

# Material Science

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### Chapter 11. Applications and Processing of Polymers

Polymers play a very important role in human life. In fact, our body is made of lot of polymers, e.g. Proteins, enzymes, etc. Other naturally occurring polymers like wood, rubber, leather and silk are serving the humankind for many centuries now. Modern scientific tools revolutionized the processing of polymers thus available synthetic polymers like useful plastics, rubbers and fiber materials. As with other engineering materials (metals and ceramics), the properties of polymers are related their constituent structural elements and their arrangement. The suffix in polymer ‘mer’ is originated from Greek word *meros* – which means part. The word polymer is thus coined to mean material consisting of many parts/meros. Most of the polymers are basically organic compounds, however they can be inorganic (e.g. silicones based on Si-O network). This chapter introduces classification of polymers, processing and synthesis of polymers, followed by mechanism of deformation and mechanical behavior of polymers.

#### 11.1 Polymer types and Polymer synthesis & processing

Polymers are classified in several ways – by how the molecules are synthesized, by their molecular structure, or by their chemical family. For example, linear polymers consist of long molecular chains, while the branched polymers consist of primary long chains and secondary chains that stem from these main chains. However, linear does not mean straight lines. The better way to classify polymers is according to their mechanical and thermal behavior. Industrially polymers are classified into two main classes – *plastics* and *elastomers*.

Plastics are moldable organic resins. These are either natural or synthetic, and are processed by forming or molding into shapes. Plastics are important engineering materials for many reasons. They have a wide range of properties, some of which are unattainable from any other materials, and in most cases they are relatively low in cost. Following is the brief list of properties of plastics: light weight, wide range of colors, low thermal and electrical conductivity, less brittle, good toughness, good resistance to acids, bases and moisture, high dielectric strength (use in electrical insulation), etc. Plastics are

again classified in two groups depending on their mechanical and thermal behavior as *thermoplasts* (thermoplastic polymers) and *thermosets* (thermosetting polymers).

Thermoplasts: These plastics soften when heated and harden when cooled – processes that are totally reversible and may be repeated. These materials are normally fabricated by the simultaneous application of heat and pressure. They are linear polymers without any cross-linking in structure where long molecular chains are bonded to each other by secondary bonds and/or inter-wined. They have the property of increasing plasticity with increasing temperature which breaks the secondary bonds between individual chains. Common thermoplasts are: acrylics, PVC, nylons, polypropylene, polystyrene, polymethyl methacrylate (plastic lenses or perspex), etc.

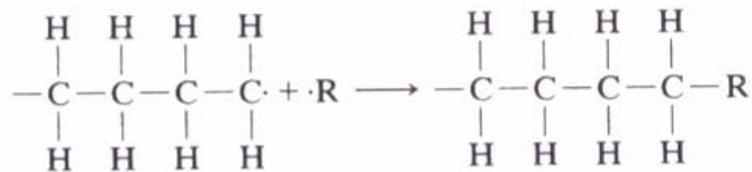
Thermosets: These plastics require heat and pressure to mold them into shape. They are formed into a permanent shape and cured or ‘set’ by chemical reactions such as extensive cross-linking. They cannot be re-melted or reformed into another shape but decompose upon being heated to too high a temperature. Thus thermosets cannot be recycled, whereas thermoplasts can be recycled. The term thermoset implies that heat is required to permanently set the plastic. Most thermosets composed of long chains that are strongly cross-linked (and/or covalently bonded) to one another to form 3-D network structures to form a rigid solid. Thermosets are generally stronger, but more brittle than thermoplasts. Advantages of thermosets for engineering design applications include one or more of the following: high thermal stability, high dimensional stability, high rigidity, light weight, high electrical and thermal insulating properties and resistance to creep and deformation under load. There are two methods whereby cross-linking reaction can be initiated – cross-linking can be accomplished by heating the resin in a suitable mold (e.g. bakelite), or resins such as epoxies (araldite) are cured at low temperature by the addition of a suitable cross-linking agent, an amine. Epoxies, vulcanized rubbers, phenolics, unsaturated polyester resins, and amino resins (ureas and melamines) are examples of thermosets.

Elastomers: Also known as rubbers, these are polymers which can undergo large elongations under load, at room temperature, and return to their original shape when the load is released. There are number of man-made elastomers in addition to natural rubber. These consist of coil-like polymer chains those can reversibly stretch by applying a force.

