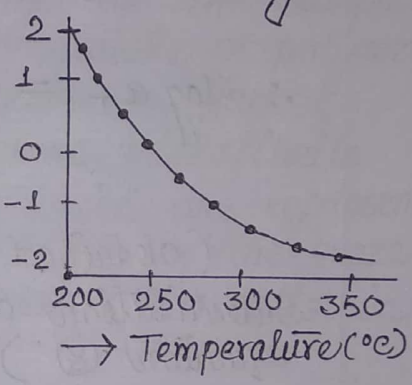
where c_1 and c_2 are constants for a polymer and T_r is the reference temperature. When $T_r = T_g$, c_1 and c_2 may be approximated by the ~~univar~~ 'universal' values of 17.44 and 51.6, respectively, although significant deviations from those values may exist for some polymer.

The temperature dependence of melt viscosity can be obtained by the WLF equation as

$$\log\left[\frac{\eta(T)}{\eta(T_g)}\right] = \log a_T = \frac{-c_1(T-T_g)}{c_2+T-T_g} \quad \text{——} \; (3)$$

When $\eta(T)$ and $\eta(T_g)$ are the viscosity at T and T_g respectively. A typical WLF fit (curve) of the shift factor, $a_T = \eta(T)/\eta(260°C)$, for polycarbonate at a ref. temp^r of 260 °C is shown in adjacent figure.



We know that, the glass transition ~~tem~~ represent a state of isoviscous and isofree volume at T_g. Therefore, the above equation provides a means of relating the WLF ~~pr~~ parameters, c_1 and c_2, to the free volume, V_f, and thermal-expansion coefficient α, of the polymer.

▸ Relationship between the WLF Parameters and free volume :

The Doolittle equation relates viscosity to the fractional free volume, f, which is defined as

$$f = \frac{V_f}{V} \quad \text{——} \; (4)$$

where V = actual volume of the polymer at temp^r T.

The Doolittle equation is given by ——

$$\ln \eta(T) = \ln A + B\left(\frac{1}{f} - 1\right) \quad \text{——} \; (5)$$

, where A & B are constant.

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When $T = T_g$

$$\ln \eta(T_g) = \ln A + B\left(\frac{1}{f_g} - 1\right); \quad \text{——— (6)}$$

[f_g = fractional free volume at T_g]

The fractional free volume, f, at a given temperature, T, is related to f_g as

$$f = f_g + \alpha_f (T - T_g); \quad \text{——— (7)}$$

[α_f = thermal-expansion coefficient of the free-volume]

$$\alpha_f = \left(\frac{\partial v_f}{\partial T}\right)_P \quad \text{——— (8)}$$

$$\therefore \log a_T = \log \frac{\eta(T)}{\eta(T_g)} = -\left(\frac{8}{2.303 f_g}\right)\left[\frac{T - T_g}{(f_g/\alpha_f) + T - T_g}\right] \quad \text{——— (9)}$$

(obtained by ~~combination of equation (5)~~ - Substitution of equation (5) – equation (7) into equation (8))

comparing equation (2) and equation (9), we get the WLF parameters -

$$c_1 = \frac{B}{2.303 f_g}$$

and $$c_2 = \frac{f_g}{\alpha_f}$$

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Mechanical Properties :

ⓐ Mechanism of deformation : At low strain (i.e <1%), the deformation of most polymers is elastic meaning that the deformation is homogeneous and full recovery can occur over a finite time. At higher strains, the deformation of glassy polymers occurs by either crazing or by shear banding.

▸ **Crazing :** When some polymers are deformed to a certain level, the critical strain (ε_c), what appears to be small cracks develop in a direction perpendicular to the principle direction of deformation. These ~~ca~~ crazes (cracks) reflect light and result in visual cloudiness or whitening of the sample. A craze is a unique morphological feature of polymer and is morphologically different from a true crack. A craze consists of polymers microfibrils are surrounded by void space, which are represent as much as 90% of the total volume of the craze. This anisotropic morphology of a craze results in the scattering of light.

▸ **Shear Banding :**

While some polymers such as polystyrene will readily craze when strained in tension, crazes may not develop in other polymers such as polycarbonate under identical conditions. Instead these polymers will form region of localized shear deformation. These regions are called shear bands, which develops at angle of 45° to the stretch direction. In general, shear-band formation is a dominant mode of deformation during tensile yielding of ductile polymers.

ⓑ Typical stress - strain behavior :

The mechanical behavior of a polymer can be characterized by its stress - strain properties. This often involves observing the behavior of a polymer as one applies tension stress to it in order to elongate (strain) it to the point where it ruptures (pull apart).

