Physical properties of polymers

- Strength
- Deformation (Plastic and Elastic)
- Chemical Resistance and Solubility
- Physical state of Polymers

(Crystalline, Amorphous and Semicrystaline)

- Effect of Heat (Glass Transition Temperature Tg)

Strength of polymer

In cross-linked polymer, the units are linked by interchain covalent bonds forming giant, three dimensional structure and they are strong and tough as the movement of inter molecular chains are totally restricted.

Strength of straight chain polymers depends on the chain length. Polymers of low mol. wt. are soft and gummy but brittle. But higher-chain length polymers are tougher and more heat resistant. Presence of polar groups along the chain length also increases the intermolecular forces and increases the strength of polymer.

Plastic deformation

Polymers consisting of linear-chain molecules are always soluble and *thermoplastic*, even for very high molecular weight.

Three-dimensional polymer molecules are insoluble in any conventional solvent and are *thermosetting*. Hence, thermoplastic and thermosetting qualities of polymer depend on structure of the polymers. Artificially creating crosslinking converts thermoplastic material into thermosetting.

Physical state

Random arrangement of molecules in the polymer leads to amorphous state whereas regular arrangements of molecules or chains in a polymer lead to crystalline state.

The regular arrangement increases the intermolecular forces of attraction and leads to higher softening point, greater rigidity, brittleness and strength of the polymer. The amorphous nature of polymer provides flexibility.

Very long chain polymers having free rotating groups form irregularly coiled and entangled snorts, which can be stretched and again returned back to its original state giving rise to elastic character to the polymer.

Solubility and chemical resistance

Polymer containing polar groups are more soluble in polar solvents like water, alcohol but are chemically resistant to non-polar solvents like benzene, toluene, CCl_4 etc. Similarly, non-polar group containing polymers are chemically resistant to polar solvents but are soluble in non-polar solvents, particularly the greater the degree of cross-linking, less is the solubility of the polymer in a solvent.

➢ Strength

- It depends upon the magnitude of force of attraction between polymeric chains
- Two types (a) Primary or chemical bond and (b) Secondary or intermolecular forces (van der Wall force or hydrogen bonding)
- In a cross-linked polymers, all chains are interconnected by strong chemical covalent bond, resulting in a giant solid molecule, extending in three dimensions
- So they are strong and tough materials, since the movement of intermolecular chains are totally restricted

- In linear or branched polymers, the chains are held together by weak intermolecular force of attraction (secondary), strength increases with increase in chain length or molecular weight
- Polymers of lower chain length are soft and gummy, while higher chain polymers are hard and strong
- By controlling the chain length, the strength of the polymer can be varied from *soft and flexible* to *hard and born* like substances
- Strength of the polymer can be increased by increasing the intermolecular force by the introduction of groups like carboxyl, hydroxyl, chlorine, fluorine, nitrile along the chain

- Strength of linear chain polymers also depends upon the slipping power of one chain over the other

- *Shape of the polymer affects the resistance to slip and consequently the deformation of the polymer*

- Take PE and PVC, PE is simple and uniform, but PVC has large lumps of *Cl* atoms, periodically along its chains with results that (i) movement of chains is restricted (ii) Strong secondary intermolecular force of attraction due to the electronegativity difference between H and *Cl* atoms

- So PVC is more hard and strong polymer than PE

Deformation

- Deformation is the slipping of one chain over the other *(on the application of heat or pressure or both)* or stretching and recoverance of original shape of the polymeric chains *(after the removal of stress)*
- Two types
  - ☐ Plastic Deformation (Plasticity)
  - ☐ Elastic Deformation (Elasticity)

- ***Plastic Deformation (Plasticity)*** is the slipping of one chain over the other on the application of heat or pressure or both
- It occurs only when the weak secondary intermolecular force is operating between the polymeric chains, when sufficient load is applied permanent deformation occurs as slippage
- The linear or branched polymers show the greatest degree of plastic deformation

- This type of material, in heated state, readily takes the shape of the mould, when it is injected into under pressure, called thermoplastic

- At high temperature, polymers deform easily due to the weakening of secondary intermolecular force between chains so the chains can easily slip over each other

- On cooling, the polymer becomes rigid in the moulded shape, because plasticity decreases with fall of temperature

- So plasticity of the polymer is reversible

- ***Elastic Deformation (Elasticity)*** is the stretching and recoverance of original shape of the polymeric chains after the removal of stress
- It arises from the fact that long polymeric chains having free rotating groups which assume peculiar configuration of irregularly coiled and entangled snarls in unstressed condition, lead to amorphous state of polymer
- When such a polymer is stretched, the snarls begin to disentangle (like a spring) and straighten out, which in turn enhances the attraction force between chains, thereby causing stiffening of polymer
- When stress is released, the stretched snarls return to their original arrangement

Chemical Resistance and Solubility

- Chemical attack is internal, causing softening , swelling and loss of strength of polymer
- The chemical nature of monomeric units and their molecular arrangement determines the chemical resistance of the polymer
- Polymers having polar groups (-OH, –COOH, or Cl) swollen or even dissolved in polar solvents whereas polymers having non-polar groups (-CH_3 or -C_6H_5) swollen or even dissolved in non polar solvents
- polymers of more aliphatic character are more soluble in aliphatic solvents whereas polymers of more aromatic character are more soluble in aromatic solvents

- The tendency to swell or solubility of polymers decreases with the increase in chain length or molecular weight of polymer
- High molecular weight polymers, on dissolving yield solutions of high viscosities
- In crystalline polymers, denser close packing of polymeric chains makes the penetration of solvents or chemical reagents in the polymeric material more difficult, so crystalline polymers exhibit more chemical resistance or lesser solubilty
- Greater the degree cross-linking in the polymer, lesser is its solubility and greater is its chemical resistance

Physical state of Polymers

- Relative arrangement of polymeric chains with respect to each other may result in an amorphous or crystalline state of polymer
- An amorphous state is characterized by a completely random, irregular, and dissymmetrical arrangement of polymeric chains e.g., rubber, thermosetting
- A crystalline state is characterized by a completely regular, symmetrical and ordered arrangement of polymeric chains with uniaxial orientation e.g., fibers
- A semi-crystalline state consists of crystalline region called crystallites (ordered arrangement of polymeric chains) embedded in an amorphous matrix, e.g., thermoplastic

Crystallinity in Polymers

- The degree to which chains of a polymer are arranged in orderly pattern with respect to each other, is a measure of crystallinity

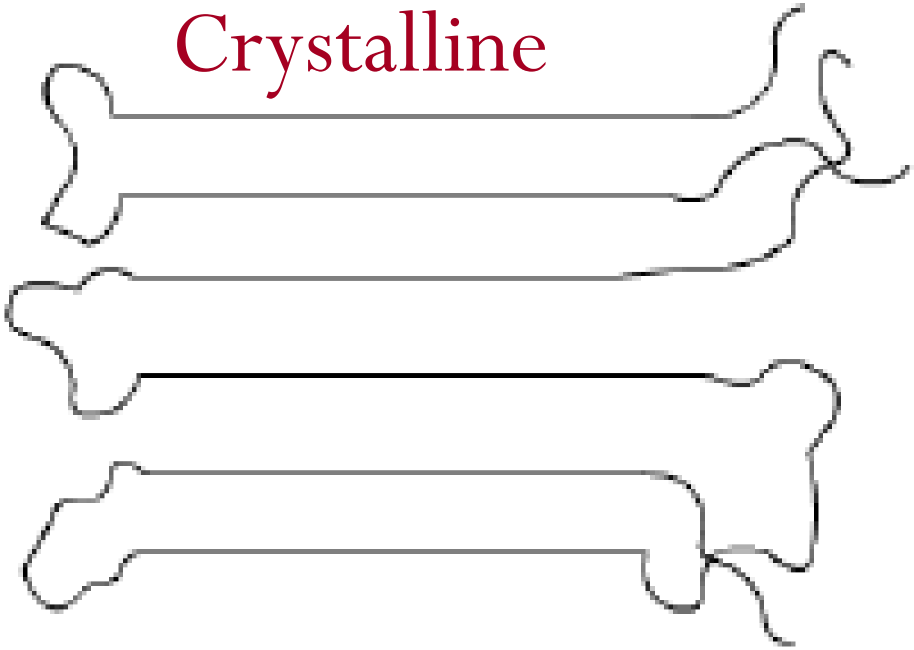
- As solidification begins, the viscosity of the polymer rises, and the chains find more and more difficulty in arranging their long chains in the regular pattern needed for crystal formation

