Properties of Polymers

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Physical Properties

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Degree of Polymerization and Molecular Weight

- Degree of polymerization

The degree of polymerization(DP)-n in a polymer molecule is defined as the number of repeating units in the polymer chain.

$$-(-CH_2 - CH_2-)-_n$$

The molecular weight of a polymer molecule is the product of the degree of polymerization and the molecular weight of the repeating unit.

❑ Molecular Weight Averages

There are different ways that molecular weights of a polymer can be expressed; by the number of the chains, by the weight of the chains (the chain size), or by viscosity.

❖Number-Average Molecular Weight

$$\overline{M_n} = \frac{\sum M_i N_i}{N_i} = \frac{(M_1N_1) + (M_2N_2) + (M_3N_3) + (M_4N_4) + \cdots}{N_1 + N_2 + N_3 + N_4 + \cdots}$$

$$\text{Degree of polymerization} = \frac{\text{Number average molecular weight}}{\text{Molecular weight of the repeat unit}}$$

❖Weight-Average Molecular Weight

$$\overline{M_w} = \frac{\sum M_i^2 N_i}{\sum M_i N_i} = \frac{(M_1^2N_1) + (M_2^2N_2) + (M_3^2N_3) + (M_4^2N_4) + \cdots}{(M_1N_1) + (M_2N_2) + (M_3N_3) + (M_4N_4) + \cdots}$$

Polydispersity

The ratio of the weight-average molecular weights to the number-average molecular weights is called polydispersity index (PDI) or heterogeneity index, which measures the polydispersity of the polymer mixture.

$$\text{PDI} = \frac{M_w}{M_n}$$

❑Polymer Crystallinity

Crystalline and Amorphous Polymers

❖The polymers having simple structural chains as linear chains and slow cooling rate will result in good crystallinity.

❖Polymer strength and stiffness increases with crystallinity as a result of increased intermolecular interactions.

❖Polymers having high degree of crystallinity are rigid and have high melting point, but their impact resistance is low.

❖Crystallinity increases the barrier properties of the polymer.

❖Polymer mass suddenly melts at a certain temperature so they have sharp melting point.

The % crystallinity is given by

$$\%\text{Crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

ρ_c =density of the completely crystalline polymer,
ρ_a =density of the completely amorphous polymer,
ρ_s =density of the sample

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- Amorphous structure is formed due to either rapid cooling of a polymer melt in which crystallization is prevented by quenching or due to the lack of structural regularity in the polymer structure.
- Amorphous or glassy polymers do not generally display a sharp melting point; instead, they soften over a wide temperature range.
- Example-Polystyrene and poly (vinyl acetate) are amorphous with melting range of 35°C to 85°C and 70°C to 115°C, respectively.

Thermal properties of polymer

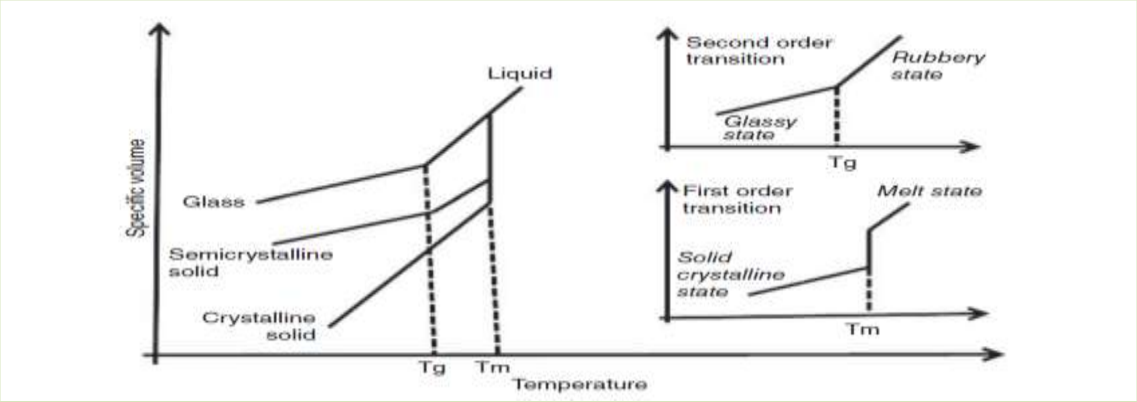
- **Glassy state**
- In this state, the polymer is brittle, hard and rigid analogous to glass. Hence the name glassy state.
- The glassy state is similar to a super cooled liquid where the molecular motion is in the frozen state.
- The glassy state shows hard, rigid, and brittle nature analogous to a crystalline solid with molecular disorder as a liquid.

