Non-Metallic Materials

CHAPTER 4

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4.1. POLYMERS AND POLYMERISATION

The **polymers** *are composed of a large number of repeating units (small molecules) called* **monomers**. A polymer is, therefore, made up of thousands of monomers joined together to form a large molecule of colloidal dimension, called *macromolecule.* The *unique feature of a polymer is that each molecule is either a long chain or network of repeating units all covalently bonded together.* In some cases, molecules are held together by secondary bonds.

The process of linking together of monomers is called **polymerisation**. The need to start with the process of polymerisation lies on the necessity of breaking the double bond (C=C) of the monomers. This requires considerable energy. Polymerization mechanisms may be of the following two types:

1. Addition polymerisation.
2. Condensation polymerisation.

1. Addition polymerisation :

This polymerisation process is of simplest form. When a large number of simple molecules are chemically added together to increase the average molecule size without wastage, process of addition polymerisation takes place. Such a polymerisation takes place by three steps namely. (*i*) *Initiation* (*ii*) *Chain propagation* and (*iii*) *Termination.*

Example. Addition polymerisation of ethylene (Fig. 4.1).

Once polymerisation process is initiated, it does not continue indefinitely since it is impossible to link all the monomers in a plastic one long continuous chain. The polymerisation is terminated by a collision between the active ends of two chains or by addition of a terminator, such as free radicals from the catalyst.

Copolymerization. It is another type of addition polymerisation.

Copolymerization is the addition polymerisation of two or more chemically different monomers. Many monomers will not polymerise with themselves but will copolymerise with other compounds.

Copolymerisation has been applied extensively, in the *artificial rubbers.*

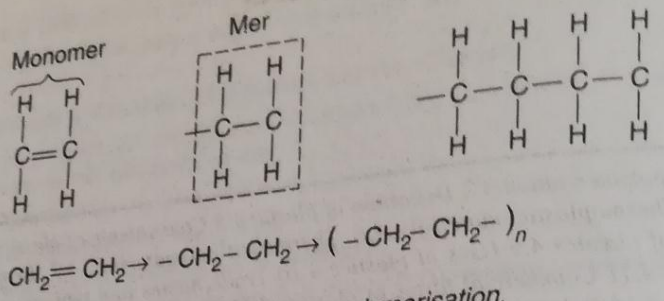


Fig. 4.1. *Addition polymerisation.*

2. Condensation polymerisation :

Condensation polymerisation *is defined as the process of linking together of uni monomers accompanied by splitting off a small molecule. This process usually requires a catal*

In comparison to *addition* reaction in which a simple molecular summation occu *condensation* reactions result in *splitting out of* simple monopolymerisable molecules, *e.g.* wa which are considered to be *by-products* of the process. Thus when a phenol and formaldehy monomers are polymerised, water is released, and the resulting product is polymerised phe formaldehyde, more commonly known as *Bakelite.*

Comparison between Addition and Condensation polymerisation

S.No.	*Addition polymerisation*	*Condensation polymerisation*
1.	It requires molecules which are unsaturated.	It requires two unlike molecules.
2.	It does not yield a by-product.	It yields a by-product.
3.	Reaction is very fast and may take 10^{-2} to 10^{-6} sec.	Reaction normally takes hours and days to complete.
4.	It is kinetic chain reaction.	It involves inter-molecular reaction.

4.2. DEFINITION OF PLASTIC

- A **plastic** *can be broadly defined as any non-metallic material that can be moulded t desired shape*
- The most common definition for plastics is that they are *natural or synthetic resins, o their compounds, which can be moulded, extruded, cast or used as films or coatings.*

– Most plastics are of organic nature composed of *hydrogen, oxygen, carbon* and *nitroge*

– The synthetic plastic development dates from 1900 when Dr. Beekland announced th production of phenol formaldehyde. Since then several new plastics have been developed

– In order to give desired properties to the finished plastic articles, certain moulding compounds like *fillers, plasticizers, solvents, pigments etc. are added.*

– The basic raw materials used in the manufacture of plastics are generally obtained from the following natural substances:

(*i*) Coal (*ii*) Petroleum (*iii*) Limestone
(*iv*) Salt (*v*) Sulphur (*vi*) Air
(*vii*) Water (*viii*) Cellulose from cotton and wood.