- Some parts of structure align during cooling to form crystalline regions (places where the polymer chains are orderly arranged, they align along side with each other, they lie in close proximity and are held together by strong intermolecular interactions) called crystallites, around crystallites get amorphous regions (places where the polymer chains are randomly arranged, resulting in weak intermolecular interactions)

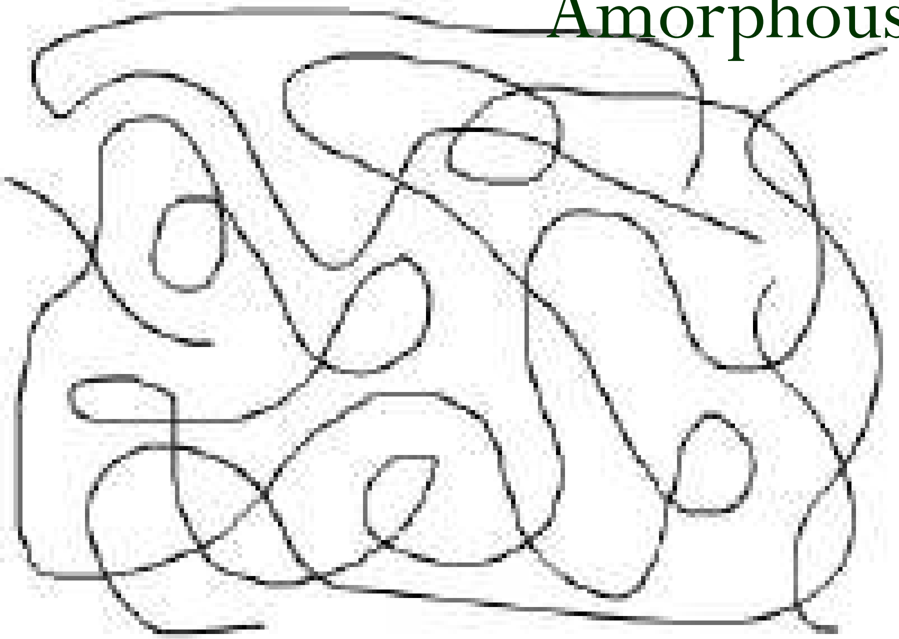
- In fact polymers have regions of crystallinity, called crystallites, embedded in an amorphous matrix

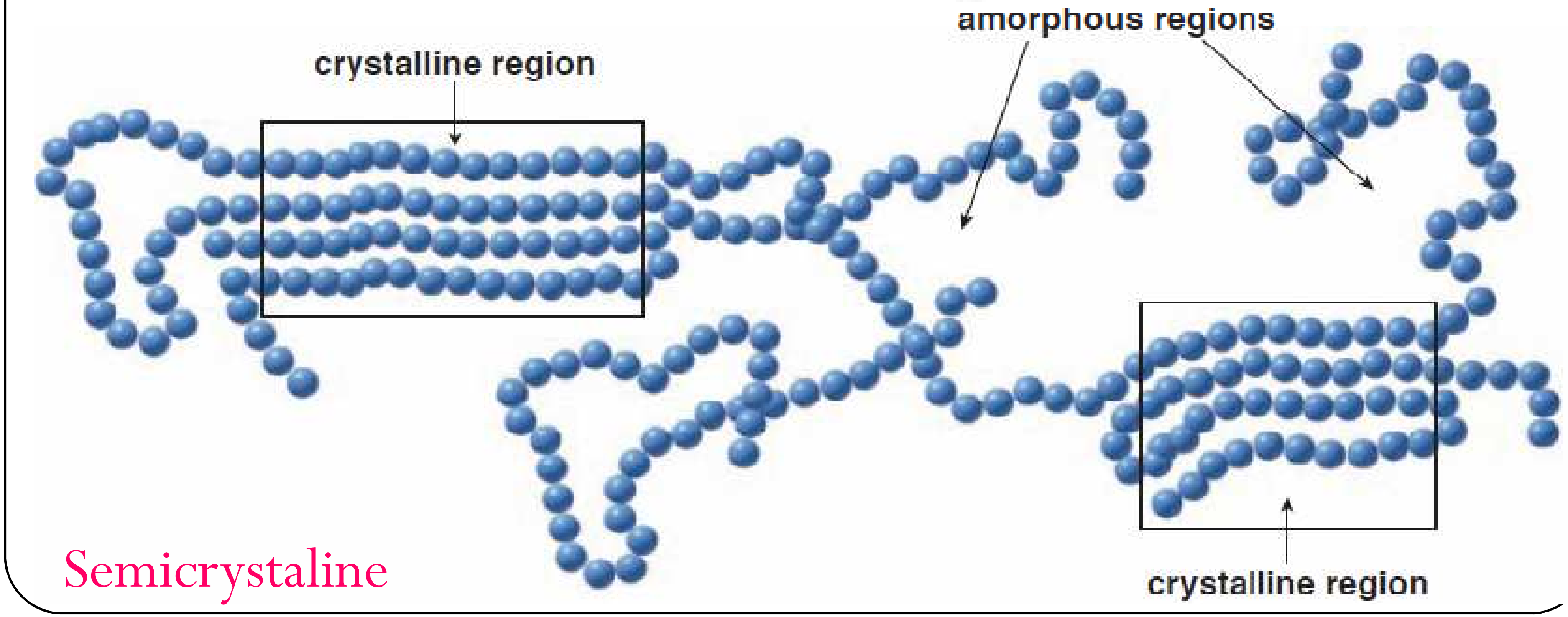
- The crystalline material shows a high degree of order formed by folding and stacking of the polymer chains
- An amorphous solid is formed when the chains have little orientation throughout the bulk polymer, the chains are tangled and organized in disordered pattern
- There are some polymers that are completely amorphous, but most are a combination with the tangled and disordered regions (amorphous regions) surrounding the crystalline areas called semicrystaline

