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 theromplasts.

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 inter-winding.

- 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 an 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 then 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 '<u>degree of polymerization</u>'.
- It si defined as number of mer units in molecular chain or ration 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 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

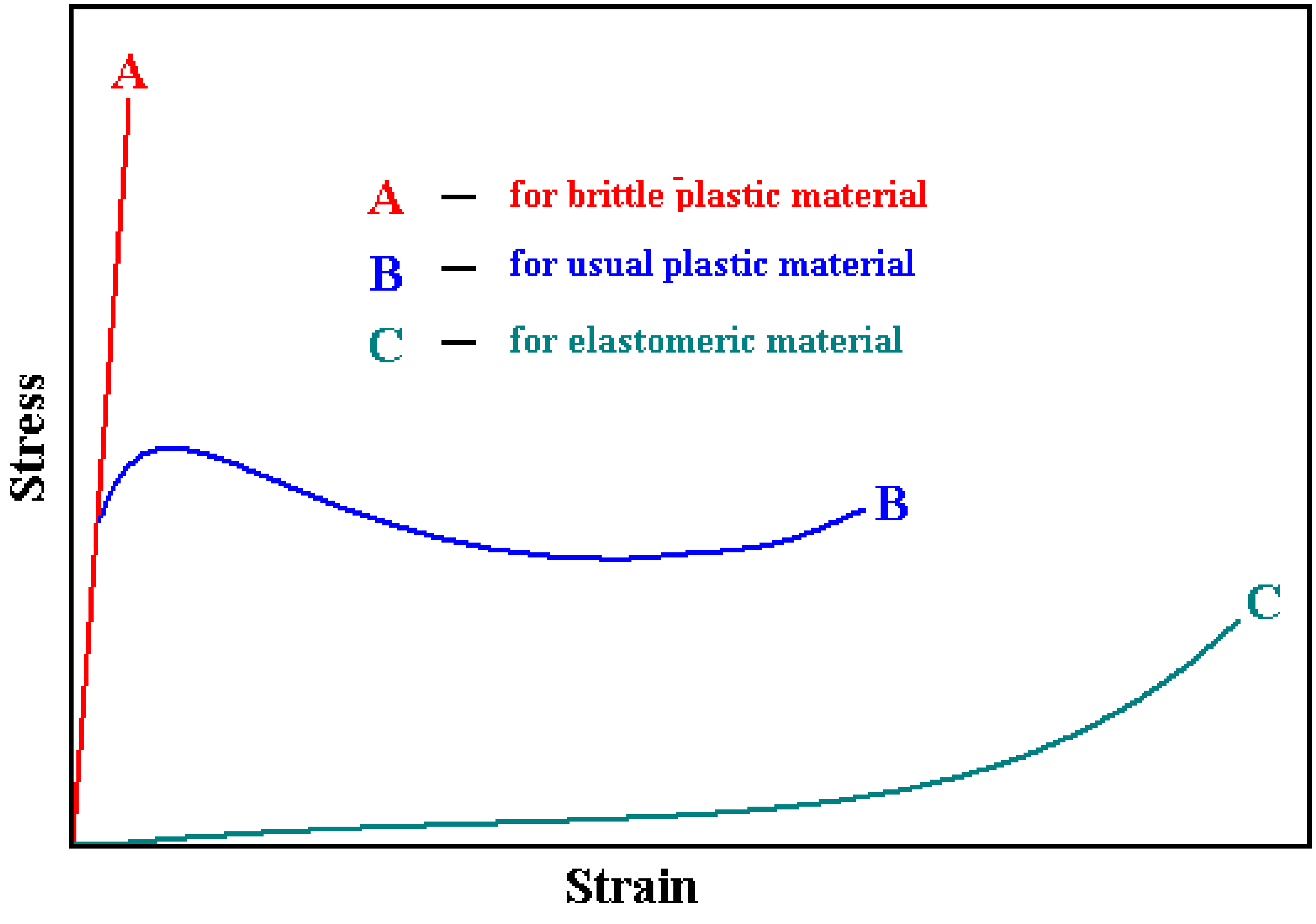
- To an large extant, mechanical behavior of polymers is similar to metals and ceramics.
- However, polymers are distinct in the sense that parameters namely temperature, strain rate, and morphology of polymers has strong influence on mechanical behavior of polymers.
- Mechanical properties of polymers 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 occurs 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 mechanisms, applicable to both thermoplasts and thermosets.
- Fibers used as reinforcements are made of either glass, carbon or aramid.
- Glass fibers are two verities – 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 application including protection from ballasts, ropes, aerospace, marine, and many other industrial applications.