POLYMERS

Introduction, Nomenclature, Functionality,

Types of Polymerization, Mechanism of Addition Polymerization, Thermosetting & Thermoplastic Polymers,

Methods of Moulding of Plastics,

Thermoplastic Resins: Polyethylene, Polypropylene, Polyvinylchloride, Polyvinyl Acetate, Polystyrene, PolymethylMethacrylate, PolytetrafluoroEthylene, Nylon-6:6, Kevlar.

Thermosetting Resins, Polyurethane, Epoxy Resin, etc.: Bakelite, Silicone Resins, Polymer Composites.

Rubber: Classification, Vulcanization, Synthetic Rubbers (Buna-S, Buna-N), PANVC, ABS etc.

- Polymers: Compounds of very high molecular weights formed by the combination of a large number of small repeating units.
- Derived from the Greek word poly meaning 'many' and mer meaning 'repeating unit'.
- Polymerisation: The process by which the simple molecules (monomers) are converted into polymers.
- Degree of polymerization: The number of repeating units in a polymeric chain, denoted by 'n'.
- Polymers are also called macromolecules because of their big size.

Classification of Polymers

1. On the basis of origin:

(a) Natural polymers: which occur in nature.

For example, starch (polymer of a-D-glucose), cellulose (a polymer of b-D-glucose), proteins (polymer of a-amino acids) and natural rubber (a polymer of poly-cis-isoprene).

(b) **Synthetic polymers**: which are prepared artificially in the laboratory.

For example, polyethylene (PE), polyvinylchloride (PVC), nylon, terylene, bakelite, synthetic rubber, etc.

2. On the basis of monomer composition

• (a) Homopolymer: If a polymer consists of identical monomers, it is termed as homopolymer.

$$nA \rightarrow (A)_{n}$$
 $nCH_{2} = CH_{2} \rightarrow (CH_{2} - CH_{2})_{n}$

ethylene polythene

 $nCH_{2} = CHCl \rightarrow (CH_{2} - CH)_{n}$

Vinyl chloride Cl

Polyvinyl chloride

• **(b) Copolymer:** If a polymer is made up of more than one type of monomers it is called a copolymer

$$n A + m B \longrightarrow A - A - B - B - A - B$$

Depending on the arrangement of the monomeric units, the copolymers may be further classified as

(i) Random copolymers The monomeric units are randomly arranged.

(ii) Alternating copolymers The monomeric units are arranged in an alternating manner.

(iii) Block copolymers The monomeric units are arranged in blocks.

(iv) Graft copolymers They are branched copolymers in which the backbone is formed of one type of monomer and the branches are formed of the other types of monomers.

3. On the basis of chain structure

(i) Linear polymer: no branching (other than the pendant groups associated with the monomer).

well packed, high densities. For example, polythene, nylons, polyesters.

(ii) **Branched polymers**: the monomers are joined to form long chains with side chains or branches of different lengths.

irregularly packed, low densities.

If the side chain is different from parent chain, they are called graft polymers. For example, low-density polyethene, glycogen, etc.

(iii) Cross-linked polymers (network polymers): the monomer units are linked together to form a three-dimensional network.

hard, rigid and brittle. For example, bakelite, vulcanised rubber, etc.

4. Based on chain composition

- (i) Homochain polymer: all carbon atoms along their backbone are called homochain polymers. For example, polyethene, PVC, rubber, etc.
- (ii) **Heterochain polymer**: If the polymeric chain contains a heteroatom, then they are called heterochain polymers. For example, nylon (polymeric chain contains nitrogen atom) and terylene (polymeric chain contains oxygen atom).

5. Based on polymerisation mechanism

- (i) Addition polymers: obtained by the addition of monomeric units.
- The molecular weight of such a polymer is an exact multiple of the molecular weight of the monomer.
- For example, polyethene, PVC, etc.

- (ii) Condensation polymers: formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia and hydrochloric acid.
- The molecular weight of such a polymer is not an exact multiple of the molecular weight of the monomer.
- For example, Nylon 66 is obtained by the condensation of two monomers, hexamethylenediamine and adipic acid with the loss of water molecules.

$$n \operatorname{H}_{2} \operatorname{N} - (\operatorname{CH}_{2})_{6} - \operatorname{NH}_{2} + n \operatorname{HOOC} - (\operatorname{CH}_{2})_{4} - \operatorname{COOH} \xrightarrow{-n \operatorname{H}_{2} \operatorname{O}}$$

$$\overset{\operatorname{O}}{\longleftarrow} \operatorname{NH} - (\operatorname{CH}_{2})_{6} - \operatorname{NH} - \overset{\operatorname{C}}{\longleftarrow} (\operatorname{CH}_{2})_{4} - \operatorname{CO} \xrightarrow{n}_{n}$$

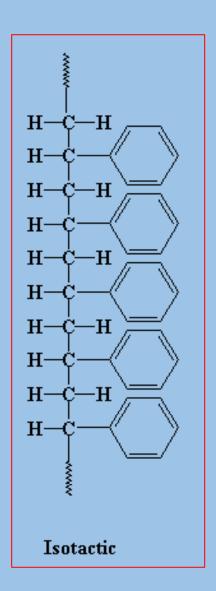
6. Based on molecular forces

- (i) Elastomers: polymers held by weakest intermolecular forces and have elastic behavior.
- These can be stretched to at least thrice their original length but return to their original shape and dimension as soon as the stretching force is removed.
- For example, natural rubber.
- (ii) Fibres: polymers whose polymeric chains are held together by strong intermolecular forces like hydrogen bonds or dipole—dipole interactions.
- They are crystalline in nature and have high tensile strength.
- For example, nylon 66, polyster, silk, etc.