Crystalline



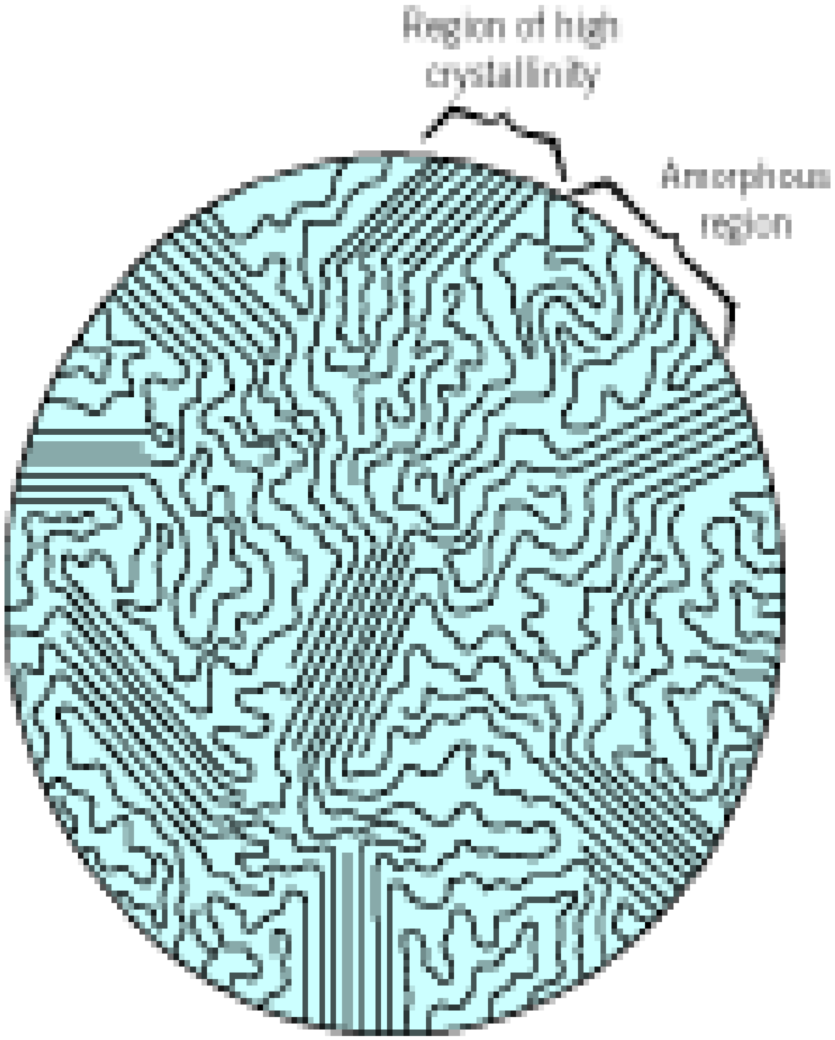
Amorphous

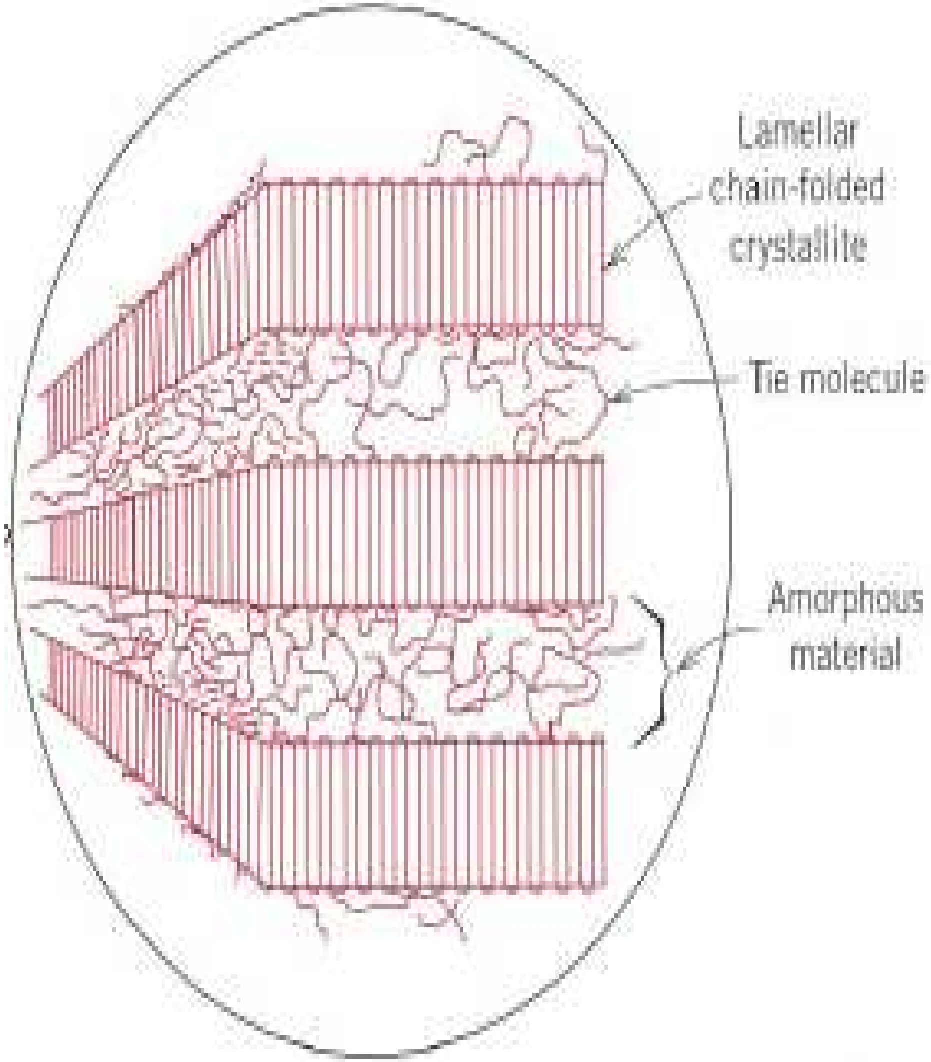




Semicrystaline

Semicrystaline





- In such polymers, the crystallites provide required hardness, rigidity and heat resistance, whereas the amorphous matrix provide flexibility, Crystalline regions impart toughness to a polymer, while amorphous regions impart flexibility
- The greater the Crystallinity of a polymer—that is, the larger the percentage of ordered regions—amorphous and, since the harder the polymer

Factors affecting Crystallinity

- [1] Polymer Morphology
- [2] Chain length or Molecular weight
- [3] Symmetry of the repeating unit
- [4] Chain branching
- [5] Cross-linking
- [6] Rate of cooling

[1] Polymer Morphology

- The polymer morphology is the size and shape of the monomers' substituent groups
- If the monomers are large and irregular, it is difficult for the polymer chains to arrange themselves in an ordered manner, resulting in a more amorphous solid
- Likewise, smaller monomers, and monomers that have a very regular structure (e.g. rod-like) will form more crystalline polymers
- Polymers having bulky side groups are attached at random to the main chain are typically amorphous

[2] Chain length or Molecular weight

- The crystallization tendency of a polymer depends on the ease with which the chains can be aligned in an orderly arrangement
- In the crystallization process, it has been observed that relatively short chains organize themselves into crystalline structures more readily than longer molecules
- Polymers with a high chain length have difficulty organizing into layers because they tend to become tangled
- Large number of entanglement of polymeric chains which impose restriction to the growth of crystallites

- Therefore, the chain length is an important factor in determining the Crystallinity of a polymer
- With increase in chain length or molecular weight of the polymer chain, % of crystallinity decreases

[3] Symmetry of the repeating unit

- Symmetrical repeating unit structure facilitate the formation of crystallites
- Polymer with a low degree of symmetry do not crystallize easily, so they form amorphous structures, crystallization tendency decreases by copolymerization, because it lowers structural symmetry
- Random copolymers do not crystallize due to the irregularity of the repeating unit
- Geometrical regularity is also desired in a polymer for it to show crystallinity
- Only the configurational regular forms (isotactic and syndiotactic) polymers crystallize, but actatic polymer is amorphous

[4] Chain branching

- Linear and branched polymers do not form crystalline solids because their long chains prevent efficient packing in a crystal lattice
- In branched polymers, branching prevents chains from packing closely, so they are softer, too
- HDPE has almost perfectly linear structure and therefore it can be obtained in a highly crystalline state (80-85% crystallinity)
- LDPE has a number of short chain and long chain branches, so it can only achieve 55% crystallinity

➢ [5] Cross-linking

- A polymer with highly cross linked structure is devoid of crystallinity due to the presence of a dense array of cross-links effectively eliminates crystallinity
- But a few cross links may improve the crystallinity obtained on stretching of a polymer, since orientation is increased by restricting the flow of polymer chains

➢ [6] Rate of cooling

- The cooling rate also influences the amount of Crystallinity
- Slow cooling provides time for greater amounts of crystallization to occur
- Fast rates, on the other hand, such as rapid quenches, yield highly amorphous polymerss
- Average cooling provides semi-crystalline polymers

➢ Crystallinity Vs Properties

- Crystallization imparts a denser packing of chains, thereby increasing the intermolecular forces of attraction, so higher and sharper softening point, greater rigidity and strength, and greater density of the crystalline polymer
- Short chains polymers are generally weaker in strength, although they are crystalline, only weak van der Waals forces hold the lattice together, this allows the crystalline layers to slip past one another causing a break in the material
- High chain length (amorphous) polymers, however, have greater strength because the molecules become tangled between layers

➢ With increase in % of crystallinity

- (a) Strength and stiffness of polymer increases but brittleness also increases
- (b) Solubility and permeability decreases but chemical resistance increases
- (c) Density and melting point increases
- (d) Opacity of the polymer increases

Effect of Heat on Polymers

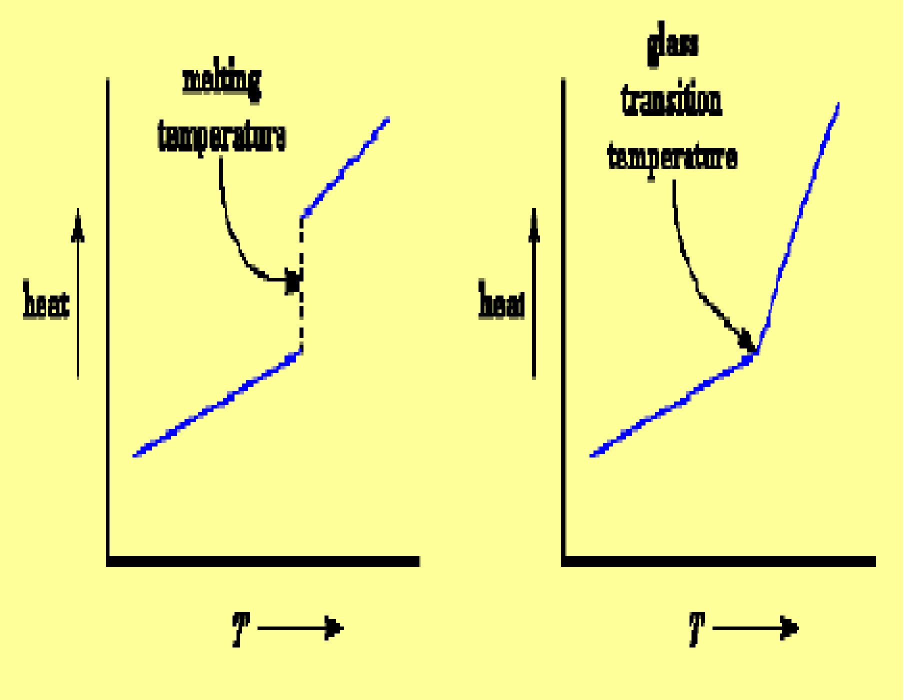
- The thermal phase behavior of polymers differs markedly from that of common low molecular weight compounds
- Amorphous polymers do not possess any clear melting point, but crystalline polymers have clear melting point
- Highly crystalline polymers undergo first order transition from solid to liquid state (melt) at sharp melting point
- Amorphous and semicrystaline polymers undergo second order transition from solid to viscous fluid at a broader range of temperature