Processing of polymers mainly involves preparing a particular polymer by synthesis of available raw materials, followed by forming into various shapes. Raw materials for polymerization are usually derived from coal and petroleum products. The large molecules of many commercially useful polymers must be synthesized from substances having smaller molecules. The synthesis of the large molecule polymers is known as polymerization in which monomer units are joined over and over to become a large molecule. More upon, properties of a polymer can be enhanced or modified with the addition of special materials. This is followed by forming operation. Addition polymerization and condensation polymerization are the two main ways of polymerization.

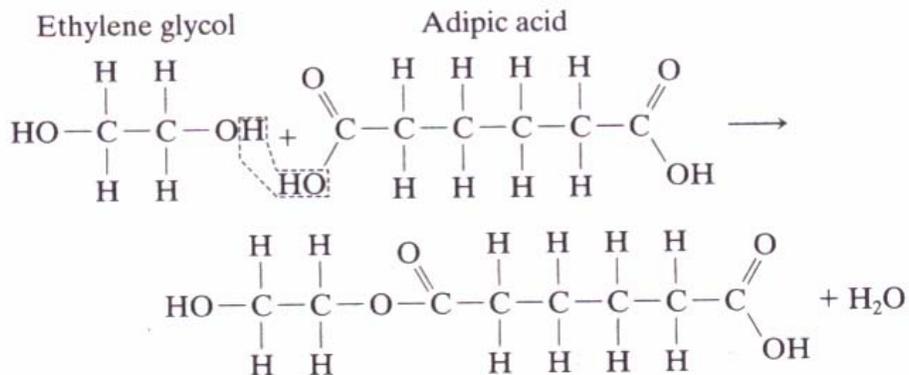


thus terminating the growth of each chain or an active chain end may react with an initiator or other chemical species having a single active bond, as follows:



with the resultant cessation of chain growth. Polyethylene, polypropylene, PVC, and polystyrene are synthesized using addition polymerization.

Condensation polymerization, also known as step growth polymerization, involves more than one monomer species; and there is usually a small molecular weight by-product such as water, which is eliminated. The repeat unit here forms from original monomers, and no product has the chemical formula of mere one mer repeat unit. The polymerization of dimethyl terephthalate and ethylene glycol to produce polyester is an important example. The by-product, methyl alcohol, is condensed off and the two monomers combine to produce a larger molecule (mer repeat unit). Another example, consider the formation of a polyester from the reaction between ethylene glycol and adipic acid; the intermolecular reaction is as follows:



This stepwise process is successively repeated, producing, in this case, a linear molecule. The intermolecular reaction occurs every time a mer repeat unit is formed. Reaction times for condensation are generally longer than for addition polymerization. Polyesters, phenol-formaldehyde, nylons, polycarbonates etc are produced by condensation polymerization. Condensation polymerization reactions also occur in sol-gel processing of ceramic materials. Some polymers such as nylon may be polymerized by either technique.

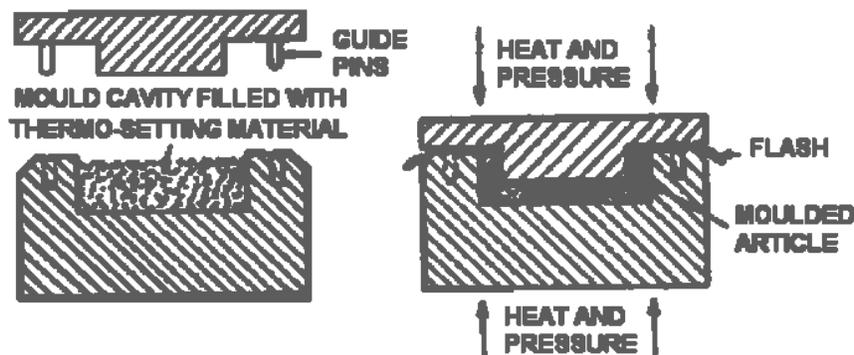
Polymers, unlike organic/inorganic compounds, do not have a fixed molecular weight. It is specified in terms of *degree of polymerization* – number of repeat units in the chain or ratio of average molecular weight of polymer to molecular weight of repeat unit. Average molecular weight is however defined in two ways. *Weight average molecular*

*weight* is obtained by dividing the chains into size ranges and determining the fraction of chains having molecular weights within that range. *Number average molecular weight* is based on the number fraction, rather than the weight fraction, of the chains within each size range. It is always smaller than the weight average molecular weight.

