

Module-11

Applications and Processing of Polymers



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- 1) Polymer types and polymer synthesis and processing
- 2) Crystallization, melting and glass transition
- 3) Mechanical behavior of polymers
- 4) Mechanisms of deformation and strengthening of polymers

Introduction – Polymers

- The word ‘polymer’ is originated from Greek word *meros*, which means ‘a part’.
- Polymers are primarily organic compounds, however few polymers are made of inorganic compounds.
- Characteristics of ceramics are:
 - low temperature stability
 - low hardness
 - low mechanical strength
 - high elongation under application of stress
 - low thermal and electrical conductivities
 - high sensitivity of properties to their morphology

Classification – Polymers

- Ceramics are classified in many ways. The prime classification based on their industrial usage is: plastics and elastomers.
- Plastic polymers are again classified based on their temperature dependence of their structure as follows:
 - thermoplasts and
 - thermosets

Thermoplasts

- Plastics which softens up on heating and hardens up on cooling where the softening and hardening are totally reversible processes. Hence thermoplasts can be recycled.
- They consist of linear molecular chains bonded together by weak secondary bonds or by inter-winding.
- Cross-linking between molecular chains is absent in thermoplasts.

E.g.: Acrylics, PVC, Nylons, Perspex glass, etc.

Thermosets

- Plastics which are ‘set’ under the application of heat and/or pressure. This process is not reversible, hence thermosets can not be recycled.
- They consist of 3-D network structures based on strong covalent bonds to form rigid solids. linear molecular chains bonded together by weak secondary bonds or by interwinding.
- Characterized by high modulus / rigidity / dimensional stability when compared with thermoplasts.

E.g.: Epoxies, Amino resins, some polyester resins, etc.

Elastomers

- These polymers are known for their high elongations, which are reversible upon release of applied loads.
- They consist of coil-like molecular chains, which straightens up on application of load.
- Characterized by low modulus / rigidity / strength, but high toughness.

E.g.: natural and synthetic rubber.

Polymer synthesis

- Processing of polymers primarily limits to synthesis followed by forming.
- Polymers are synthesized by process known as polymerization.
- Polymerization is process in which multi-functional monomers are attached to form linear/3-D macro molecular chains.
- When polymerization process involves single kind of monomers i.e. in Additional polymerization, resultant macro-molecule's composition is an exact multiplication of composition of individual monomer.

Polymer synthesis

- Additional polymerization process involves three stages namely initiation, propagation and termination.
- Initiation process will be started by an initiator (e.g. benzoyl peroxide) which forms a reactive site where carbon atom of another monomer is attracted, upon which reaction site transfers to different place leading to molecular chain growth.
- As molecular chain grows longer, reaction rate decreases. However the growth process is terminated either by the combination *or* disproportionation process.

Polymer synthesis

- Condensation polymerization process involves more than one monomer species. This process is also known as step growth polymerization.
- In condensation polymerization, smaller macro-molecule by-product such as water is eliminated.
- No resultant product has the chemical formula of mere one monomer.
- Repeat unit in condensation process itself is product of polymerization involving basic constituents.
- Reaction times for condensation polymerization is usually longer than those for additional polymerization.

Degree of polymerization

- Extant of polymerization is characterized in terms of 'degree of polymerization'.
- It is defined as number of mer units in molecular chain or ratio of average molecular weight of polymer to molecular weight of repeat unit.
- Average molecular weight is defined in two ways: *Weight average molecular weight* (based on weight fraction) and *Number average molecular weight* (based on the number fraction).
- Number average molecular weight is always smaller than the weight average molecular weight.

Polymer forming

- Thermoplasts usually formed above their glass transition temperatures under application of pressure which ensures detailed product shape.
- Thermosets are formed in two stages – making liquid polymer and then molding it.
- Different molding techniques are employed to mold polymers –
 - compression molding
 - transfer molding
 - injection molding
 - blow molding
 - extrusion

Polymer forming mechanics

- Polymer forming involves melting, cooling upon which crystallization takes place. In addition, glass transition occurs in polymers.
- Crystallization rate depends on temperature and molecular weight. It decrease with increase in molecular weight.
- Polymer melting is different from that of metals as it takes place over a temperature range.
- Glass transition occurs in amorphous and semi-crystalline polymers. Upon cooling, this transformation corresponds to gradual change of liquid to rubbery material, and then rigid solid.

Polymer forming mechanics

- Polymer melting and glass transition is heavily dependent on polymer morphology.
- Following factors has marked effect on these:
 - chain stiffness (e.g., single vs. double bonds)
 - size, shape of side groups
 - size of molecule
 - side branches, defects
 - cross-linking