- (iii) **Thermoplastics**: They are linear, long-chain polymers that soften on heating and harden when cooled.
- The intermolecular forces of these polymers are intermediate between those of elastomers and fibres.
- There is no cross-linking between the polymeric chains.
- They can be processed again and again.
- For example, polyethene (PE), polystyrene, PVC, teflon, polypropylene, etc.
- (iv) Thermosetting plastics: They are polymers that can change irreversibly into hard and rigid materials on heating and cannot be reshaped once they set.
- They form hard, infusible, insoluble products because of cross-linkages.
- For example, bakelite, melamine, etc.

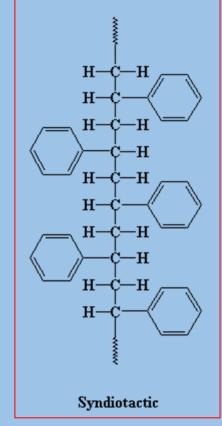
7. Based on tacticity

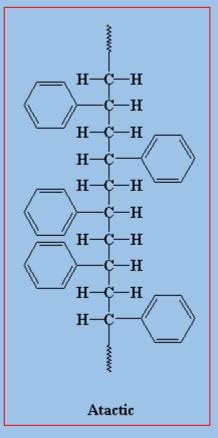
- Tacticity is defined as the spatial arrangement of the substituent groups on the asymmetric carbon atom.
- Based on the orientation of side groups in space the polymers can be of three types:
- (i) **Isotactic polymers**: When the orientation of side groups (R) on all asymmetric carbon atoms is the same.



- (ii) Syndiotactic polymers: When the orientation of the side groups on alternate asymmetric carbon atoms is the same.
- (iii) Atactic polymers: When the side groups have no preferential arrangement and are randomly arranged.

• In general, isotactic and syndiotactic polymers are partially crystalline, whereas atactic polymers are amorphous, indicating the absence of crystalline order.





- 8. Based on degree of polymerisation
- (i) Oligopolymers: Polymers with low degree of polymerisation.
- (ii) Macromolecules: Polymers with a high degree of polymerization.

 They have very high molecular weights.

9. Based on chemical composition

(i) Organic polymers: backbone chain is made mainly of carbon atoms and the side chains consist of oxygen, nitrogen, sulphur, etc.

Examples include polythene, PVC, nylon, etc.

(ii) Inorganic polymers: do not have a carbon backbone chain.

Examples include silicone rubbers, phosphazene, etc.

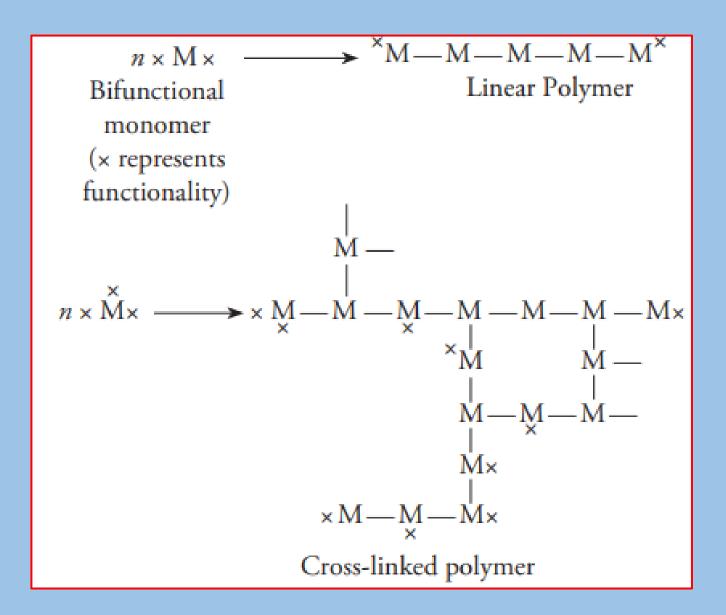
Functionality

- The number of reactive sites in a molecule is termed as its functionality.
- For a molecule to act as a monomer it must have at least two reactive sites, that is, its functionality should be two.
- For example, ethylene can add two molecules of hydrogen or halogen. Hence, it is bifunctional (functionality two).

$$CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$$

- Similarly, acetylene has a functionality of four (tetrafunctional), as it can react with four atoms of hydrogen or halogen.
- Phenol has three reaction sites (2-ortho and one para). It undergoes substitution reaction at these sites. Hence, it is trifunctional.

- If the monomer is bifunctional (ethylene, propylene, vinyl chloride, styrene, etc.), a linear polymer is formed.
- A trifunctional monomer leads to the formation of a crosslinked polymer.
- A mixture of bifunctional and trifunctional monomer may form branched or cross-linked polymer.



Mechanism of Polymerisation

There are two types of polymerisation processes:

- 1. Addition polymerisation or chain polymerisation
- 2. Condensation polymerisation

Addition polymerisation

The monomer molecules are added to each other without the formation of any byproduct.

The elemental composition of polymer is similar to that of the monomer and its molecular weight is an exact multiple of the molecular weight of the original monomeric molecule.

Bifunctional molecules like ethylene, propylene (olefins) generally undergo this type of polymerisation.