- **Rubbery state**
- When the polymer is heated, the polymer chains are able to wiggle around each other, and the polymer becomes soft and flexible similar to rubber. This state is called the rubbery state.

- **Glass Transition Temperature(Tg)**
- The temperature at which the glassy state makes a transition to rubbery state is called the glass transition temperature Tg.
- As a consequence of this transition, the polymer undergoes anabrupt change in properties. Among these are coefficient of expansion, permeability, heat content, refractive index, and hardness.

Melting Point and Glass Transition Temperature

- The glass transition temperature is the property of the amorphous region of the polymer, whereas the crystalline region is characterized by the melting point.
- In thermodynamics, the transitions are described as first and second order transitions.
- Glass transition temperature is the second order transition, whereas the melting point is the first order transition.
- The semi-crystalline polymer shows both the transitions corresponding to their crystalline and amorphous regions.
- The semi-crystalline polymers have true melting temperatures (Tm) at which the ordered phase turns to disordered phase, whereas the amorphous regions soften over a temperature range known as the glass transition (Tg).



Factors Affecting the Glass Transition Temperature

- **Intermolecular** -Forces. Strong intermolecular forces cause higher Tg.

- **Chain Stiffness-**The presence of the stiffening groups *(*such as amide, sulfone, carbonyl, p-phenylene etc.) in the polymer chain reduces the flexibility of the chain, leading to higher glass transition temperature.

- **Cross-Linking-**The cross-links between chains restrict rotational motion and raise the glass transition temperature. Hence, higher cross-linked molecule will show higher *Tg* than that with lower cross-linked molecule.

- **Pendant groups-**The presence of pendent group can change the glass transition temperature.
  - **Bulky pendant groups***:* The presence of bulky pendant group, such as a benzene ring, can restrict rotational freedom, leading to higher glass transition temperature.
  - **Flexible pendant groups***:* The presence of flexible pendant groups, for example, aliphatic chains, limits the packing of the chains and hence increases the rotational motion, tending to less *Tg* value.

- **Plasticizers**

  Plasticizers *are* added to polymers to increase their chain flexibility. They reduce the intermolecular cohesive forces between the polymer chains, which in turn decrease *Tg*.

- **Molecular Weight**

  Tg is increases with the molecular weight. The molecular weight is related to the glass transition temperature by the Fox–Flory Equation:

$$T_g = T_{g,\infty} - \frac{K}{M_n} \qquad \text{(Fox–Flory Equation)}$$

Where $T_{g,\infty}$ is the glass transition temperature at the molecular weight of infinity, and K is the empirical parameter called Fox–Flory parameter related to the free volume inside the polymer.

Mechanical Properties

- **Tensile strength**: Ability to resist against stretching or the resistance of a polymer to breaking under tension .

- **Compressive strength**: The strength of the compacted polymer; in other words, a polymer can withstand loads tending to reduce size.

- **Flexural strength**: It is also known as bend strength or modulus of rupture. It is the ability of the material to bend .

- **Impact strength**: It is the resistance of a polymer to fracture under a sudden impact or shock; it is the ability to withstand sudden stress.

Factors Affecting the Strength of Polymers

- Molecular Weight
- Cross-linking
- Crystallinity

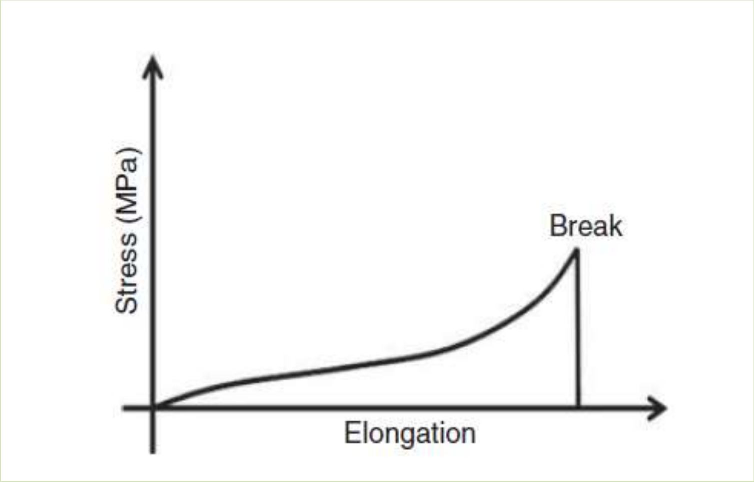
- **Percent Elongation to Break (Ultimate Elongation)**

