

Transition Phenomena in high polymers (1)

Raising or lowering of temperature, just application or withdrawal of stress, greatly influenced the physical structure and properties of polymers.

As the temperature is changed, a high polymer material usually passes two transitions characterized by

(i) Melting point or first order transition corresponding to the melting temperature denoted by T_m

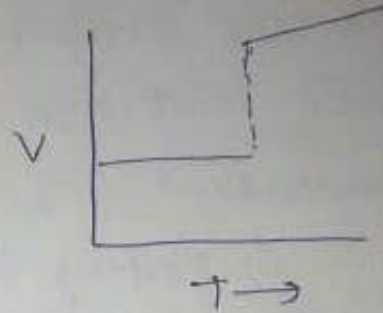
(ii) the second order transition or the glass transition corresponding to the temperature denoted by T_g

(i) Melting Point and First order Transition

Melting of a crystalline ~~or~~ solid or boiling of a liquid is associated with the change of phase. Many high polymers possess enough molecular symmetry and / or structural regularity that they crystallize sufficiently to produce a solid-liquid phase transition phenomena or melting, i.e., they have a crystalline melting point T_m . The melting is quite sharp for a few polymers such as, the nylons, while in most other cases as for polystyrene, different rubbers, etc., the phase change takes place over a range of temperature. Phase transitions of this kind, particularly in low molecular weight materials being associated with sharp

(2)

discontinuities in some primary physical properties such as the density or volume, V , [$V = (\partial G/\partial P)_T$] and entropy, S , [$-S = (\partial G/\partial T)_P$] which are the first derivatives of free energy, are commonly called first order transitions. ~~Although not~~ ~~observed~~



(ii) Glass Transition or Second Order Transition

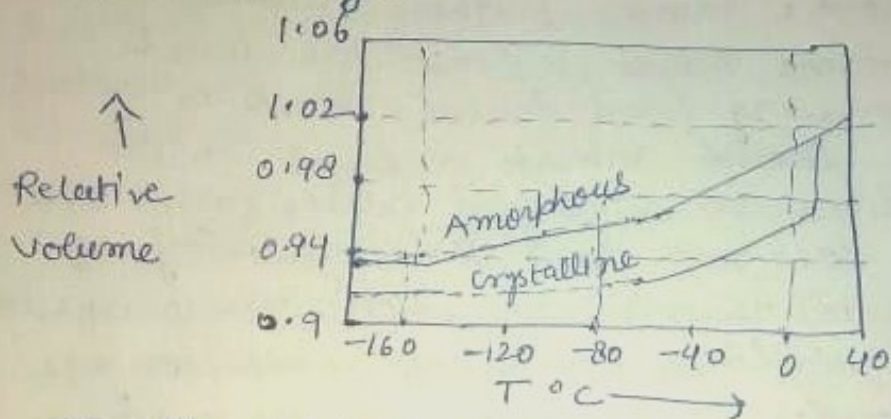
Glass transition is not a phase transition and almost each polymeric or high polymeric material is characterized by a specific glass transition temperature (T_g), appearing well below its crystalline melting point T_m .

Below this temp (T_g) normally rubber like polymers become rigid, hard and dimensionally stable and they are considered to be in a glassy state while above this temperature, all normally rigid, hard and stiff polymers become soft and readily susceptible to cold flow or creep and they turn into a rubbery state.

The Glassy state and the glass transition ②

All amorphous polymers assume at sufficiently low temperatures the characteristics of glasses, including hardness, stiffness, and brittleness.

One property associated with the glassy state is a low volume coefficient of expansion. This low coefficient occurs as the result of a change in slope of the curve of volume versus temperature at the point called the glass transition temperature T_g .



In the high temperature region, the slope of the curve (expansion coefficient) is characteristic of a rubber, below T_g at about -70°C , it is characteristic of a glass.

From the fig, the another general phenomena: The amorphous region in partially crystalline polymers also assume a glassy state, T_g being independent of degree of crystallinity to a first approximation.

In contrast to crystalline melting at a temperature T_m , there is not an abrupt change in volume at T_g , but only a change in the volume temperature curve.

Measurement of T_g

The glass transition temperature can be detected in a variety of experiments, like Bulk properties, molecular motion, phenomena related to T_g , Time effect near T_g , molecular interpretation of T_g , molecular motion below T_g .

FREE VOLUME THEORY

In the glassy state, large-scale molecular motion does not take place, rather, atoms and small groups of atoms move against the local restraints of secondary bond forces, much as atoms ~~move against the local~~ vibrate around their equilibrium positions in a crystal lattice, except that the glassy state does not have the irregularity of the crystalline state. The glass transition corresponds to the onset of liquid-like motion of much longer segments of molecules, characteristic of the rubbery state. This motion requires more free volume than the short range excursions of atoms in the glassy states. The rise in the relative free volume with increasing temperature above T_g leads to the higher observed volume expansion coefficient in this region, since the fully extended chain is the conformation of minimum energy, it tends to be assumed more frequently as the temperature is lowered.

As the molecules thus straighten out, the free volume decreases. As a result, flow becomes more difficult. The glass transition (observed at infinite time) or alternatively, the onset of crystallization where possible - is taken as the point where the number of possible conformations

of the amorphous phase decreases sharply towards one. ⑤

The fraction f of "free" volume may be defined as

$$\begin{aligned} f &= f_g + (T - T_g) \Delta\alpha & T \geq T_g \\ f &= f_g & T < T_g \end{aligned} \quad \text{--- ①}$$

Thus f is constant at the value f_g for all temperatures below T_g . Hence the volume expansion coefficient α is that resulting 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.

WLF EQUATION

Williams, Landel and Ferry proposed that \log viscosity varies linearly with $1/f$ above T_g , so that

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

Substitute eq ① in eq ② leads to

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

This is WLF equation, the numerical constants for a and b given there being determined by fitting literature data on the viscosity-temperature behaviour of many glass forming substances.

The shift factor a_T is seen to be just the ratio of the viscosity at T relative to that at T_g . Equation ③ also implies that both the viscosity of the polymer and the activation energy for

viscous flow $\Delta G = 2.3R d(\log \eta) / d(1/T)$
 should become infinite at $T = T_g - b = T_g - 51.6$.
 Thus by extrapolating downward from behaviour
 well above T_g , one would predict that all molecular
 motion should become completely frozen at
 $T < T_g - 51.6$, the new mechanisms of deformation
 take over more or less sharply as this critical
 range is approached in fact at T_g

Reference - (1) Book

Polymer science by Billmeyer

(2) Polymer science by
 Premomoy Ghosh