Addition polymerisation consists of three important steps:

- (i) Chain initiation: This step involves the formation of active molecules called chain initiators.
- These chain initiators then attack the monomer to initiate the chain formation.

(ii) Chain propagation The initiated chain then attacks more monomeric molecules leading to the increase in the length of the chain.

Hence the polymeric chain propagates.

(iii) Chain termination The active centers are removed or they combine with each other and the chain propagation comes to an end.

$$I - M - M - M^{\dagger} + \dot{M} - M - I \longrightarrow I - M - M - M - M - M - I$$

The addition polymerization reaction can take place by three methods.

- 1. Free radical mechanism
- 2. Ionic mechanism (anionic and cationic)
- 3. Coordination mechanism
- 1. Free radical addition polymerization: It has three steps:
- (i) Chain initiation step: It involves the formation of free radicals in the initiation step.

The free radicals are formed as a result of homolytic dissociation of the initiator in the presence of heat, light or catalyst.

Commonly used free radical initiators are azo compounds (- N N-), disulphides (- S - S -), peroxides (- O - O -), hydroperoxides peracids and peresters.

• An important example of a free radical initiator is benzoyl peroxide that dissociates as follows:

$$C_6H_5$$
 C_6H_5 C_6H_5 C_6H_5 C_6H_5 C_6H_5 C_6 C_6

Here, half arrow (\(\sigma \)) represents single electron shift. In C₆H₅, the dot (\(\bullet \)) represents single electron.

In general, the dissociation of the initiator (I—I) to form free radical species can be represented as

In the second step of initiation, a monomer molecule (M) is attached to the initiator radical. Considering vinyl as the monomer, this step can be represented as

$$I' + CH_2 = CH \longrightarrow I - CH_2 - \dot{C}H$$
 X

(Monomer)

X

(Initiated monomer species)

(ii) Chain propagation step In this step, the initiated monomer species adds additional monomer units as follows:

$$I-CH_2-\dot{C}H+\dot{CH_2}=\dot{C}H \longrightarrow I-CH_2-CH-CH_2-\dot{C}H$$

$$X X X X X X X X$$

The propagation continues until the chain growth is stopped by <u>some impurities</u> or by <u>termination process</u> or till there is <u>no further monomer</u> left for attack.

The structure of the growing chain can be represented as

n and the wavy line both denotes the number of monomeric units added up in the chain. If the CH₂ part of monomeric chain is called head and CH X part is termed as tail, then four modes of addition can take place.

(i)
$$\longrightarrow$$
 CH₂— $\overset{.}{C}$ H+CH₂= $\overset{.}{C}$ H \longrightarrow CH₂— $\overset{.}{C}$ H \longrightarrow Head to tail X

(ii) \longrightarrow CH₂— $\overset{.}{C}$ H+CH= $\overset{.}{C}$ H+ $\overset{.}{C}$ H= $\overset{.}{C}$

- (iii) <u>Chain termination</u>: This is the last step of polymerization process where the growth of the chain is arrested. It can occur as follows:
- (a) By coupling: As the decomposition of the initiator produces many free radicals at the same time, many chains are initiated and propagated simultaneously.

The two growing chains can come close, collide and get deactivated.

(b) By disproportionation: The hydrogen from one growing chain is abstracted by the other growing chain and results in the formation of two polymer molecules, one saturated and the other unsaturated.

Contrary to the first type where a long-chain polymer is obtained, by this method we obtain two polymer molecules of shorter chain length.

The products formed do not contain any reactive sites and may be termed as 'dead' polymer chain.

$$I = \begin{bmatrix} CH_2 - CH + CH_2 - CH + CH_2 + CH - CH_2 \end{bmatrix} \begin{bmatrix} CH_2 - CH_2 - CH_2 \end{bmatrix} \begin{bmatrix} CH_2 - CH_2 \end{bmatrix} \begin{bmatrix} CH_2 - CH_2 + CH_2 \end{bmatrix} \begin{bmatrix} CH_2 - CH_2 + CH_2 \end{bmatrix} \begin{bmatrix} CH_2 - CH_2 + CH_2 \end{bmatrix} \begin{bmatrix} CH_2 - CH_2 \end{bmatrix} \begin{bmatrix} CH_2 - CH_2 + CH_2 \end{bmatrix} \begin{bmatrix} CH_2 - CH_2 \end{bmatrix} \begin{bmatrix} CH_2 -$$

(c) Chain transfer: The growth of one polymer chain is stopped forming a dead polymer but there is simultaneous generation of a new free radical capable of initiating a fresh polymer chain growth.

This reaction takes place by hydrogen abstraction from either solvent or some impurities present in the system.

The chain can also be terminated by the addition of certain compounds, which are called inhibitors.

E.g. Hydroquinone, nitrobenzene and dinitrobenzene

$$R + CH_{2} - CH + CH_{2} - \dot{C}H + SH \longrightarrow R + CH_{2} - CH + \dot{S}H_{2} - CH_{2} + \dot{S}H_{2} + \dot{S}H_{2} + \dot{S}H_{3} + \dot{S}H_{4} + \dot{S}H_{5} + \dot{S}H_{5}$$

2. Ionic addition polymerization: It follow the same basic steps.

The chain is initiated either by a carbocation or carbanion.

(i) Cationic polymerization

In this mechanism, the reaction is initiated by an electrophile resulting in the formation of a carbocation as intermediate.

The reaction can be terminated by a nucleophile.