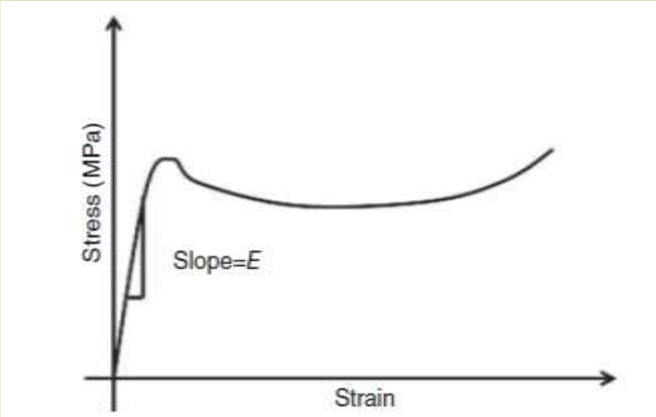
- It is the strain in the material on its breakage, It measures the percentage change in the length of the material before fracture.

- **Young’s Modulus (Modulus of Elasticity or Tensile Modulus):**

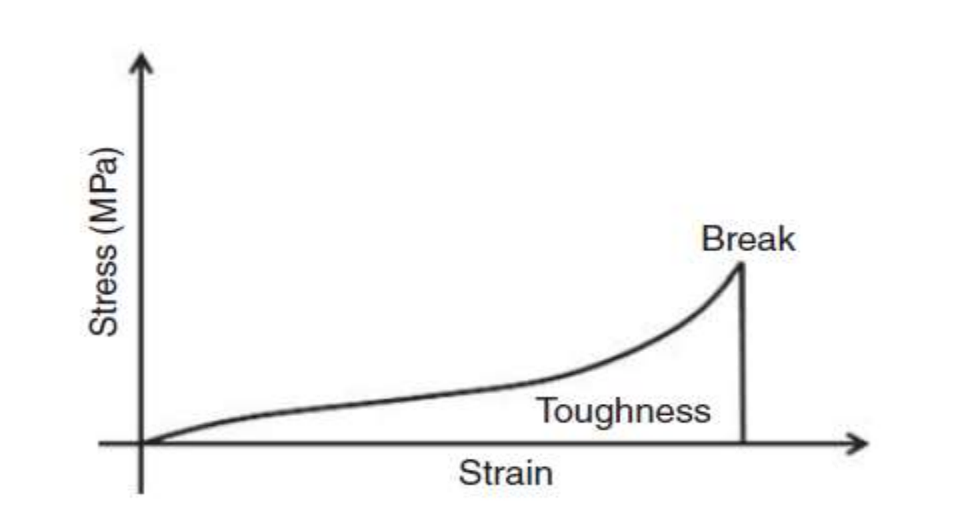
- *Young’s Modulus* is the ratio of stress to the strain in the linearly elastic region . Elastic modulus is a measure of the stiffness of the material.

$$E = \frac{\text{Tensile Stress}(\sigma)}{\text{Tensile Strain}(\varepsilon)}$$





- **Toughness**: The toughness of a material is given by the area under a stress–strain curve.
- **Fatigue**: It refers to the weakening of a material caused by repeatedly applied loads or dynamic loading .



Viscoelastic Properties

The elastic behavior of polymers shows that they can disperse the stored energy, hence it can be said that most of the polymers are a viscoelastic material.

- ❖**Creep test**: In this test the polymer is loaded with a certain weight and its deformation is measured with time.

- ❖**Stress relaxation test**: In this test the polymer is deformed to a certain extent, then its stress (internal stress) relaxation is measured with time.

Application of Polymer

- Modified drug release dosage forms
- Extended release dosage forms
- Gastro retentive Dosage forms
- Polymers used as colon targeted drug delivery
- Polymers as floating drug delivery system
- Polymers used in mucoadhesive drug delivery system
- Polymers in implantable drug delivery
- Polymers in tissue engineering
- Polymers used in micro and nanoparticles for targeted drug delivery
- Polymer drug conjugate