Most of polymer properties are intrinsic i.e. characteristic of a specific polymer. Foreign substances called additives are intentionally introduced to enhance or modify these properties. These include – fillers, plasticizers, stabilizers, colorants, and flame retardants. Fillers are used to improve tensile and compressive strength, abrasion resistance, dimensional stability etc. wood flour, sand, clay, talc etc are example for fillers. Plasticizers aid in improving flexibility, ductility and toughness of polymers by lowering glass transition temperature of a polymer. These are generally liquids of low molecular weight. Stabilizers are additives which counteract deteriorative processes such as oxidation, radiation, and environmental deterioration. Colorants impart a specific color to a polymer, added in form of either dyes (dissolves) or pigments (remains as a separate phase). Flame retardants are used to enhance flammability resistance of combustible polymers. They serve the purpose by interfering with the combustion through the gas phase or chemical reaction.

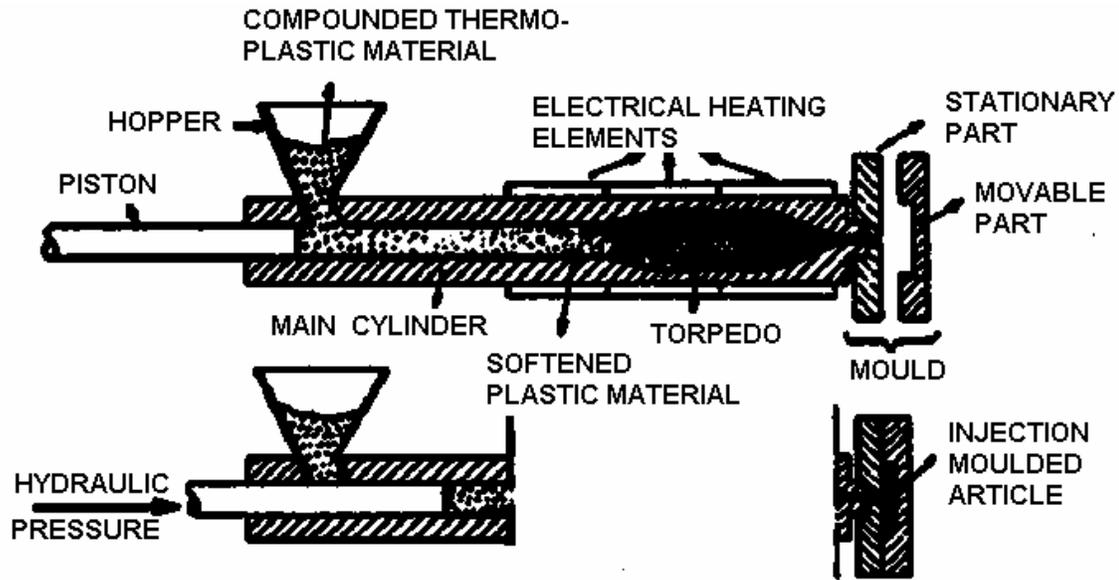
Polymeric materials are formed by quite many different techniques depending on (a) whether the material is thermoplast or thermoset, (b) melting/degradation temperature, (c) atmospheric stability, and (d) shape and intricacy of the product. Polymers are often formed at elevated temperatures under pressure. Thermoplasts are formed above their glass transition temperatures while applied pressure ensures that the product retain its shape. Thermosets are formed in two stages – making liquid polymer, then molding it.

Different molding techniques are employed in fabrication of polymers. *Compression molding* involves placing appropriate amount of polymer with additives between heated male and female mold parts. After pouring polymer, mold is closed, and heat and pressure are applied, causing viscous plastic to attain the mold shape. *Figure-11.1* shows a typical mould employed for compression molding.