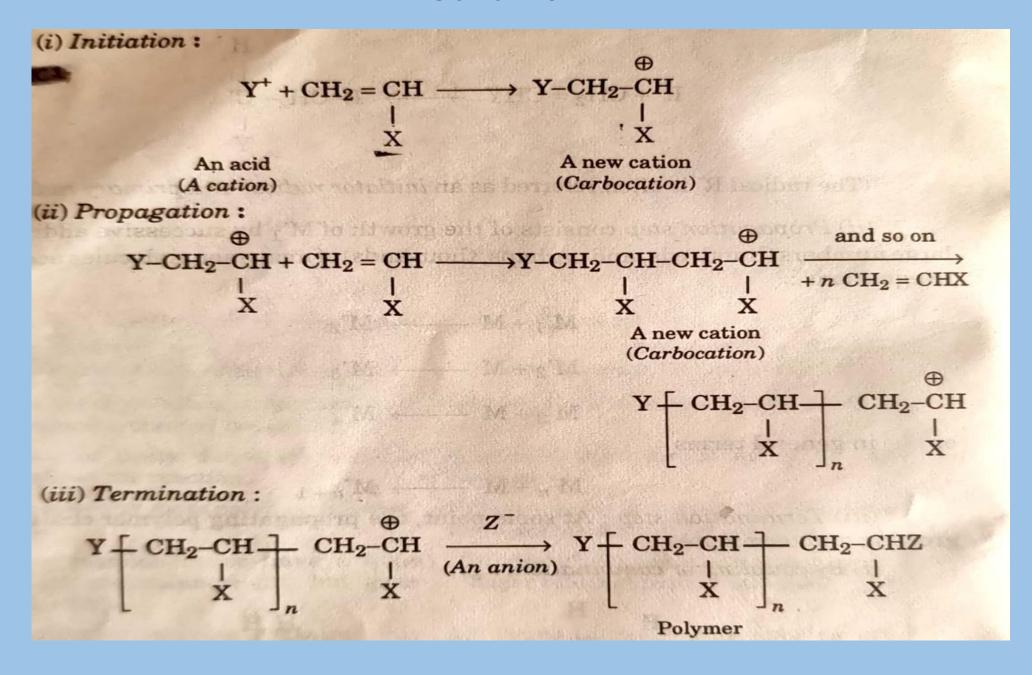
In this reaction,

Initiator is Electrophile,

Intermediate is Carbocation,

Inhibitor (Terminator) is Nucleophile.

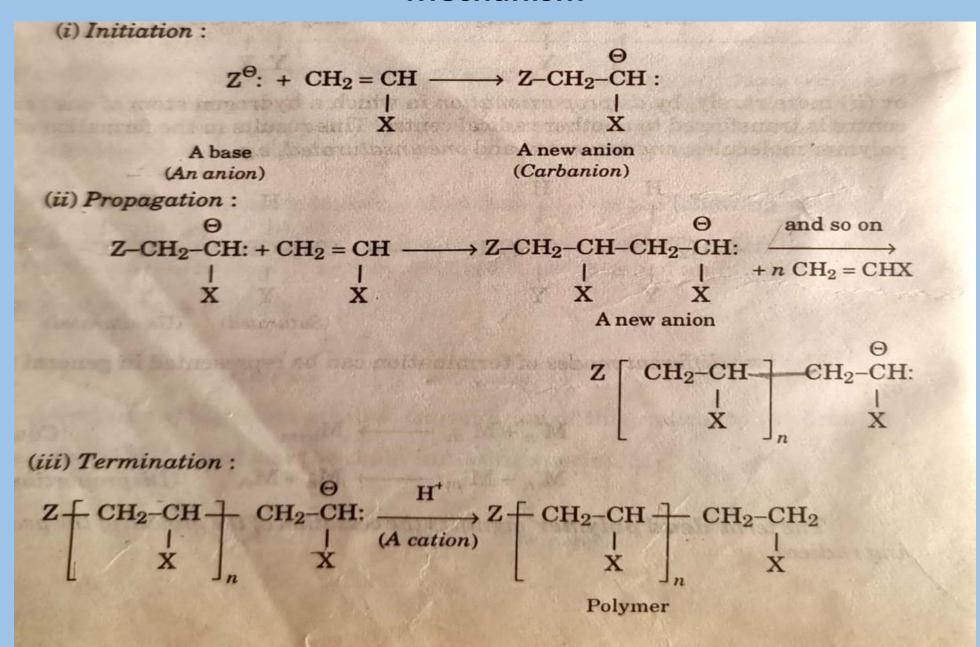
Mechanism



(ii) Anionic polymerization

- The reaction is initiated by a nucleophile resulting in the formation of a carbanion as intermediate.
- The reaction can be terminated by an electrophile.
- In this reaction,
 - Initiator is Nucleophile,
 - Intermediate is Carbanion,
 - Inhibitor (Terminator) is Electrophile.

Mechanism



3. Coordination Polymerization:

It is another variant of addition polymerization which is neither free radical nor simply ionic.

The monomers with side groups are attached to the growing chain in a highly defined spatial arrangement (stereoregular).

The significant feature of this mechanism is the ability to orient each monomer and join it to the growing polymer chain in a very specific configuration.

These are polymerization reactions taking place in the presence of organometallic compounds as catalysts.

Karl Ziegler (1953) and Giulio Natta (1955) discovered that an organometallic compound in combination with transition metal halide (Titanium tetrachloride $TiCl_4$ and Titanium(III) chloride $TiCl_3$) can be used to prepare stereospecific polymers.