- Amorphous polymers do not melt but soften
- At low temp, polymer behave as glassy materials where there chains cannot move all, on heating, the polymers soften and becomes more flexible
- In this state, polymer chains gain sufficient energy to move slightly, this occurs at the glass transition temperature (Tg)
- Beyond Tg, amorphous and semi-crystalline polymers behave differently

- In amorphous or semicrystalline polymers, polymeric chains are disorderly arranged due to the entanglement of chains, which prevent the close packing of polymeric chains, so fee volume increases, hence the internal movement of polymeric chains becomes easy, so they have Tg
- In semicrystalline polymers, amorphous region shows Tg and crystallites show Tm

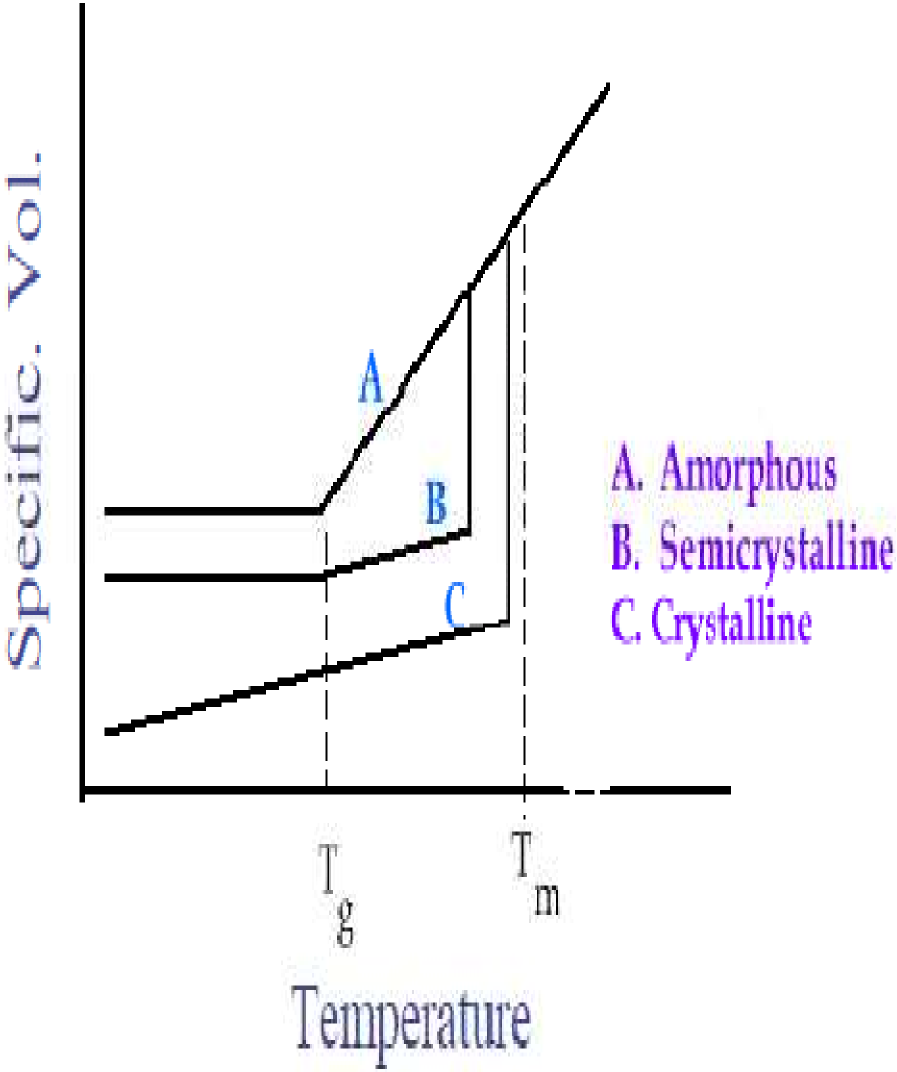
- In crystalline polymers, polymeric chains are orderly arranged, which lead to dense close packing of polymeric chains, so fee volume becomes zero, hence the internal movement of polymeric chains is prevented, so the crystalline polymers have no Tg
- In cross linked polymers, polymeric chains are connected through cross links or chemical bond, so the internal movement of polymeric chains is prevented, so the they have infinite value of Tg