Mechanical behavior of polymers

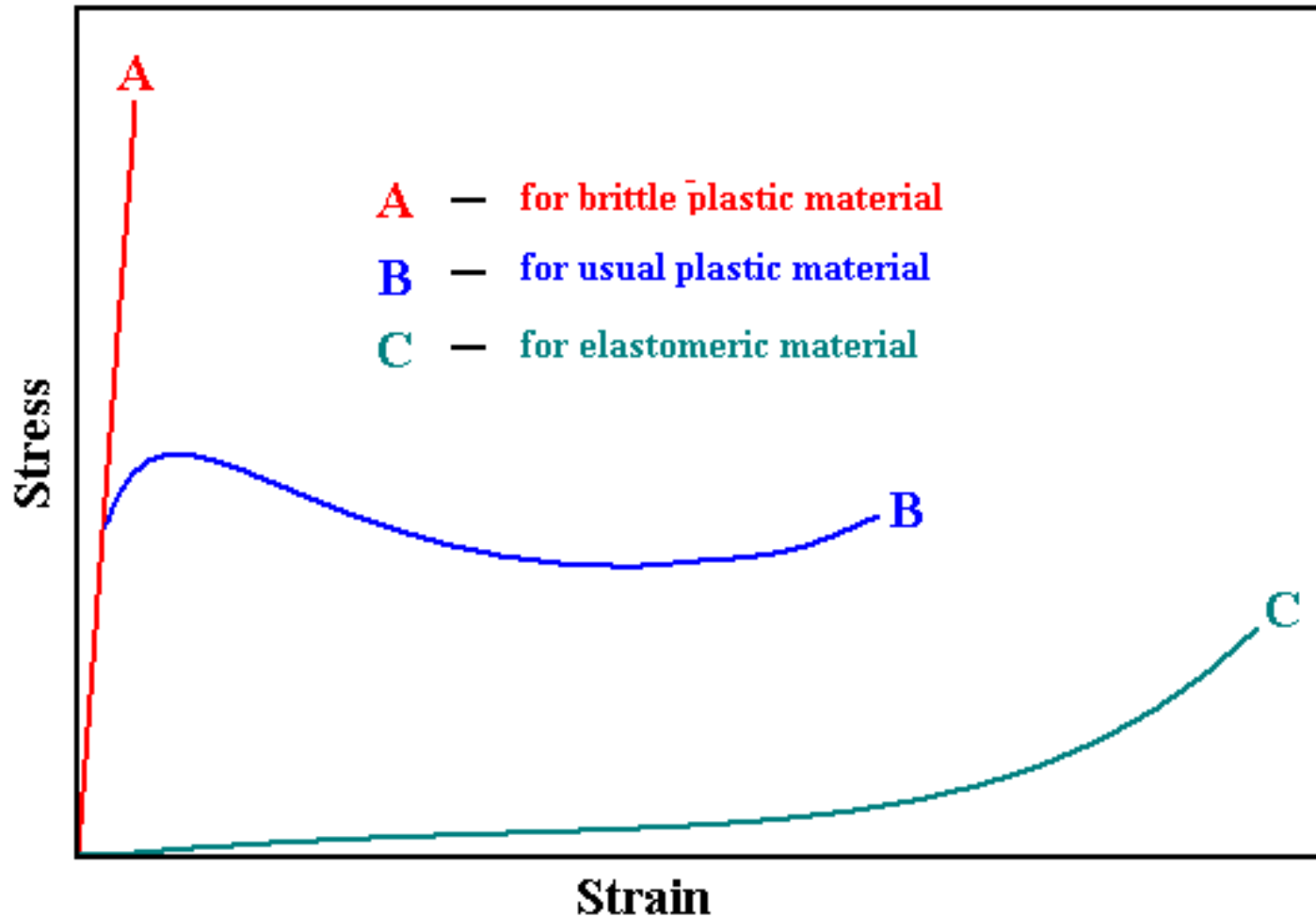
- To an large extant, mechanical behavior of polymers is similar to metals and ceramics.
- However, polymers are distinct in the sense that parameters namely temperature, strain rate, and morphology of polymers has strong influence on mechanical behavior of polymers.
- Mechanical properties of polymers change dramatically with temperature, going from glass-like brittle behavior at low temperatures to a rubber-like behavior at high temperatures.

Mechanical behavior of polymers

- Highly crystalline polymers behave in a brittle manner, whereas amorphous polymers can exhibit plastic deformation.
- Due to unique structures of cross-linked polymers, recoverable deformations up to very high strains / point of rupture are also observed with polymers (elastomers).
- Tensile modulus (modulus) and tensile strengths are orders of magnitude smaller than those of metals, but elongation can be up to 1000 % in some cases.

Mechanical behavior of polymers

➤ Typical stress-strain diagram for polymers:



Mechanisms of deformation in polymers

- Elastic deformation – bending and stretching of covalent bonds and slight adjustments of secondary van der Waals forces.
- Plastic deformation – NOT by dislocation movement, but either rotation, stretching, sliding or disentanglement of molecular chains, which may occur in several stages.
- Elastomers – simple uncoiling, and straightening of molecular chains that are highly twisted, kinked, and coiled in unstressed state. When an elastomer is stretched, causing decrease in entropy, in-turn causes the modulus of elasticity to increase with increasing temperature, which is opposite to the behavior of other materials.

Strengthening polymers

- Polymers' resistance to deformation – strength – is influenced by many parameters.
- For thermoplasts: average molecular mass, degree of crystallization, presence of side groups, presence of polar and other specific atoms, presence of phenyl rings in main chains and addition of reinforcements.
- For thermosets, its reinforcement methods.
- Every parameter that influence the strength can be used as means of strengthening the polymers.

Reinforcements for polymers

- Reinforcement strengthening in polymers is an important mechanism, applicable to both thermoplasts and thermosets.
- Fibers used as reinforcements are made of either glass, carbon or aramid.
- Glass fibers are two varieties – E-glass and S-glass. The later variety is costlier but offers more strength than former.
- Aramid (aromatic polyamide) fibers – also known as Kevlar – are commercially highly successful fibers. They are used with plastics in many applications including protection from ballistics, ropes, aerospace, marine, and many other industrial applications.