The commonly used Ziegler–Natta catalyst is triethylaluminium in combination with titanium trichloride or titanium tetrachloride.

$$Cat-R' + CH_2 = CHR \longrightarrow Cat-CH_2CH(R)R'$$

(Complex catalyst) (Monomer)

Propagation:

Cat-CH₂-CH-R' +
$$n$$
 CH₂ = CHR' \longrightarrow Cat-CH₂-C $+$ CH₂-CH \longrightarrow R'
R

Termination (with active hydrogen compound):

$$\begin{array}{c} \text{Cat-CH}_2\text{-CH} \leftarrow \text{CH}_2\text{-CH} \rightarrow \text{R'} + \text{HX} \longrightarrow \text{Cat-X} + \text{CH}_3\text{-CH} \leftarrow \text{CH}_2\text{-CH} \rightarrow \text{R'} \\ \downarrow \\ R & R & \end{pmatrix}_n \end{array}$$

Condensation polymerization / Step polymerization

The polymerization reaction proceeds step by step through reaction between the functional groups of the monomers with the removal of small molecules like water.

For example, consider the formation of Nylon 6, 6:

Nylon 66 is obtained by the condensation of two monomers, hexamethylenediamine and adipic acid with the loss of water molecules.

nHO
$$-$$
 C $-$ (CH₂)₄ $-$ C $-$ OH $+$ nH₂N $-$ (CH₂)₆ $-$ NH₂ \longrightarrow

Adipic acid Hexamethylene diamine
$$\begin{bmatrix}
O & O \\
- C - (CH2)4 - C - NH(CH2)6 - NH \\
- C - (CH2)4 - C - NH(CH2)6 - NH \\
- C - (CH2)4 - C - NH(CH2)6 - NH \\
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- (CH2)4 - C - NH(CH2)6 - NH \\
- (CH2)4 - C - NH(CH2)6$$

Addition Polymerization	Condensation Polymerization
Eg. PVC	Eg. Nylon 6,6
Otherwise known as "Chain growth	Otherwise known as "Step wise
Polymerization".	Polymerization".
Monomers are adding together to form polymers.	Monomers are condensed to form polymer.
No elimination of other molecules.	Elimination of smaller molecules occur.
At least one multiple bond presence is essential	Monomers must have two or more functional
condition.	groups.
Homo polymers are formed.	Hetero polymers are formed.
Thermoplastics are formed.	Thermo set plastics are formed.
Molecular weight of the polymer is the integral	Need not be so.
multiple of monomers.	
Monomers disappear slow and steadily.	Monomers disappear at the initial stage of the
	reaction.
Longer processing time is needed to increase	Longer time is essential for increasing
yield.	molecular weight.

Plastics

 The term 'plastic' refers to the class of polymers that can be shaped into hard and tough utility articles by the application of heat and pressure.

The reason for using plastics over metals is:

- They are light in weight and at the same time possess good strength, toughness and rigidity.
- They are corrosion-resistant and also resist the action of chemicals.
- They are less brittle than glass and can be made equally smooth and transparent.
- They do not absorb moisture.
- They can be easily molded into desired shape.
- They can take a variety of colors, are heat-resistant and abrasion-resistant, and have good dimensional stability.
- Their maintenance cost is low.

Thermoplastics

- They are plastic materials that soften on heating and can be molded into desired shape.
- On cooling, they become hard. However, they can be resoftened and remolded by the application of heat and pressure.
- The reason for resoftening of thermoplastic is that they are composed of linear or long-chain molecules.
- On heating the intermolecular bonds weaken, the material softens and thus can be molded again without any damage.
- Common examples of thermoplastics are polyethene, polypropylene, polystyrene, teflon, polyamides, etc.

Thermosetting plastics

- They are those plastic materials that, when subjected to heat and pressure, change into a hard and rigid substance. Once they set, they cannot be softened again by the application of heat.
- The reason is that during molding they acquire three-dimensional cross-linked structure.
- Such three-dimensional polymers will not soften when heated but may decompose or disintegrate at high temperatures.
- Common examples are bakelite, melamine formaldehyde, epoxy resins, etc.

THERMOPLASTICS	THERMOSETTING PLASTIC
Eg.PVC, Polyethylene	Polyester, Bakelite
Plastics which are melted at high	They cannot be remoulded after their first
temperature, solidified at low temperature	usage.
They can be remelted and remoulded into	
any desired shapes for any number of times.	
Scrap can be used again.	Scrap cannot be used again.
Formed by addition polymerization	Formed by condensation polymerization
The bond strength is low	The bond strength is high
Molecular weight is low	Molecular weight is high
Soluble in organic solvents.	Insoluble in organic solvents.
Prepared by Injection moulding	Prepared by compression moulding.
They have linear structure	They have complex 3D structure.

Molding constituents of a plastics

- 1. **Resin**: These are substances that hold the different constituents together. Usually thermosetting resins are used.
- 2. Plasticizers: These materials increase the plasticity and flexibility.

They neutralize the intermolecular forces of attraction and impart greater freedom of movement between the polymeric macromolecules.

Commonly used plasticizers are vegetable oils, camphor, esters (of stearic, oleic or phthalic acids) and phosphates like tricresylphosphate.

3. **Fillers**: These are added to improve the hardness, tensile strength, opacity and workability of the plastic.