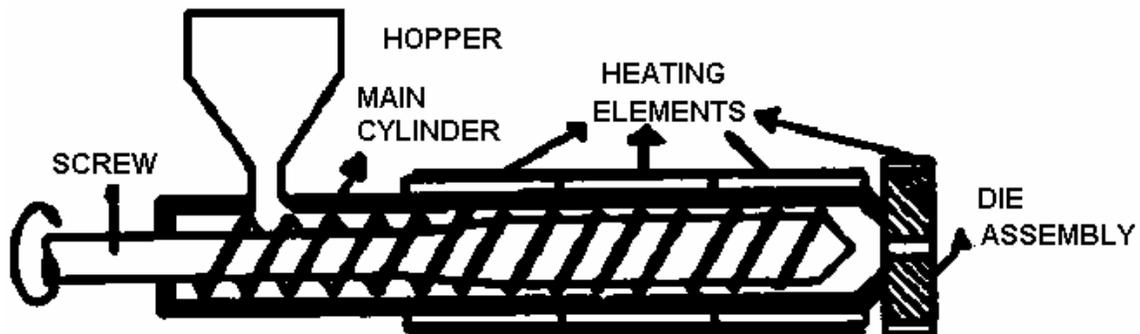
**Figure 11.1:** Schematic diagram of a mould employed for compression molding

*Transfer molding* differs from compression molding in how the materials is introduced into the mold cavities. In transfer molding the plastic resin is not fed directly into the mold cavity but into a chamber outside the mold cavities. When the mold is closed, a plunger forces the plastic resin into the mold cavities, where and molded material cures. In *injection molding*, palletized materials is fed with use of hopper into a cylinder where charge is pushed towards heating chamber where plastic material melts, and then molten plastic is impelled through nozzle into the enclosed mold cavity where product attains its shape. Most outstanding characteristic of this process is the cycle time which is very short. The schematic diagram of injection-molding machine is shown in *figure-11.2*



**Figure 11.2:** Schematic diagram of injection-molding machine

*Extrusion* is another kind of injection molding, in which a thermoplastic material is forced through a die orifice, similar to the extrusion of metals. This technique is especially adapted to produce continuous lengths with constant cross-section. The schematic diagram of a simple extrusion machine is shown in *figure- 11.3*



**Figure 11.3:** Schematic diagram of a simple extrusion machine

*Blow molding* of plastics is similar to blowing of glass bottles. Polymeric materials may be cast similar to metals and ceramics.

## **11.2 Crystallization, melting and glass transition**

Polymers are known by their high sensitivity of mechanical and/or thermal properties. This section explains their thermal behavior. During processing of polymers, they are cooled with/without presence of presence from liquid state to form final product. During cooling, an ordered solid phase may be formed having a highly random molecular structure. This process is called crystallization. The melting occurs when a polymer is heated. If the polymer during cooling retains amorphous or non-crystalline state i.e. disordered molecular structure, rigid solid may be considered as frozen liquid resulting from glass transition. Thus, enhancement of either mechanical and/or thermal properties needs to consider crystallization, melting, and the glass transition.

Crystallization and the mechanism involved play an important role as it influences the properties of plastics. As in solidification of metals, polymer crystallization involves nucleation and growth. Near to solidification temperature at favorable places, nuclei forms, and then nuclei grow by the continued ordering and alignment of additional molecular segments. Extent of crystallization is measured by volume change as there will be a considerable change in volume during solidification of a polymer. Crystallization rate is dependent on crystallization temperature and also on the molecular weight of the polymer. Crystallization rate decreases with increasing molecular weight.

Melting of polymer involves transformation of solid polymer to viscous liquid upon heating at melting temperature,  $T_m$ . Polymer melting is distinctive from that of metals in many respects – melting takes place over a temperature range; melting behavior depends on history of the polymer; melting behavior is a function of rate of heating, where increasing rate results in an elevation of melting temperature. During melting there occurs rearrangement of the molecules from ordered state to disordered state. This is influenced by molecular chemistry and structure (degree of branching) along with chain stiffness and molecular weight.

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. The temperature range at which the transition from rubbery to rigid state occurs is termed as glass transition temperature,  $T_g$ . This temperature has its significance as abrupt changes in other physical properties occur at this temperature. Glass transition temperature is also influenced by molecular weight, with increase of which glass transition temperature increases. Degree of cross-linking also influences the glass transition such that polymers with very high degree of cross-linking do not experience a glass transition. The glass transition temperature is typically 0.5 to 0.75 times the absolute melting temperature. Above the glass transition, non-crystalline polymers show viscous behavior, and below the glass transition they show glass-brittle behavior (as chain motion is very restricted), hence the name glass transition.

