**Polymers/Plastics**

The word polymer (‘mer’) is originated from Greek word *meros* – which means part. The word polymer is thus coined to mean material consisting of many parts/mers. Most of the polymers are basically organic compounds, however they can be inorganic (e.g. silicones based on Si-O network).The polymers are composed of a large number of repeating units (small molecules) called monomers. *A polymer is, therefore, a long chain or network made up of thousands of monomers all covalently bonded together.*

The size of a polymer is determined by dividing the molecular weight by the mer weights. The number is called degree of polarization, DP.

$$DP= \frac{Molecular weight}{Mer weight}$$

At DP values of above 10 to 20, the substance formed is *light oil*. As the DP increases the substance becomes *greasy,* then waxy, and finally at a value of DP of about 1000 the substance becomes a solid.

**Mechanism of Polymerization**

The process of linking together of monomers is called the polymerization. Polymerization mechanisms may be of the following two types:

***Addition polymerization****, also known as chain reaction polymerization, is a process in which multi-functional monomer units are attached one at a time in chainlike fashion to form linear/3-D macro-molecules. The composition of the macro-molecule is an exact multiple of for that of the original reactant monomer*.

This kind of polymerization involves three distinct stages – initiation, propagation and termination. To initiate the process, an initiator is added to the monomer. This forms free radicals with a reactive site that attracts one of the carbon atoms of the monomer. When this occurs, the reactive site is transferred to the other carbon atom in the monomer and a chain begins to form in propagation stage. A common initiator is *benzyl peroxide*. When polymerization is nearly complete, remaining monomers must diffuse a long distance to reach reactive site, thus the growth rate decreases.

The process for polyethylene is as follows



Here R. represents the active initiator. Propagation involves the linear growth of the molecule as monomer units become attached to one another in succession to produce the chain molecule, which is represented, again for polyethylene, as follows



As we need polymers with controlled molecular weight, polymerization needs to be terminated at some stage. Propagation may end or terminate in different ways. First, the active ends of two propagating chains may react or link together to form a non-reactive molecule, as follows:



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, with the resultant cessation of chain growth as follows:



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 di-methyl 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 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.

**Deploymerisation:** *A reversal of the polymerization reaction is known as depolymerisation.* It may happen due to the thermal vibrations which may disrupt the inter-molecular bonds within the molecules. Depolymerisation is commercially used for cracking petroleum into more combustible, light molecules.

**Characteristics of Polymers**

1. *Strength-to-weight ratio:* Plastics are generally light in weight but their strength to weight ratio compares favorably with many light alloys.
2. *Low rigidity*
3. 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.
4. 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.
5. Highly crystalline polymers behave in a brittle manner; where as amorphous polymers can exhibit plastic deformation.
6. Due to unique structures of cross-linked polymers, recoverable deformations up to very high strains/point of rupture are also observed with polymers (elastomers).
7. Tensile modulus (modulus) and tensile strengths are order s of magnitude smaller than those of metals, but elongation can be upto1000% in some cases.

Typical stress-strain diagram for polymers:



1. Corrosion resistance of plastics is very high.
2. Low Thermal conductivity
3. Thermal expansion of plastics is very high.
4. Plastics are good electrical insulators.

**Classification of Polymers**

Polymers are classified in many ways. The prime classification based on their industrial usage is: *Plastics and Elastomers*.

1. Plastic polymers are again classified based on their temperature dependence of their structure as follows:
* *thermoplasts and*
* *thermosets*
* Thermoplasts
* Plastics which softens upon heating and hardens upon 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 cannot 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.
1. 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 straighten up on application of load.
* Characterized by low modulus/rigidity/strength, but high toughness.
* E.g.: natural and synthetic rubber.

***Characteristics and typical applications of few plastics 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 260o 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 150o C; may be compounded with a large number of resins, fillers, etc.; inexpensive. *Application:* Motor housing, telephones, auto distributors, electrical fixtures.

**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 involves melting, cooling upon which crystallization takes place. In addition, glass transition occurs in polymers.
* Crystallization rate depends on temperature and molecular weight. It decreases 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 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