For example, addition of carbon black to natural rubber increases its tensile strength and makes it abrasion-resistant.

Addition of asbestos to a plastic material provides heat and corrosion resistance.

- 4. **Lubricants**: Lubricants like waxes, oils and soaps prevent the plastic material from sticking to the mold. They also impart flawless, glossy finish to the final products.
- 5. **Catalysts or accelerators**: They are added to accelerate the polymerization process. They are particularly used for thermosetting plastics. Commonly used catalysts are hydrogen peroxide, benzoyl peroxides, metals like Ag, Cu and Pb and oxides like ZnO.
- 6. **Stabilizers**: They improve the thermal stability during processing. For example, vinyl polymers. Commonly used stabilizers are salts of lead and stearates of lead, cadmium and barium.
- 7. **Coloring materials**: Organic dye stuffs and opaque inorganic pigments are commonly used to impart color to the plastic products.

Plastic molding processes

• Plastic materials supplied in granular, powder or other forms are molded into articles by various methods.

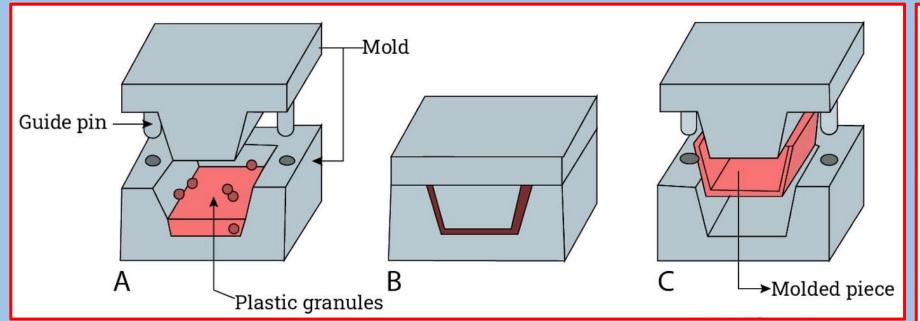
The commonly used methods are as follows:

- (a) Compression molding
- (b) Transfer molding
- (c) Injection molding
- (d) Extrusion molding



Compression molding

- It is widely used to produce articles from thermosetting plastics.
- It is used for manufacturing electrical parts such as switches, switch boards, cooker handles, etc.
- The mold used for the purpose is made up of two halves.
- The upper half has a projection, whereas the lower half has a cavity.
- The material to be molded is placed in the lower cavity and is heated continuously by steam or electricity.
- The movable bolster is raised so that the lower mold portion contacts the upper die, which is also heated.
- As the mold closes down under pressure, the excess material flows out of the mold as flash.





- Under the influence of heat, the compacted material gets cured and hardened.
- The mold is opened while it is still hot to release the molded product.



Transfer molding

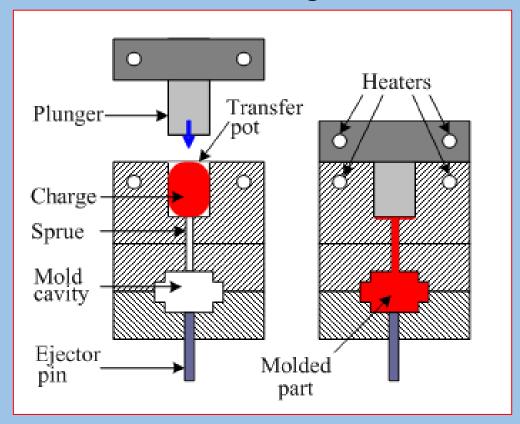
It is used for molding thermosetting materials.

The molded material is preheated and loaded into a chamber known as the pot.

A plunger (piston) forces the molten material into the mold cavities through channels known as sprue and runner system.

The mold remains closed as the material is inserted.

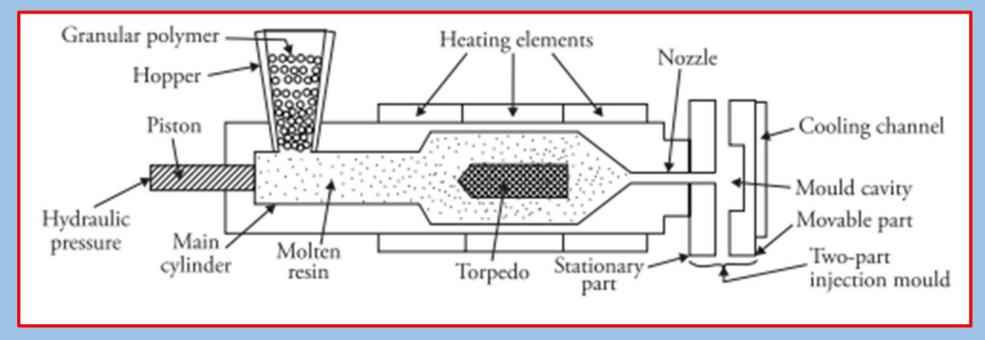
The molten material sets, gets cured and is released by opening the mold.





Injection molding

• It is used for producing articles made of **thermoplastic** materials like mugs, buckets, dust bins, chairs, etc.