T_m T_g



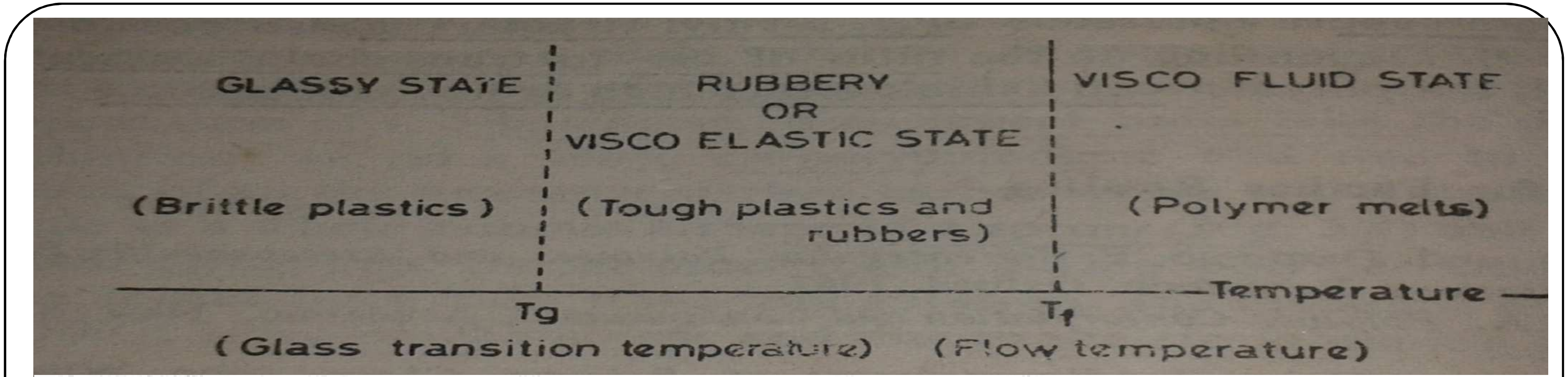
crystalline amorphous

1st order transformation 2nd order transformation

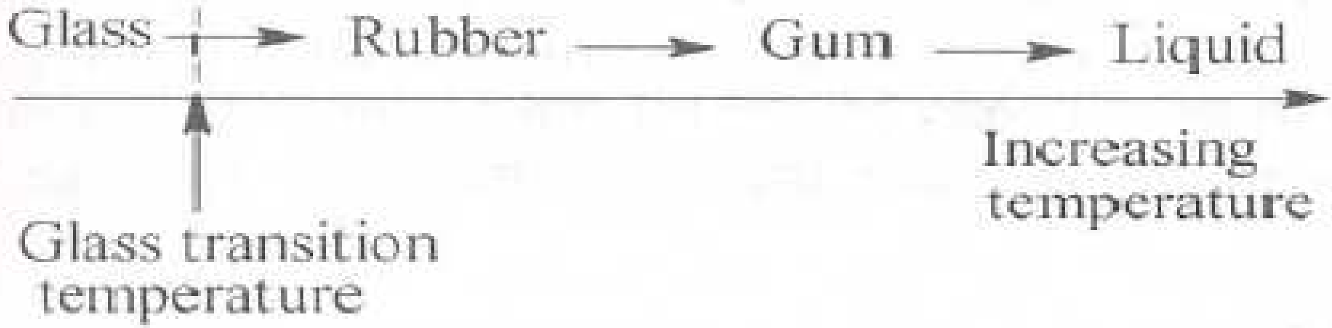


Glass Transition Temperature or Tg

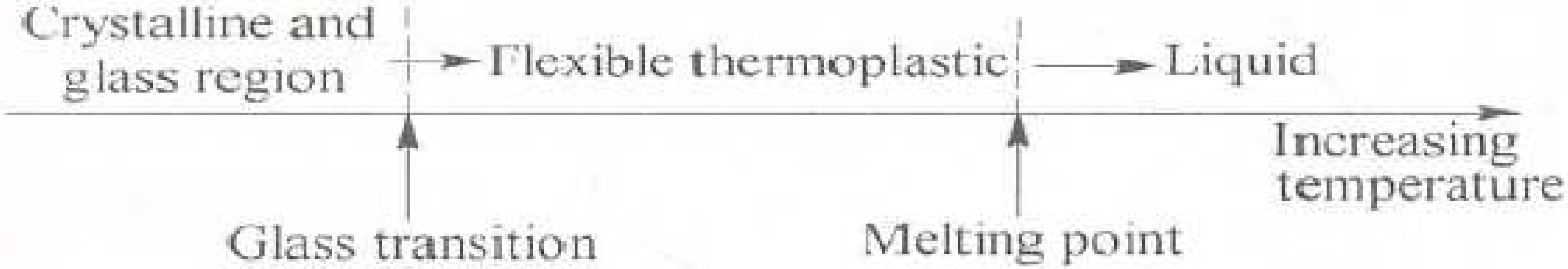
- The *glass transition temperature* (T_g) is the temperature at which the internal energy of the chains of the polymer increases such as extends that the chains just starts leaving their lattice sites
- Below glass transition temperature (T_g), polymers are usually hard, brittle and glass-like in mechanical behavior
- Above glass transition (T_g), polymers are usually more soft, flexible and rubbery (elastic)-like in mechanical behavior
- Tg is the temperature at which transformation of a polymer from a rigid material to one that has rubber like characteristics and temperature has large effect on chain flexibility