– In the field *building construction*, plastics have been found very useful for a variety of purpose *e.g. fittings, fixtures, structural component parts*, etc.

4.3. CONSTITUENTS OF PLASTICS

As earlier stated that the basic raw materials for producing plastics are obtained from coal, petroleum, air and water. A moulding composition for plastics is prepared from the following raw material groups :

1. Binder. Binders may be either *resins* (synthetic or natural) or *cellulose derivatives* (polymeric compounds), chemically both kinds of materials may be described as *substances made up of compounds of very large molecular weight.*

2. Fillers. The *materials added to the plastics to improve their mechanical properties and to make them economical* are called '*fillers*'. These are powder, fibrous and laminated fillers.

(*i*) ***Powder fillers:*** Quartz powder, chalk, talcum and organic substances (ground saw dust).

- These fillers improve hardness, durability, heat resistance and acid resistance of plastics and reduce cost.

(*ii*) ***Fibrous fillers:*** Asbestos, wood wool, saw dust and glass fibres.

- They increase strength, reduce brittleness and enhance thermal resistance and impact strength of plastics.

(*iii*) ***Laminated fillers:*** Paper, cotton and fibre glass cloths, asbestos, card board and wood veneer.

- They increase mechanical strength of plastics. Asbestos and cardboards also increase heat and acid resistance properties.

3. Plasticizers. *The chemicals added to plastics to make them soft; to improve their toughness at finished stage and to make them flexible* are called **plasticizers**. A plasticizer should be *chemically inert, non-volatile and non-toxic.*

Common plasticizers are: *Vegetable oils, aluminium stearates and dibutyl phthalate and camphor.*

4. Colouring matter. This is usually in the form of pigment and dyes and often added to monomers and gives the required colour to the plastics. The Colouring matter should be durable and adequately fast to light.

Commonly used dyes are: *Organic* (AZO dyes, anthraquinone vat dyes) and *mineral pigments* (ochre, chromium oxide and ultramarine).

5. Lubricants. Common lubricants are: Mosallic soaps and stearates.

- They facilitate moulding operation by increasing the flow of plastic mix in the die and also prevent sticking of plastic to moulds.

6. Catalysts. These compounds are added to accelerate the chemical reaction during the process of polymerisation of plastics. These compounds also act as hardeners and accelerators.

4. CLASSIFICATION OF PLASTICS

Most commonly, plastics are classified into,

1. Thermoplastic, and
2. Thermosetting.

Thermoplastic materials *are those which soften on the application of heat, with or without pressure and require cooling to be set to a shape.*

- They can be *heated and cooled any number of times,* only they *should not be heated above* their *decomposition temperatures.*
- They are main long chain straight or slightly branched molecules and the chains are held close to each other by secondary weak forces of type Vander Waal's forces. During heating, as the temperature increases the secondary forces are reduced and the sliding of these long chain molecules can easily occur one over the other at a reduced stress level.

- They are highly plastic and are easy for moulding or shaping.
- They have low melting temperatures and are not so strong as the thermosetting plastics.
- Since they can be repeatedly used, they have a resale value.
- Some commercial thermoplastics are: **Polythene, Polyvinyl chloride (PVC), Polystrene, Polytetrafluroethylene (PTEE) etc.**

Thermosetting materials are those plastics *which require heat and pressure to mould them into shape.*

- They cannot be resoftened once they have set and hardened.
- They are ideal for moulding into components which require rigidity, strength and some resistance to heat.
- In general, resins formed by condensation are thermosetting.
- Thermosetting resins have *three-dimensional molecular structure and have very high molecular weights.*
- Due to *cross-linking* thermosetting resins are hard, tough, non-swelling and brittle. Hence they cannot be softened or remoulded as in the case of thermoplastic resins. Moulding and casting are the processes often used with such materials.
- Some important commercial examples of this type are: **Phenolics, Polyesters, Epoxies, Silicones etc.**

The *difference between thermoplastic and thermosetting materials* may be explained *in terms of molecular structure.* The thermoplastics are essentially long chain macromolecules with a limited number of cross links. When heated and compressed, the chains glide over each other and fluid materials take the shape of any mould in which they are placed. The thermosetting plastics are characterised by strong cross links between the chains; once these are formed by heat and pressure, the plastics set to a rigid infusible solid.