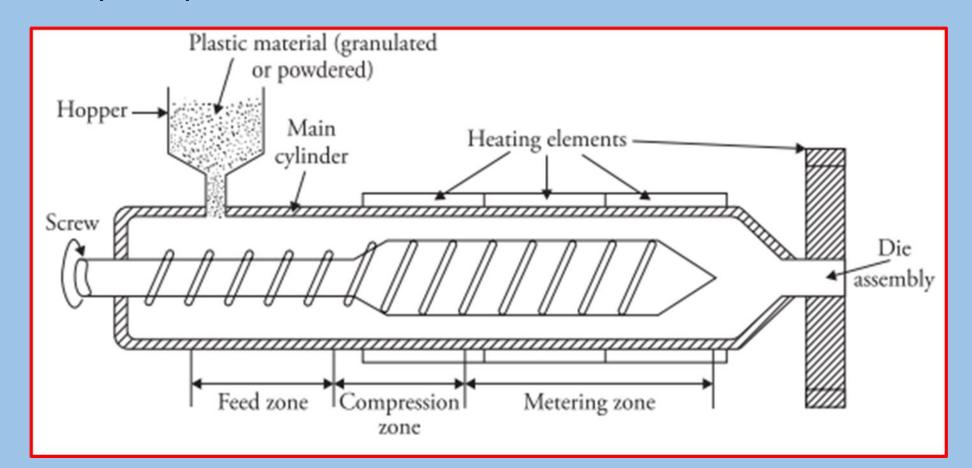
- The mold consists of a two-part system; one part is movable and the other is stationary.
- The stationary part is fixed to the end of the cylinder, whereas the movable part can be opened or closed on to the stationary part.

- In this process, a correct amount of plastic material as granules, pellets or powder is fed from the hopper into the cylinder.
- The piston pushes the plastic material into the heating chamber where it melts to form a viscous liquid.
- Again with the help of the piston the molten plastic material is injected through the nozzle into the mold cavity.
- Pressure is maintained in the mold cavity.
- The material is cooled by water circulation.
- It solidifies.
- Finally, the mold is opened, the piece is ejected, the mold is closed and the entire cycle is repeated.
- The most outstanding feature of this technique is the speed with which the pieces may be produced.



Extrusion molding (for Thermoplastics)

- This method is used for making elongated and continuous articles such as rods, pipes, tubes, hose pipes, filaments and sheets.
- An extruder resembles the injection molding apparatus, except that the mold cavity is replaced with a die.



- In this process, the compounded plastic material in the form of powder or granules is fed into the electrically heated cylinder using a hopper.
- A helically rotating screw inside the cylinder further works the plastic charge.
- During the journey from hopper to the die, the plastic material passes through three zones namely feed zone, compression zone and metering zone.
- The feed zone receives the charge from the hopper.
- No heating takes place in the feed zone.
- In the compression zone, the powdered charge melts because of heating and compression by the moving screw.
- The pasty molten mass enters the metering zone.
- The pressure in this region enables the molten polymer to enter the die and come out of it with the desired shaped.
- The material extruded out of the die is quite hot (usually 125–350 °C) and is carried over the conveyor belt through a tub containing cold water.

- The process of extrusion is also used for coating wires and cables with PVC or rubber.
- This method gives products of good surface finish and dimensional stability.



Thermoplastic Resins: Polyethylene (Polyethene)

- The most popular plastic in the world (34%).
- Prepared by injection moulding
- The most common types of polyethylene are:
- Low-density polyethylene (LDPE)
- High-density polyethylene (HDPE)
- Linear low-density polyethylene (LLDPE)
- Very-low-density polyethylene (VLDPE)
- Ultra High-molecular-weight polyethylene (UHMWPE)
- Among the above 5 forms of polyethylene, the two most common kinds of PE are HDPE and LDPE.
- Prepared by the addition polymerization of ethylene.

(a) Low-density polyethene (LDPE)

 Preparation: Polymerization of ethylene at high pressure (1000–3000 atmospheres) at 250 °C in the presence of free radical initiators like benzoyl peroxide. Traces of oxygen catalyze the reaction.

$$n(CH_2 = CH_2)$$
 $\xrightarrow{1000-3000 \text{ atmosphere}}$ $+(CH_2 - CH_2)_n$ $\xrightarrow{\text{free radical initiators like benzoyl peroxide and traces of } O_2}$ $+(CH_2 - CH_2)_n$

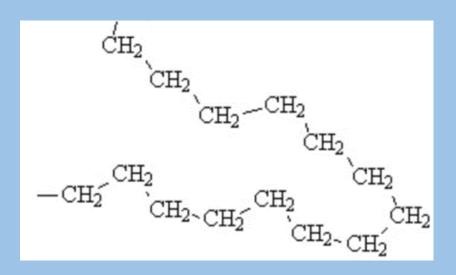
- Properties: It is a waxy solid that floats on water and has a linear branched structure. It is produced through a single monomer, ethylene which makes it a homopolymer.
- The chemical structure of LDPE includes many short branches and is composed of 4,000-40,000 carbon atoms. Its molecules are more loosely packed than other variants of Polyethylenes.

- The branches do not allow the chains to pack efficiently; hence, its density is low (0.91–0.925 g/cm³).
- It is not polar and has weak intermolecular forces. It is tough, flexible, chemically inert and has excellent electrical insulation properties.
- Applications: It is used for storing a variety of foodstuffs. It is used for making carrier bags, films for general packing, molded toys, mugs and ink tubes for pens.

- (b) High-density polyethylene (HDPE):
- Preparation:

Ethylene is polymerized under 6–8 atmospheric pressure at 60–70 °C in the presence of Ziegler–Natta catalyst (triethylaluminium and titanium tetrachloride).