(a) Effect of temperature on amorphous polymer

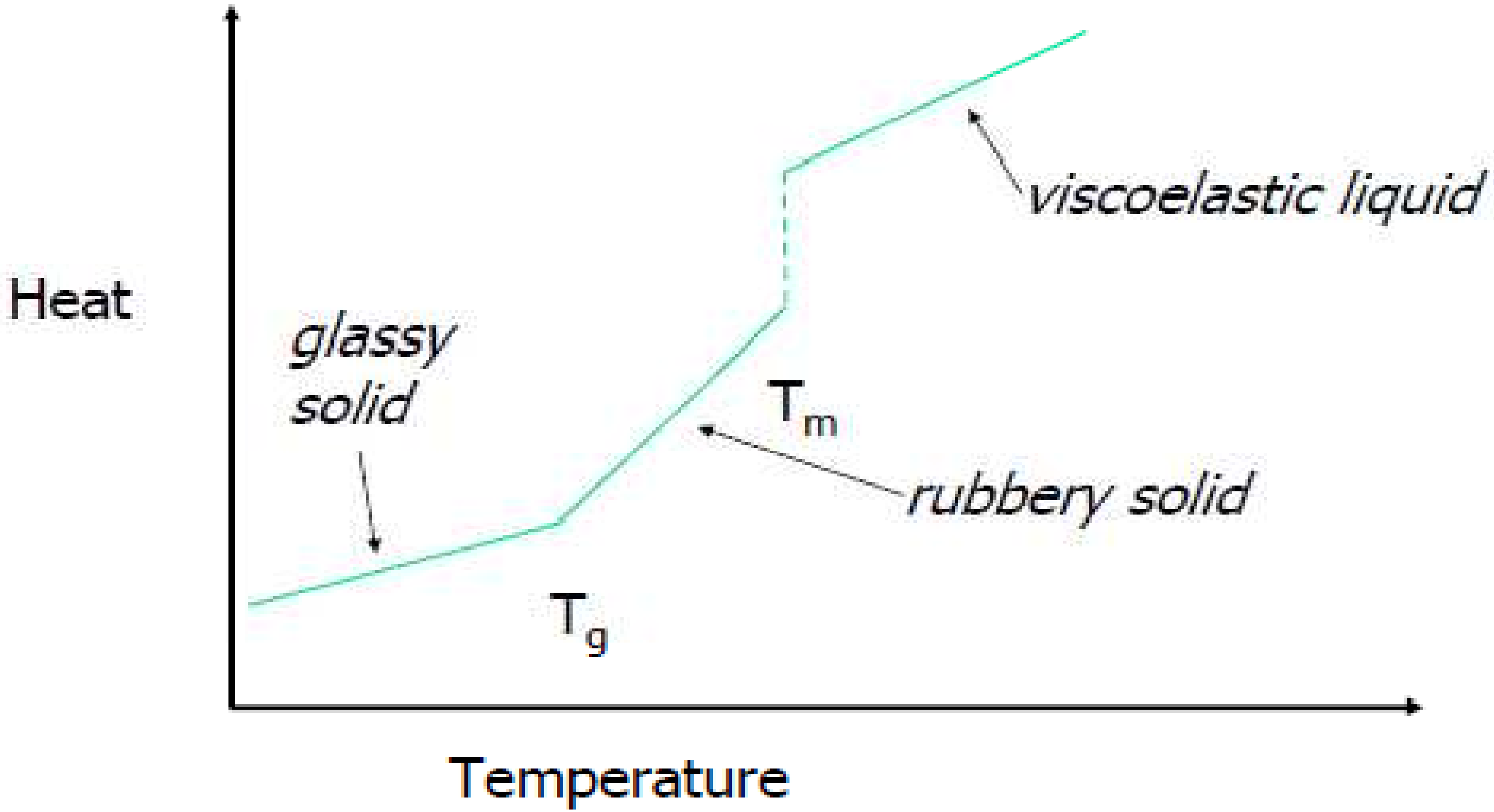


(b) Effect of temperature on crystalline polymer

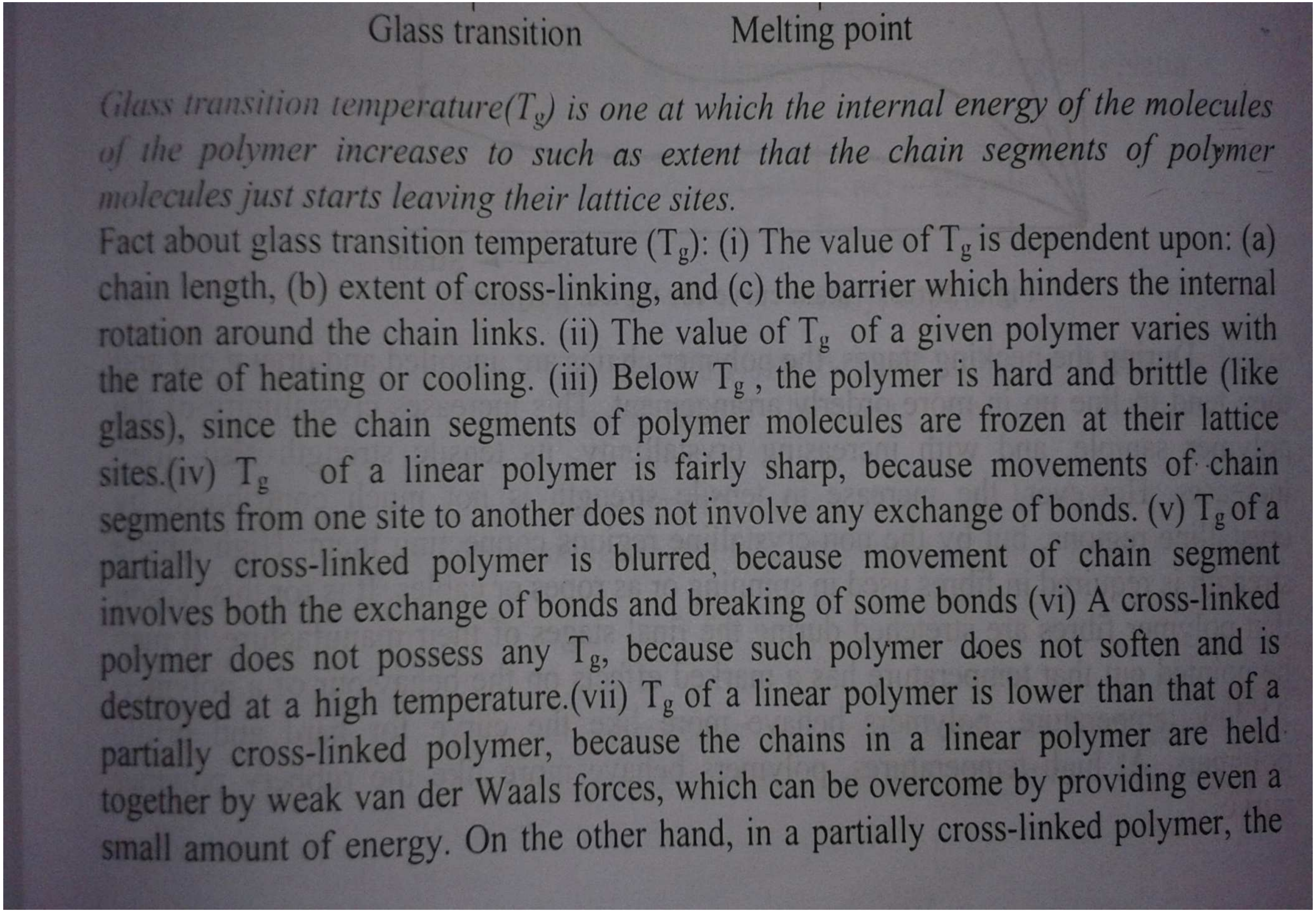


Semicrystalline polymers

- These materials exhibit both a glass transition and a melting temperature



➢ Factors affecting glass transition temperature:



Glass transition Melting point

Glass transition temperature(T_g) is one at which the internal energy of the molecules of the polymer increases to such as extent that the chain segments of polymer molecules just starts leaving their lattice sites.

Fact about glass transition temperature (T_g): (i) The value of T_g is dependent upon: (a) chain length, (b) extent of cross-linking, and (c) the barrier which hinders the internal rotation around the chain links. (ii) The value of T_g of a given polymer varies with the rate of heating or cooling. (iii) Below T_g , the polymer is hard and brittle (like glass), since the chain segments of polymer molecules are frozen at their lattice sites.(iv) T_g of a linear polymer is fairly sharp, because movements of chain segments from one site to another does not involve any exchange of bonds. (v) T_g of a partially cross-linked polymer is blurred, because movement of chain segment involves both the exchange of bonds and breaking of some bonds (vi) A cross-linked polymer does not possess any T_g, because such polymer does not soften and is destroyed at a high temperature.(vii) T_g of a linear polymer is lower than that of a partially cross-linked polymer, because the chains in a linear polymer are held together by weak van der Waals forces, which can be overcome by providing even a small amount of energy. On the other hand, in a partially cross-linked polymer, the

- [1] Chain Flexibility
- [2] Geometric Factors
- [3] Inter-chain Attractive Forces
- [4] Copolymerization
- [5] Chain Length
- [6] Cross-Linking and Branching
- [7] Crystallinity
- [8] Plasticization

[1] Chain Flexibility

- Chain flexibility is determined by the ease with which rotation occurs about primary valence bonds
- Polymers with low hindrance to internal rotation have low T_g values
- Long-chain aliphatic groups — ether and ester linkages — enhance chain flexibility, while rigid groups like cyclic structures stiffen the backbone

[2] Geometric Factors

- Geometric factors, such as the symmetry of the backbone and the presence of double bonds on the main chain, affect T_g
- Polymers that have symmetrical structure have lower T_g than those with asymmetric structures
- Additional groups near the backbone for the symmetrical polymer would enhance steric hindrance and consequently raise T_g
- Double bonds in the cis form reduce the energy barrier for rotation of adjacent bonds, “soften” the chain, and hence reduce T_g

➢[3] Inter-chain Attractive Forces

- The presence of strong secondary attractive forces in a polymer chain, i.e., a high value of cohesive energy density, will significantly increase T_g
- The steric effects of the groups like CH_3, –Cl, and –CN are similar, but the polarity increases, consequently, T_g is increased
- Secondary bonding forces are effective only over short molecular distances. Therefore, any structural feature that tends to increase the distance between polymer chains decreases the cohesive energy density and hence reduces T_g

[4] Copolymerization

- It is desirable to be able to control T_g, however, this is often impossible, polymer chemists have circumvented this problem to some extent by copolymerization
- A copolymer system may be characterized by the arrangement of the different monomers (random, alternating, graft, or block)
- The increased disorder resulting from the random or alternating distribution of monomers enhances the free volume and consequently reduces T_g

➢[5] Chain Length

- Since chain end segments are restricted only at one end, they have relatively higher mobility than the internal segments, which are constrained at both ends
- At a given temperature, therefore, chain ends provide a higher free volume for molecular motion
- As the number of chain ends increases (means short chain polymers), the available free volume increases, and consequently there is a depression of T_g.

➢ [6] Cross-Linking and Branching

- By definition, cross-linking involves the formation intermolecular connections through chemical bonds, this process necessarily results in reduction in chain mobility. Consequently, T_g increases
- For lightly cross-linked systems like vulcanized rubber, T_g shows a moderate increase over the uncross-linked polymer
- For highly cross-linked systems like phenolics and epoxy resins, the glass transition is virtually infinite
- Like long and flexible side chains, branching increases the separation between chains, enhances the free volume, and therefore decreases T_g

➢[7] Crystallinity

- In semicrystaline polymers, the crystallites may be regarded as physical cross-links that tend to reinforce or stiffen the structure
- Viewed this way, it is easy to visualize that T_g will increase with increasing degree of crystallinity

➢ [8] Plasticization

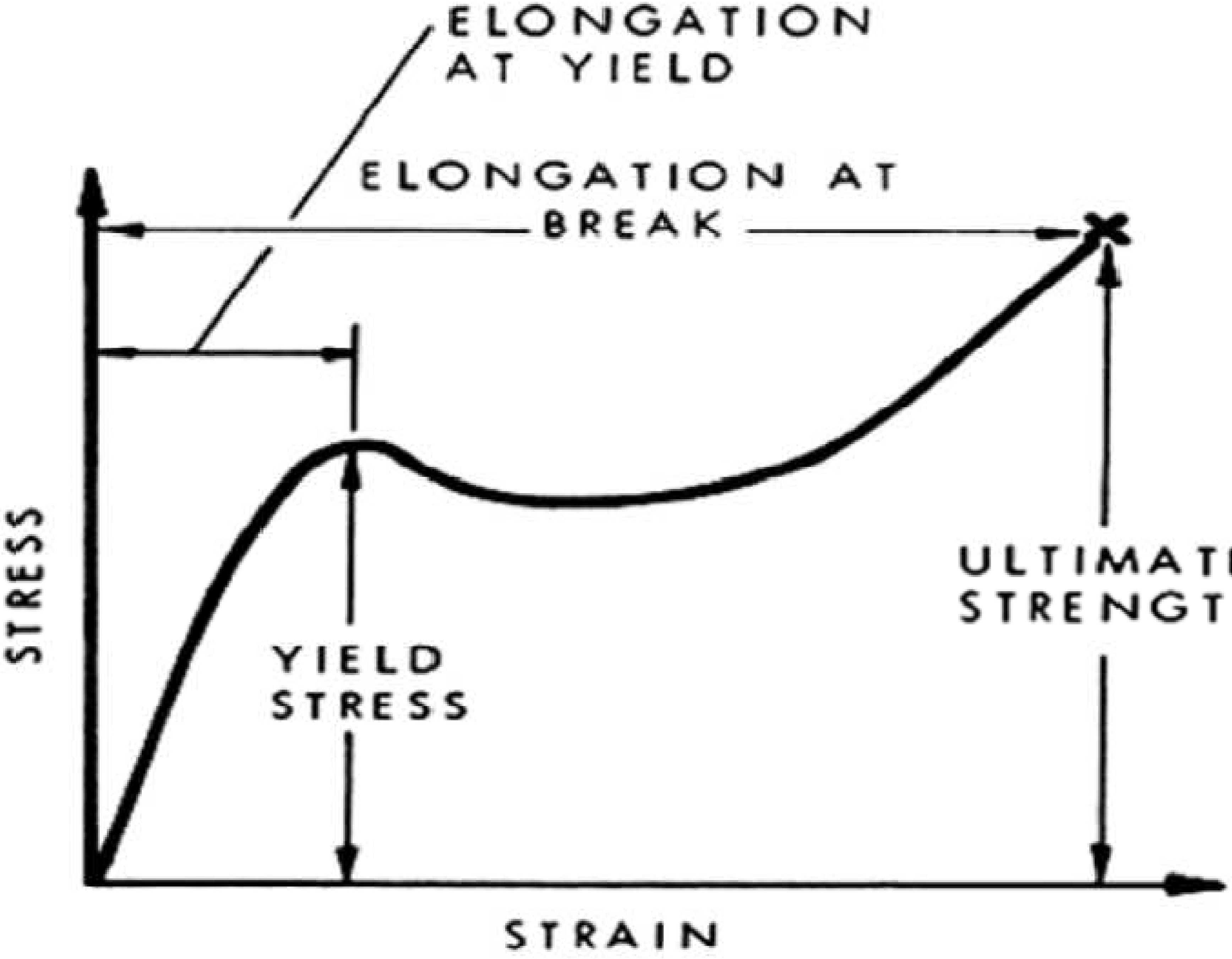
- Plasticization is the process of inducing plasticity in a material
- In polymers, this can be achieved by the addition of low-molecular-weight organic compounds referred to as plasticizers which are usually nonpolymeric, organic liquids of high boiling points and they are miscible with polymers Addition of plasticizers to a polymer, even in very small quantities, drastically reduces the Tg of the polymer
- Plasticizers function through a solvating action by increasing intermolecular distance, thereby decreasing intermolecular bonding forces