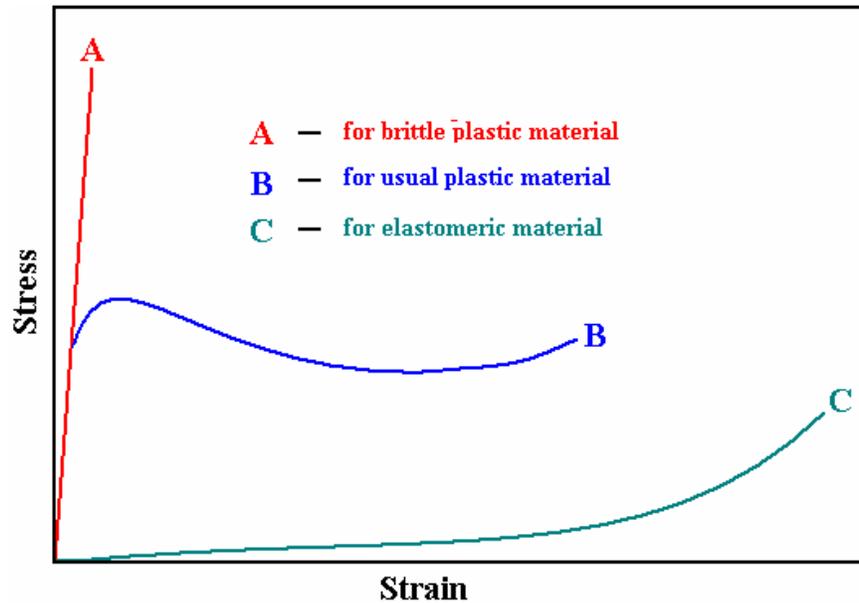
Melting involves breaking of the inter-chain bonds, so the glass- and melting-temperatures depend on:

- chain stiffness (e.g., single vs. double bonds)
- size, shape of side groups
- size of molecule
- side branches, defects
- cross-linking

### **11.3 Mechanical behavior of polymers**

Polymer mechanical properties can be specified with many of the same parameters that are used for metals such as modulus of elasticity, tensile/impact/fatigue strengths, etc. However, polymers are, in many respects, mechanically dissimilar to metals. To a much greater extent than either metals or ceramics, both thermal and mechanical properties of polymers show a marked dependence on parameters namely temperature, strain rate, and morphology. In addition, molecular weight and temperature relative to the glass transition play an important role that are absent for other type of materials.

A simple stress- strain curve can describe different mechanical behavior of various polymers. As shown in *figure – 11.4*, the stress-strain behavior can be brittle, plastic and highly elastic (elastomeric or rubber-like). 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. Highly crystalline polymers behave in a brittle manner, whereas amorphous polymers can exhibit plastic deformation. These phenomena are highly temperature dependent, even more so with polymers than they are with metals and ceramics. 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. The tensile strength is defined at the fracture point and can be lower than the yield strength.



**Figure-11.4:** *Typical stress-strain curves for polymers.*

As the temperature increases, both the rigidity and the yield strength decrease, while the elongation increases. Thus, if high rigidity and toughness are the requirements, the temperature consideration is important. In general, decreasing the strain rate has the same influence on the strain-strength characteristics as increasing the temperature: the material becomes softer and more ductile. Despite the similarities in yield behavior with temperature and strain rate between polymers, metals, and ceramics, the mechanisms are quite different. Specifically, the necking of polymers is affected by two physical factors that are not significant in metals: dissipation of mechanical energy as heat, causing softening magnitude of which increases with strain rate; deformation resistance of the neck, resulting in strain-rate dependence of yield strength. The relative importance of these two factors depends on materials, specimen dimensions and strain rate. The effect of temperature relative to the glass transition is depicted in terms of decline in modulus values. Shallow decline of modulus is attributed to thermal expansion, whereas abrupt changes are attributable to viscoelastic relaxation processes.

Together molecular weight and crystallinity influence a great number of mechanical properties of polymers including hardness, fatigue resistance, elongation at neck, and even impact strength. The chance of brittle failure is reduced by raising molecular weight, which increases brittle strength, and by reducing crystallinity. As the degree of crystallinity decreases with temperature close to melting point, stiffness, hardness and yield strength decrease. These factors often set limits on the temperature at which a polymer is useful for mechanical purposes.