Difference between Thermosetting Thermoplastic materials

S.No.	*Thermosetting materials*	*Thermoplastic materials*
1.	They have three dimensional network of primary covalent bonds with cross-linking between chains.	They are linear polymers without cross-linking and branching.
2.	They are more stronger and harder than thermoplastic resins.	They are comparatively softer and less strong.
3.	Once hardened and set they do not soften with the application of heat.	They can be repeatedly softened by heat and hardened by cooling.
4.	Objects made by thermosetting resins can be used at comparatively higher temperature without damage.	Objects made by thermoplastic resins cannot be used at comparatively higher temperatures as they will tend to soften under heat.
5.	They are usually supplied in a monomeric or partially polymerized form in which they are either liquid or partially thermoplastic solids.	They are usually supplied as granular materials.
6.	It is difficult to fill an intricate mould with such plastics.	They can fill the complicated mould quite easily.
7.	They cannot be recycled.	The scrap of these plastics can be recycled again and thus they are *economical.*
	Uses: *Telephone receivers, electric plugs, radio & TV cabinets, camera bodies, automobile parts, circuit breaker switch panels etc.*	**Uses:** *Toys, combs, toilet goods, photographic films, insulating tapes, hoses, electric insulation, etc.*

Important thermoplastic materials are described here under :

1. Polyethylene or Polythene $(C_2H_4)_n$:

This material originated in England was produced commercially in the United States in 1943.

Polyethylenes are obtainable *as various liquids, gums and tough flexible solids suitable for* moulding.

Properties:

(*i*) They are wax like in appearance, transluscent, odourless and one of the lightest plastics.
(*ii*) Flexible over a wide temperature range.
(*iii*) High resistivity and dielectric strength.
(*iv*) Chemically resistant.
(*v*) Do not absorb moisture.
(*vi*) Dielectric losses and dielectric constant are low.
(*vii*) They are relatively low in cost.

Uses:

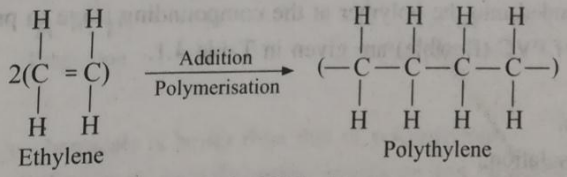
(*i*) High voltage (upto 30 kV) applications.
(*ii*) Coaxial cables.
(*iii*) Packaging.
(*iv*) Moisture proofing.
(*v*) Coating ice-cube trays.
(*vi*) As insulation in submarine cables and radar lines.
(*vii*) Lining for lagoons to avoid seepage of polluted water into the underground.
(*viii*) Fan and blower casing (gas filled polythene)
(*ix*) Pipes and tanks for water storage.

Two types of polyethylene are manufactured depending upon the condition of polymerisation.

(*a*) High density polyethylene (HDPE)
(*b*) Low density polyethylene (LDPE)

(*a*) High density polyethylene (HDPE) :

- This is obtained by *low pressure polymerisation process.*
- It has specific gravity 0.96 and softening temperature 120-130°C.



Ethylene — Polythylene

Typical properties of HDPE are given in Table 4.1.

(*b*) Low density polyethylene (LDPE) :

- This is obtained by high pressure process.
- It has specific gravity 0.90 and softening temperature 86°C.
- Polythene is prone to degradation and embrittlement by sunlight due to cross linking but performance can be improved by addition of black pigments such as carbon black, which absorbs rays and prevents damage.