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The result are usually shown as a plot of the stress Vs strain. The stress is usually expressed in $N cm^{-2}$ or MPa where $1 MPa = 100 N.cm^{-2}$. The strain is the fractional increase in the length of the polymer sample (i.e, $\Delta L/L$, where L is the original, unstretched sample length)

$1 MPa$ (Megapascals) $= 100 N.cm^{-2}$ (Newtons/cm^2)
$1 N cm^{-2} = 1.450$ Psi (Pounds per square inch)

Four important quantities characterize the stress - strain behavior of a polymer:

1. Modulus: The resistance to ~~determine~~ deformation as measured by the initial stress divided by $\Delta L/L$.
2. Ultimate strength or Tensile strength: The stress required to rupture the sample.
3. Ultimate elongation: The extent of elongation at the point where the sample ruptures.
4. Elastic elongation: The elasticity as measured by the extent of reversible elongation.

The ratio of ~~strain~~ stress to strain is called 'Young's modulus'. This ratio is also called the modulus of elasticity and tensile modulus.

Young's modulus = stress (Pa)/strain (mm/)

Large values of Young's modulus indicate that the material is rigid and resistant to elongation and stretching.

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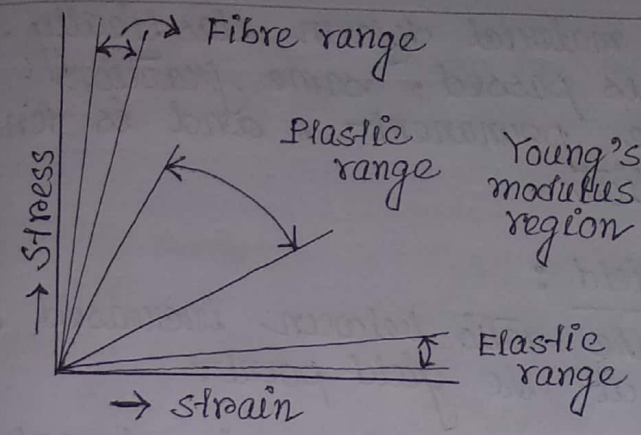

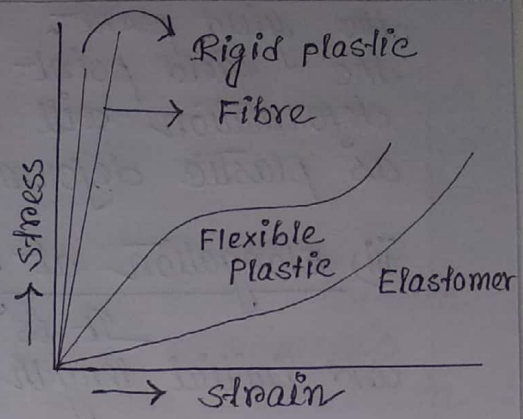

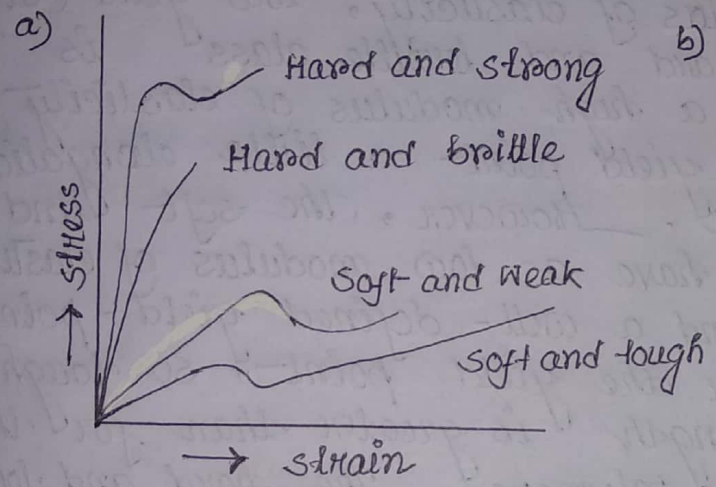

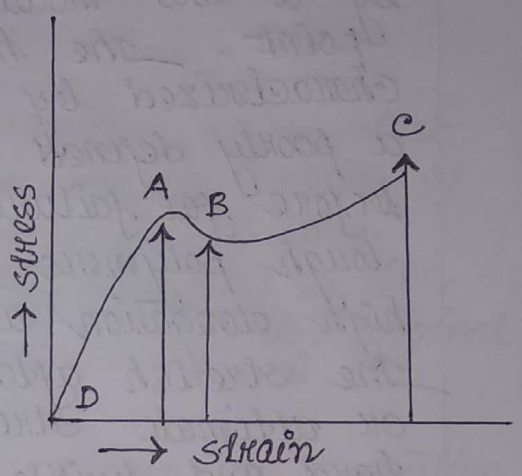

Typical stress - strain curves for plastics where (right) A is the elongation at yield point, B is the yield - stress, C is the elongation at break, and the area under the curve is the ultimate strength or densile strength.

N.B. i) Yield Point : The point at which the material begins to deform plastically.

ii) Yield stress or yield - strength :

It is the stress corresponding to the yield point at which the materials begins to deform plastically. The yield strength is often used to determine the maximum allowable load that can be applied without producing permanent deformation.

⊛ It indicates the limit of elastic behavior and the begining of plastic behavior. Before