Mechanical properties of polymers

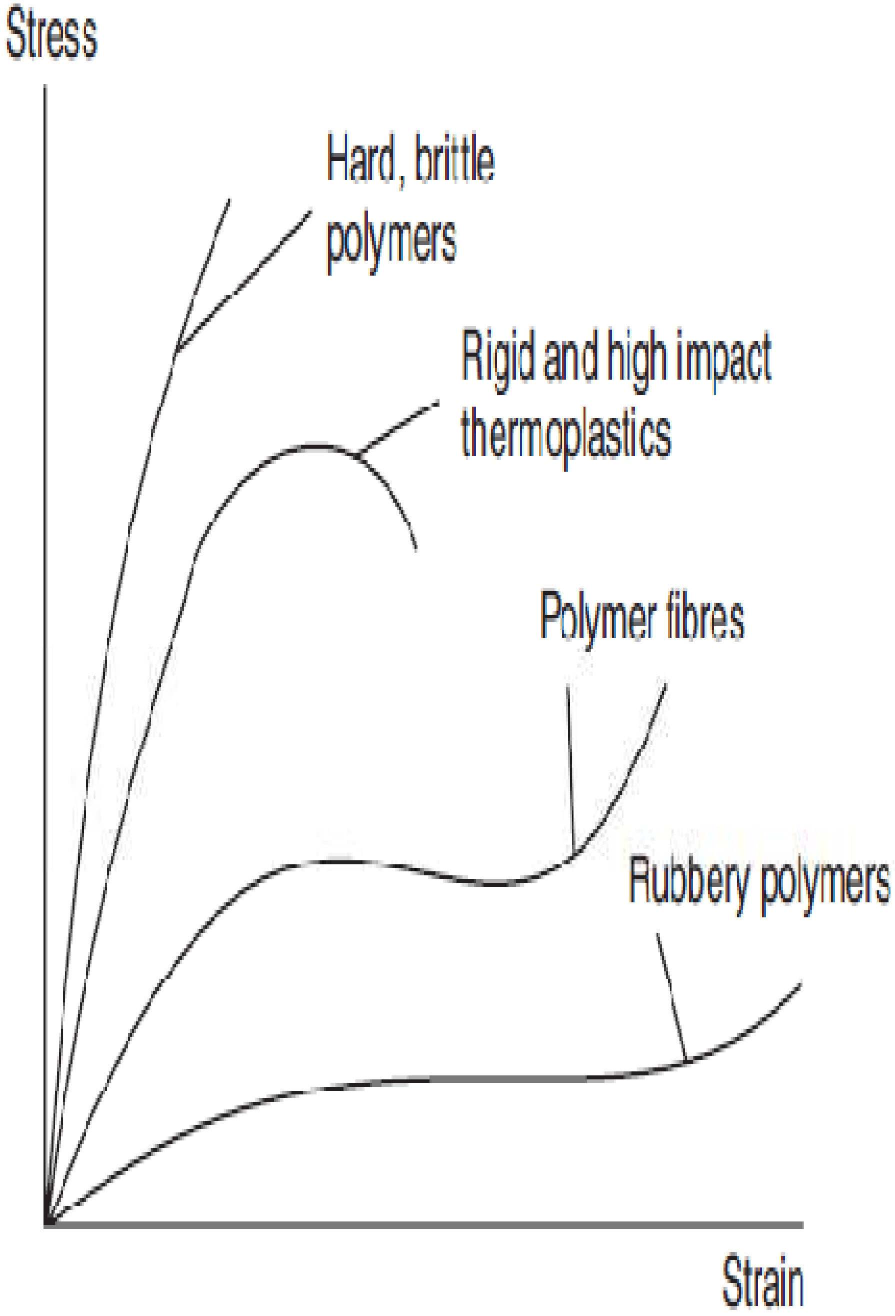
The internal arrangement of the long-chain molecules provides the forms in which the polymer may form *i.e.*, fibres, plastics and rubbers. If the internal forces between the molecules are low, molecules become bulky, form random arrangement and show rubbery character. If the internal forces are high they ultimately give rise to orderly arrangement and form fibrous nature. Intermediate forces lead to plastic nature.

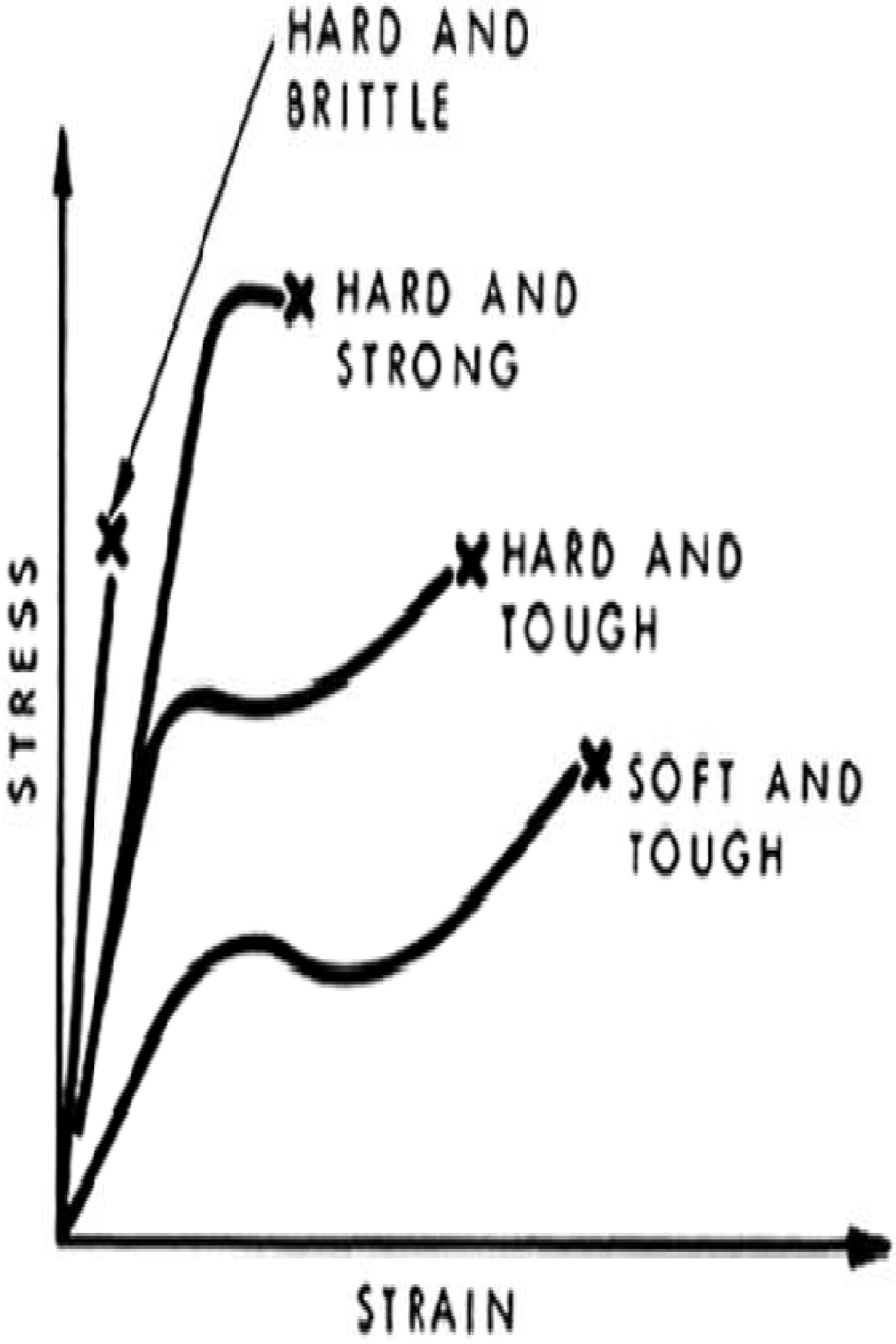
The strength of the polymer is controlled by the length of the polymer chains and its cross-linking. Strength of a polymer is estimated from typical stress-strain curves for different polymers as shown in Fig. 20.2. On increasing strain continuously ultimately the polymer chains are uncoiled and fully stretched called *necking* and after this point the polymer reaches its *break point* and yields.

