Lecture 4.1: Thermoplastics and Thermosets

The word plastic comes from the Greek word Plastikos, meaning “able to be shaped and molded”. Plastics can be broadly classified into two major groups on the basis of their chemical structure i.e. thermoplastics and thermosetting plastics.

Thermoplastics
The material that softens when heated above the glass transition temperature or melting temperature and becomes hard after cooling is called thermoplastics. Thermoplastics can be reversibly melted by heating and solidified by cooling in limited number of cycles without affecting the mechanical properties. On increasing the number of recycling of thermoplastics may result in color degradation, thereby affecting their appearance and properties. In the molten state, they are liquids, and in the mushy state they are glassy or partially crystalline. The molecules are joined end-to-end into a series of long chains, each chain being independent of the other. Above the melting temperature, all crystalline structure disappears and the long chain becomes randomly scattered.

The molecular structure of thermoplastic (figure 1) has an influence on the chemical resistance and resistance against environmental effects like UV radiation. The properties may also vary from optical transparency to opaque, depending on the molecular structure. The important properties of the thermoplastics are high strength and toughness, better hardness, chemical resistance, durability, self lubrication, transparency and water proofing.

With the application of heat, thermoplastic softens and it can be molded into desired shapes. Some thermoplastics can be joined with the application of heat and pressure. There are several techniques available for the joining of thermoplastics such as mechanical fastening, fusion bonding, hot gas welding, solvent bonding, ultrasonic welding, induction welding, and dielectric welding.

The different types of thermoplastic are: Acrylonitrile Butadiene Styrene (ABS), Acetals, Acrylics, Cellulosics, Fluorocarbons, Polyamides, Polycarbonates, Polyethylene (PE), Polypropylenes (PP), Polystyrenes, Polyetheretherketone, Polyvinyl Chloride (PVC), Liquid Crystal Polymers (LCP), Polyphenylene Sulphide (PPS) and Vinlys.
Applications
Thermoplastics can be used to manufacture the dashboards and car trims, toys, phones, handles, electrical products, bearings, gears, rope, hinges and catches, glass frames, cables, hoses, sheet, and windows, etc.

Thermosets
The property of material becoming permanently hard and rigid after cooling when heated above the melting temperature is called thermosets. The solidification process of plastics is known as curing. The transformation from the liquid state to the solid state is irreversible process, further heating of thermosets result only in the chemical decomposition. It means that the thermosets can’t be recycled. During curing, the small molecules are chemically linked together to form complex inter-connected network structures (figure 2). This cross-linking prevents the slippage of individual chains. Therefore, the mechanical properties (tensile strength, compressive strength, and hardness) are not temperature dependent, as compared to thermoplastics. Hence, thermosets are generally stronger than the thermoplastics.
The joining of thermosets by thermal processes like ultrasonic welding, laser welding, and gas welding is not possible, but mechanical fastening and adhesive bonding may be used for low strength applications.

The different types of thermosets are Alkyds, Allylics, Amine, Bakelite, Epoxy, Phenolic (PF), Polyester, Silicone, Polyurethane (PUR), and Vinyl Ester.

**Applications**

Thermosets are commonly used for high temperature applications. Some of the common products are electrical equipments, motor brush holders, printed circuit boards, circuit breakers, encapsulation, kitchen utensils, handles and knobs, and spectacle lenses.

**Processing Techniques for Plastics**

Plastic materials are synthetic and semi-synthetic organic solids and it can be easily processed. The processing stages of plastics may be heating, forming and cooling in continuous or repeated cycles. The processing of plastic product depends on the shape of the final product and types of plastic material (thermoplastics or thermosets) being used. The complex plastic product can be produced in a single operation. The processing of plastic may be automated and suitable for mass production.

Thermoplastics can be processed by heating up to the glass transition temperature and formed into the desired shape with the application of pressure, for examples, thermoforming, compression molding, and blown film extrusion.
The processing of thermosets can be completed in two steps; first it can be melted and then poured into the mold to make a desired shape, for examples, casting, extrusion, and injection molding.