Elastomers, however, exhibit some unique mechanical behavior when compared to conventional plastics. The most notable characteristics are the low modulus and high deformations as elastomers exhibit large, reversible elongations under small applied stresses. Elastomers exhibit this behavior due to their unique, cross-linked structure.

Elastic modulus of elastomers (resistance to the uncoiling of randomly orientated chains) increases as with increase in temperature. Unlike non-cross-linked polymers, elastomers exhibit an increase inelastic modulus with cross-link density.

#### **11.4 Mechanisms of deformation and strengthening of polymers**

An understanding of deformation mechanisms of polymers is important in order to be able to manage the optimal use of these materials, a class of materials that continues to grow in terms of use in structural applications. Despite the similarities in ductile and brittle behavior with to metals and ceramics respectively, elastic and plastic deformation mechanisms in polymers are quite different. This is mainly due to (a) difference in structure they made of and (b) size of the entities responsible for deformation. Plastic deformation in metals and ceramics can be described in terms of dislocations and slip planes, whereas polymer chains must undergo deformation in polymers leading to different mechanism of permanent deformation. Unique to most of the polymers is the viscoelasticity – means when an external force is applied, both elastic and plastic (viscous) deformation occur. For viscoelastic materials, the rate of strain determines whether the deformation in elastic or viscous. The viscoelastic behavior of polymeric materials is dependent on both time and temperature.

Plastic polymers deform elastically by elongation of the chain molecules from their stable conformations in the direction of the applied stress by the bending and stretching of the strong covalent bonds. In addition, there is a possibility for slight displacement of adjacent molecules, which is resisted by weak secondary / van der Waals bonds. Plastic deformation in polymers is not a consequence of dislocation movement as in metals. Instead, chains rotate, stretch, slide and disentangle under load to cause permanent deformation. This permanent deformation in polymers might occur in several stages of interaction between lamellar and intervening amorphous regions. Initial stages involve elongation of amorphous tie chains, and eventual alignment in the loading direction. Continues deformation in second stage occurs by the tilting of the lamellar blocks. Next, crystalline block segments separate before blocks and tie chains become orientated in the direction of tensile axis in final stage. This leads to highly orientated structure in deformed polymers.

Elastomers, on the other hand, deform elastically by simple uncoiling, and straightening of molecular chains that are highly twisted, kinked, and coiled in unstressed state. The driving force for elastic deformation is change in entropy, which is a measure of degree of disorder in a system. When an elastomer is stretched, the system's order increases. If elastomer is released from the applied load, its entropy increases. This entropy effect results in a rise in temperature of an elastomer when stretched. It also causes the modulus of elasticity to increase with increasing temperature, which is opposite to the behavior of other materials.

Fracture of polymers is again dependent on morphology of a polymer. As a thumb rule, thermosets fracture in brittle mode. It involves formation of cracks at regions where there is a localized stress concentration. Covalent bonds are severed during the fracture.

However, both ductile and brittle modes are possible mode of fracture for thermoplasts. Many of thermoplasts can exhibit ductile-to-brittle transition assisted by reduction in temperature, increase in strain rate, presence of notch, increased specimen thickness and a modification of the polymer structure. Unique to polymer fracture is crazing – presence of regions of very localized yielding, which lead to formation of small and interconnected microvoids. Crazes form at highly stressed regions associated with scratches, flaws and molecular inhomogeneties; and they propagate perpendicular to the applied tensile stress and typically are 5  $\mu\text{m}$  or less thick. A craze is different from a crack as it can support a load across its face.

The deformation of plastic materials can be primarily elastic, plastic, or a combination of both types. The deformation mode and resistance of deformation depends on many parameters for different plastics. The following factors influence the strength of a thermoplast: 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. Effect of every one of these factor can be used to strengthen a thermoplast. Thermosets are, however, strengthened by reinforcement methods.

