubber-like state is accompanied by marked changes in the specific volume, the modulus, the heat capacity, the refractive index, and other physical properties of the polymer.

Experimental demonstration of T_g :-

If the first derivative of the prop. - temp. curve is measured, a change in the vicinity of T_g is observed. But, the precise value of T_g depends on the method used and the rate of measurement.



Schematic representation of the changes with temp. of V , H and S and the first derivative of V & H for (a) first-order, and; (b) second-order transition.

Techniques for locating T_g .

↓
Static
↓

Changes in temp.-dependence of an intensive property, such as density or heat capacity are followed and measurements carried out slowly to allow to equilibrate & relax at each observation temperature.

↓
Dynamic
↓

A rapid change in modulus is indicative of the glass transi., but none of the transi. region is dependent on the freq. of the applied force.

In dynamic method study

↓ - the location of transition region and T_g will depend on the exptl. approach used, and T_g is found to increase from 5 to 7 K for every tenfold increase in frequency of the measuring technique.

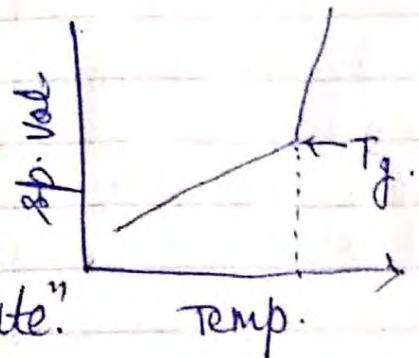
- # Factors Affecting T_g :- Magnitude of T_g varies over a wide temp. range for different polymers. As T_g depends largely on the amount of thermal energy required to keep the polymer chains moving, a number of factors that affect rotation about chain links will also influence T_g . These include:-
- 1.) Chain flexibility (i)
 - 2.) Molecular Structure (Steric effects) (d)
 - 3.) Molar Mass (constant at high M) but (d)
 - 4.) Branching & Cross-linking. (d)

FREE VOLUME THEORY:-

- Amorphous polymers go from solid glassy state to a more flexible plastic state because of the presence of sufficient energy & free volume.
- When the sample is heated, the polymer gains sufficient energy for the chain segments to become separated & begin movement, which in turn creates free or unoccupied volume that allows the chain segments to slip past one another, resulting in the material being more flexible.
- In order for chains to begin moving, the secondary forces that hold the chains together must be overcome.
- As movement begins, additional unoccupied volume is created, & this expansion with a complex maze of inter-twining chains creates additional free volume. The measure of this expansion is the thermal coefficient of expansion of that polymer.
- The temp. range, where the available free volume & energy necessary to overcome segmental chain interactions, is available, is called T_g .
- As the sp. vol. of polymers increases at T_g in order to accommodate the increased segmental chain motion, $\therefore T_g$ values can be estimated from plots

of the change in sp. vol. with Temp.

- Below the T_g , the chains are "frozen" into place and the material acts as a brittle solid, a glass hence, the name "glassy state".



- Other prop's. such as Young's modulus (stiffness), refractive index, dielectric prop's, gas permeability, X-ray Adsorption & heat capacity all change at T_g & have been used to determine the T_g .

WLF Equation:- (William-Landel-Ferry Equation)

- In this equation, the temperature-dependence of melt viscosity is expressed in terms of the glass transi. temp., T_g (or any other reference temperature) and 2 universal constants.
- The terms describing the variation of melt viscosity with temperature and with molecular weight are independent. Thus, WLF equation can be written as:-

$$\log \eta = 3.4 \log \bar{Z}_w - \frac{17.44 (T - T_g)}{51.6 + T - T_g} + K'$$

where,

η = viscosity

\bar{z}_{wo} = chain length

k' = constant depending on polymer type.

This equation holds true over the temp. range from T_g to about $T_g + 100$ K.

Other form of WLF eq? :- (In ref. to free vol. theory)

The fraction 'f' of "free" volume may be defined as:-

$$\left. \begin{aligned} f &= f_g + (T - T_g) \Delta\alpha, & T > T_g \\ f &= f_g & T < T_g \end{aligned} \right\} \text{--- (1)}$$

Thus, f is a constant at the value of f_g for all temp's. below T_g

α = volume expansion coefficient (which results from the increase in amplitude of molecular vibrations with temp.)

Above T_g , new free volume is created as the result of an increase $\Delta\alpha$ in the expansion coefficient. According to this, WLF proposed that \log viscosity varies linearly with $1/f$ above T_g , so that:-

$$\ln \left(\frac{\eta}{\eta_g} \right) = \frac{1}{f} - \frac{1}{f_g} \text{ --- (2)}$$

Substituting eqⁿ (2) in (1), we get:-

$$\log \left(\frac{\eta}{\eta_g} \right) = - \left(\frac{a(T - T_g)}{b + T - T_g} \right) \quad (3)$$

which is the WLF eqⁿ (similar to the equation done in previous section).

- The values of numerical constants 'a' & 'b' are determined by fitting literature data on the viscosity-temps behaviour of many glass forming substances.
- This equation also implies that both viscosity of the polymer and the activation energy for viscous flow, i.e., $\Delta E = 2.3 R d(\log \eta) / d(1/T)$ should become infinite at $T = T_g - b = T_g - 51.6$.
Thus, by extrapolating downward from behaviour well above T_g , it can be predicted that all mol. motion should become completely frozen at $T < T_g - 51.6$.
- At T_g , new mechanisms of deformations take ~~place~~ over more or less sharply as this critical range is approached.

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