- For engineering applications of polymers, the designer using polymeric materials must understand their mechanical behaviour with respect to the maximum permissible strains to avoid failure
- A simple tensile stress-strain curve provides a good start towards understanding the mechanical behaviour of a particular polymer
- This curve is usually established by continuously measuring the force developed as the sample is elongated at constant rate of extension until it breaks


ELONGATION AT YIELD
ELONGATION AT BREAK
STRESS
YIELD STRESS
ULTIMATE STRENGTH
STRAIN

- The initial slope provides a value for Young's modulus (or the modulus of elasticity) which is a measure of stiffness
- The curve also gives yield stress, strength and elongation at break, the area under the curve or work to break is a rough indication of the toughness of the polymeric material
- The stress at the knee in the curve (known as the yield point) is a measure of the strength of the material and resistance to permanent deformation
- The stress at the breaking point, commonly known as ultimate strength, is a measure of the force required to fracture the material completely


Stress
Hard, brittle polymers
Rigid and high impact thermoplastics
Polymer fibres
Rubbery polymers
Strain

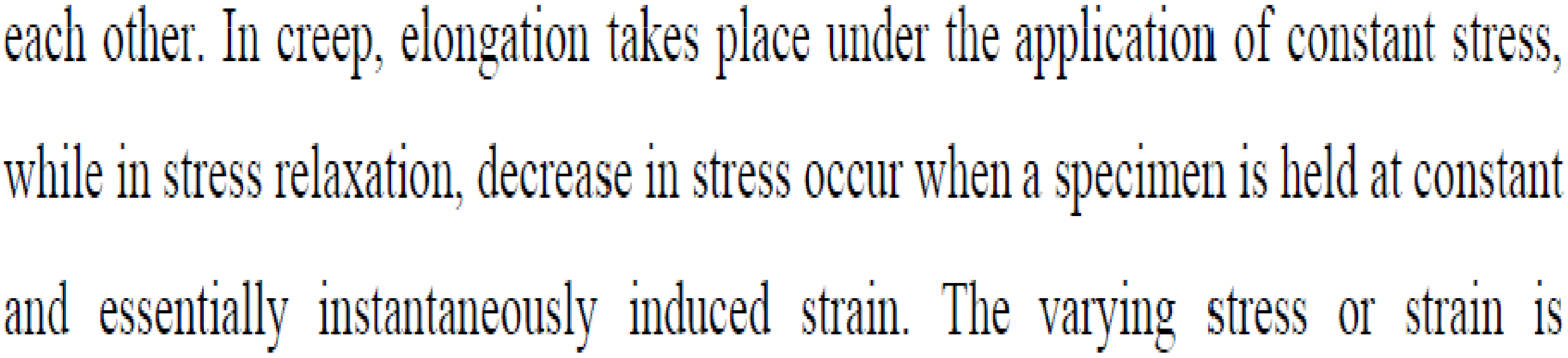

HARD AND BRITTLE
HARD AND STRONG
HARD AND TOUGH
SOFT AND TOUGH
STRESS
STRAIN

- *Hard and brittle* material such as an amorphous polymer far below its T_g, usually has an initial slope indicative of very high modulus, moderate strength, a low elongation at break, and a low area under the stress-strain curve, e.g., polystyrene, poly(methyl methacrylate) and phenol-formaldehyde resins

- ***Hard and strong*** polymers have high modulus of elasticity, high strength, and elongation at break of approximately 5 percent, e.g., poly(vinyl chloride) formulations and polystyrene polyblends

- ***Hard and tough*** polymers have high yield points, high modulus, high strengths and large elongations, e.g., cellulose acetate, cellulose nitrate and nylons

- ***Soft and tough*** polymers have low yield points, low modulus, moderate strength at break, and very high elongation ranging from 20 to 100 percent, e.g., elastomers like NR, SBR, NBR



each other. In creep, elongation takes place under the application of constant stress, while in stress relaxation, decrease in stress occur when a specimen is held at constant and essentially instantaneously induced strain. The varying stress or strain is

Important Mechanical Properties of Polymers

- [1] Hardness
- [2] Toughness
- [3] Stiffness
- [4] Density
- [5] Tensile Strength
- [6] Abrasion Resistance
- [7] Resilience
- [8] Wear and Tear

[1] Hardness

- The ability of a polymer to resist scratching, abrasion, cutting, or penetration
- It is measured by its ability to absorb energy under impact loads
- Hardness is associated with strength
- it is closely associated with material structure, composition, and other mechanical properties

[2] Toughness

- It is the amount of energy a polymer can absorb before actual fracture or failure takes place
- The ability of a polymer to withstand shock and vibrations
- It is related to impact strength which is the resistance to breakage under high velocity impact conditions, i.e., resistance to shock loading
- It is the ability of a polymer to withstand both plastic and elastic deformation

➢ *[3] Stiffness*

- The resistance of a polymer to elastic deformation, i.e., a polymer which suffers slight deformation under load has a high degree of stiffness
- Flexibility (has to do with bending) is the opposite of stiffness

➢ *[4] Density*

- Mass per unit volume (at defined temperature) Relative Density is the mass of the polymer with the mass of equal volume of a specific (reference) substance (water) Density is frequently measured as a quality control parameter
- A specimen, with smooth surfaces from crevices and dust, is weighed in air (W_1) and then in freshly boiled water (W_2), then

$$\rho_{polymer} = \frac{W_1}{W_1 - W_2} \rho_{water}$$

[5] *Tensile Strength*

- The strength of a polymer is its capacity to withstand destruction under the action of loads. It determines the ability of a polymer to withstand stress without failure
- Tensile strength or ultimate strength is the stress corresponding to the maximum load reached before rupturing the polymer

$$\text{Tensile strength or Stress} = \frac{\text{Force or Maximum Load}}{\text{Area of Cross section}}$$

➢ [6] Abrasion Resistance

- It is defined as the ability of a polymer to withstand mechanical action (such as rubbing, scrapping, or erosion) that tends progressively to remove material from its surface
- Abrasion is closely related to frictional force, load and true area of contact, an increase in any one of the three results in greater abrasion or wear
- Abrasion process also creates oxidation on the surface from the build up of localized high temperatures

➢ [7] Resilience

- It is the capacity of a polymer to absorb energy elastically
- Resilience gives capacity of the polymer to bear shocks and vibrations
- When a body is loaded, it changes its dimension, and on the removal of the load it regains its original dimensions
- In fact, the polymer behaves perfectly like a spring, so long as it remains loaded, it has stored energy in itself, on removal of the load, the energy stored is given off exactly as in a spring when the load is removed

➢ [8] Wear and Tear

- It occurs when a steady rate of increase in the use of polymers in bearing applications and in situations where there is sliding contact e.g. gears, piston rings, seals, cams, etc
- Wear and tear is characterized by fine particles of polymer being removed from the surface or the polymer becomes overheated to the extent where large troughs of melted polymer are removed

- The wear and tear of polymers is extremely complex subjects which depend markedly on the nature of the application and the properties of the material
- It is characterized by adhesion and deformation which results in frictional forces that are not proportional to load but rather to speed
- The mechanism of wear and tear is complex; the relative rates may change depending on specific circumstance

The end