Strength of a thermoplast is directly dependent on its average molecular mass since polymerization up to a certain molecular-mass range is necessary to produce a stable solid. This method is not used so often as after a critical mass range, increasing the average molecular mass does not greatly increase its strength. In general, as the degree of crystallinity increases, the strength, modulus and density all increase for a thermoplast. Another method to increase the strength is to create more resistance to chain slippage. This can be achieved by addition of bulky side groups on main chains, which results in increase of strength but reduces the ductility. Increased resistance to chain slippage can be achieved by increasing the molecular bonding forces between the polymer chains. E.g.: introducing a chlorine atom on every other carbon atom of main chain to make polyvinylchloride (PVC). Introducing an ether linkage (i.e. introduction of oxygen atom) or amide linkage (i.e. introduction of oxygen and nitrogen atoms) into the main chain can increase the rigidity of thermoplasts. One of the most important strengthening methods for thermoplasts is the introduction of phenylene rings in the main chain. It is commonly used for high-strength engineering plastics. The phenylene rings cause steric hindrance to rotation within the polymer chain and electronic attraction of resonating electrons between adjacent molecules. Another method of strengthening is introduction of reinforcements like glass fibers. Glass content ranges from 20 to 40%, depending on trade-off between desired strength, ease of processing and economics.

Thermosets are strengthened by reinforcements again. Different reinforcements are in use according to the necessity. Glass fibers are most commonly used to form structural and molding plastic compounds. Two most important types of glass fibers are E (electrical)- and S (high strength)- glasses. *E-glass* (lime-aluminium-borosilicate glass with zero or low sodium and potassium levels) is often used for continuous fibers. *S-glass* (65%SiO<sub>2</sub>, 25%Al<sub>2</sub>O<sub>3</sub> and 10% MgO) has higher strength-to-weight ratio and is more expansive thus primary applications include military and aerospace applications. Carbon fiber reinforced plastics are also often used in aerospace applications. However they are very expensive.

The other classes of reinforcements include aramid (aromatic polyamide) fibers. They are popularly known as *Kevlar*. Presently two commercial variants of Kevlar are available – Kevlar29 and Kevlar49. Kevlar29 is a low-density, high strength aramid fiber designed for applications such as ballistic protection, ropes and cables. Kevlar49 is characterized by a low density and high strength/modulus; is used in aerospace, marine, automotive and other industrial applications. Thermosets without reinforcements are strengthened by creation of network of covalent bonds throughout the structure of the material. Covalent bonds can be developed during casting or pressing under heat and pressure.

### ***11.5 Characteristics and typical applications of few plastic materials.***

#### ***a) Thermo plastics***

##### **1. Acrylonitrile-butadiene-styrene (ABS):**

*Characteristics:* Outstanding strength and toughness, resistance to heat distortion; good electrical properties; flammable and soluble in some organic solvents.

*Application:* Refrigerator lining, lawn and garden equipment, toys, highway safety devices.

##### **2. Acrylics (poly-methyl-methacrylate)**

*Characteristics:* Outstanding light transmission and resistance to weathering; only fair mechanical properties.

*Application:* Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs

##### **3. Fluorocarbons (PTFE or TFE)**

*Characteristics:* Chemically inert in almost all environments, excellent electrical properties; low coefficient of friction; may be used to 260° C; relatively weak and poor cold-flow properties.

*Application:* Anticorrosive seals, chemical pipes and valves, bearings, anti adhesive coatings, high temperature electronic parts.

##### **4. Polyamides (nylons)**

*Characteristics:* Good mechanical strength, abrasion resistance, and toughness; low coefficient of friction; absorbs water and some other liquids.

*Application:* Bearings, gears, cams, bushings, handles, and jacketing for wires and cables

##### **5. Polycarbonates**

*Characteristics:* Dimensionally stable: low water absorption; transparent; very good impact resistance and ductility.

*Application:* Safety helmets, lenses light globes, base for photographic film

##### **6. Polyethylene**

*Characteristics:* Chemically resistant and electrically insulating; tough and relatively low coefficient of friction; low strength and poor resistance to weathering.

*Application:* Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials.

### 7. Polypropylene

*Characteristics:* Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to UV light.

*Application:* Sterilizable bottles, packaging film, TV cabinets, luggage

### 8. Polystyrene

*Characteristics:* Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive

*Application:* Wall tile, battery cases, toys, indoor lighting panels, appliance housings.

### 9. Polyester (PET or PETE)

*Characteristics:* One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity acids, greases, oils and solvents

*Application:* Magnetic recording tapes, clothing, automotive tire cords, beverage containers.

## ***b) Thermo setting polymers***

### 1. Epoxies

*Characteristics:* Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties.

*Application:* Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates.

### 2. Phenolics

*Characteristics:* Excellent thermal stability to over 150° C; may be compounded with a large number of resins, fillers, etc.; inexpensive.

*Application:* Motor housing, telephones, auto distributors, electrical fixtures.

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