**Structure of Plastics**

The basic structure of plastics depends upon its molecular chains formulated during chemical reaction (figure 3). A single repeating unit in a molecular chain is called monomers. There are two different types of chemical reactions which take place during processing i.e. polyaddition and polycondensation. In polyaddition, the monomers bond to each other without the loss of any other atoms, for example alkene. In case of polycondensation, the two different monomers combine to form a single molecule with the loss of atoms, for example: formation of polyester lost hydrogen molecules.

On the basis of structure, plastics can be classified into four categories i.e. linear structure, branched structure, cross-linked structure, and network structure.

![Structure of Plastics Diagram](image)

**Linear Structure**: The monomers are linked together to form linear chains (figure 4). The van der waals interaction takes place between the linear chains. Some common examples are nylon, high density polyethylene, polyvinyl chloride, polyester.
Branched Structure: The monomers are joined to form long chains with branches of different lengths (figure 5). For examples: low density polyethylene, glycogen and starch.

Cross-linked Structure: The monomers are combined together to form cross-linked chains (figure 6). Chains are connected by covalent bonds. For example: rubber, bakelite.

Network Structure: The monomers are joined together to form a large three dimensional network, for example: epoxy, phenol formaldehyde.
Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. Isomers may be in two form i.e. stereoisomers and geometrical isomers. Further, geometrical isomers can be divided into the trans and cis isomer depending upon atoms in space, for example: 1, 2 dichloroethene (figure 8). Two chlorine atoms are joined on opposite side of the double bond is called trans isomer. If the chlorine atoms are joined on the same side is called cis isomer.

The monomers are organic carbon based molecules. Covalent bonds hold the atoms in the molecules together and secondary bonds hold groups of chains together. For example, polyethylene is made from ethylene monomers (figure 9). The two mers are joined together with the application of heat, pressure and catalyst which is called polymerization to form polyethylene chains.
The polyethylene chains are elongated thousands times greater than its crystalline structures when stretched. The mechanical properties of plastics depend upon the number of carbon atom present into the polymeric chain. Some of the common plastic monomers are shown in table 1.

Table 1 Chemical formula of plastic monomers

<table>
<thead>
<tr>
<th>Polyethylene (PE)</th>
<th>Polyvinyl chloride (PVC)</th>
<th>Polypropylene (PP)</th>
<th>Polystyrene (PS)</th>
<th>Polytetrafluoroethylene (PTFE)</th>
<th>Polymethyl methacrylate (PMMA)</th>
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<tr>
<td><img src="image" alt="Polyethylene" /></td>
<td><img src="image" alt="Polyvinyl chloride" /></td>
<td><img src="image" alt="Polypropylene" /></td>
<td><img src="image" alt="Polystyrene" /></td>
<td><img src="image" alt="Polytetrafluoroethylene" /></td>
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**Mechanical Properties of Plastics**
The mechanical properties of the plastics are given below:

(a) **Hardness:** Plastics are not very hard, their hardness being comparable to that of brass and aluminum. Generally, thermosets are harder than thermoplastics. The temperature of the material substantially affects its properties. The hardness of commonly used plastics is in the range of 5-50 BHN.

(b) **Stress-Strain Behavior:** When the plastic is subjected to uni-axial load, it deforms permanently and ultimately fails as shown in figure 10. Tensile strengths of plastics may be in the range of 10 to 100 MPa. The modulus of elasticity for plastic is in the range of 10 MPa to 4000 MPa. Tensile strength decreases with increasing temperature. Some of the plastics are brittle in nature. The mechanical properties of the plastics depend upon the strain rate, temperature, and environmental conditions.
(c) **Creep:** The molecular weight of the polymer affects its creep behavior. As the molecular weight of the polymer increases, it becomes more creep resistant. When a plastic is subjected to a constant load, it deforms continuously. The plastic will continue to deform slowly with long time or until fails. The creep depends on several factors such as: types of plastic, load applied, temperature and time.

(d) **Fatigue Behavior:** Fatigue failure of thermosets is brittle in nature, but in case of thermoplastic failure occurs due to initiation of crack propagation. The flexural fatigue strength of plastics may be in the range of $10^5 - 10^7$ numbers of cycle to failure at room temperature ($20^\circ$C).