- Properties:
- The polymeric chains are linear and hence they pack easily. Hence, it has high density (0.95–0.97 g/cm³).
- It is more stiff, hard and has greater tensile strength compared with LDPE.
- Its softening temperature is high (135 °C).



- It has excellent electrical insulation properties, has low water and gas permeability, has excellent chemical resistance and is free from odor and toxicity.
- Applications:
- It is used for making insulations, pipes, bottles for milk, household chemicals and drug packing.
- It is also used for the manufacture of crates, industrial containers and overhead tanks.
- HDPE sheets are used for packing materials and for making toys.

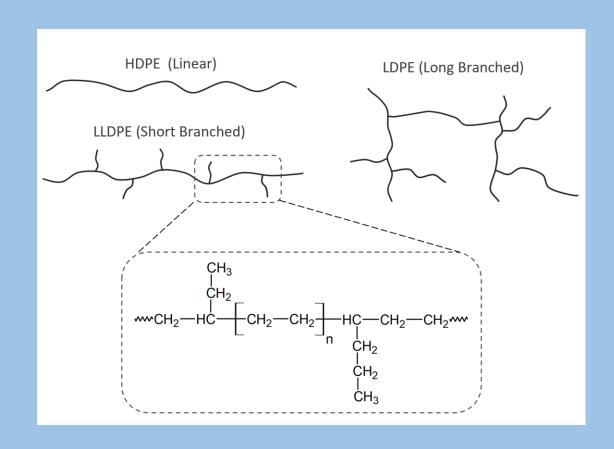


^{*}LDPE is represented by code 4

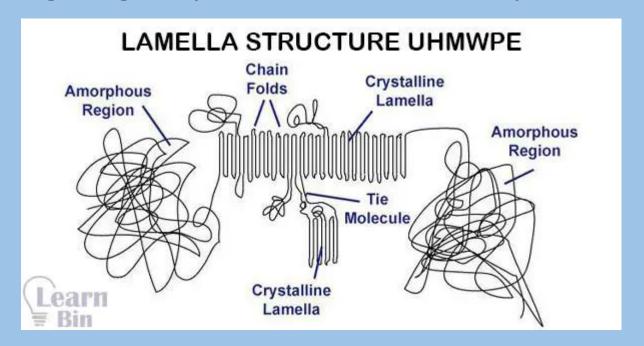
^{*}HDPE is represented by code 2

^{*}Both are considered to be safe plastics for recycling and hence, are represented with green.

- (c) Linear low-density polyethylene (LLDPE):
- It is actually a copolymer of ethylene and 1-butene manufactured with Ziegler-type catalysts.
- It requires considerably less energy to produce than LDPE.
- Uses:
- golf ball covers,
- orthopedic devices,
- blending with LDPE,
- packing films and bottles.



- (d) Ultrahigh molecular-weight polyethylene (UHMWPE):
- It is a linear (non-branching) semi-crystalline polymer which can be described as a two phase composite of crystalline and amorphous phases.
- The crystalline phase contains chains folded into highly oriented lamellae, with the crystals being orthorhombic in structure.
- Uses:
- It is used in making surgical prostheses, machine parts, heavy-duty liners.



Polypropylene (second most popular plastic in the world, 16%)

composed of an average of 5,000 to 20,000 monomer units

Obtained by polymerizing propylene in presence of Zeigler-Natta catalyst (to

get isotactic structure)

Properties:

- low density, high stiffness, heat resistance, chemical inertness
- good transparency, good impact/rigidity balance, stretchability, high gloss
- easy to weld, recyclability, good hinge property (for example where a lid and box are made together, for DVD boxes)

Uses: Molded parts, fibers for ropes, carpets, furniture, bags, water-pipes, sterilizable hospital equipment, etc.

Polyvinylchloride (third most popular plastic in the world 12%)

• It is prepared by radical polymerization of vinyl chloride to produce material composed of an average of 10,000 to 24,000 monomer units. It is atactic and therefore amorphous

$$H-C = C-H + HCl \longrightarrow H Cl \longrightarrow H H H$$

$$H-C = C \longrightarrow H Cl \longrightarrow H Cl$$

$$Vinyl chloride poly(vinyl chloride)$$

- Colorless, odorless, non-inflammable, chemically inert, resistant to light, inorganic acids and alkalis, oxygen
- Rigid PVC: high rigidity and chemical resistance, brittle. Used for making sheets
- <u>Plasticized PVC</u>: Plasticizers are often based on esters of poly carboxylic acids with linear or branched aliphatic alcohols of moderate chain length.

Applications: Window frames, floor and wall coverings, roofing sheets, water pipes and fittings, ducts for power and telecommunications.

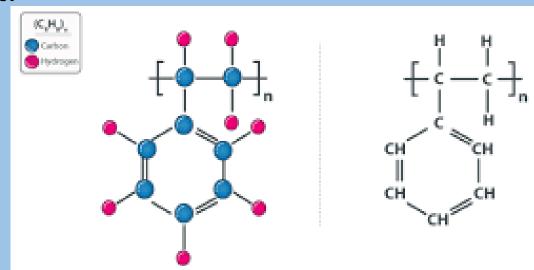
- Packaging of pharmaceuticals, water and fruit juices.
- Medical products, including blood bags, transfusion tubes and surgical gloves.

Polystyrene (9%)

Polystyrene exists in an amorphous state due to the presence of bulky phenyl groups.

 prepared by polymerization of styrene (dissolved in ethyl benzene) in presence of benzoyl peroxide as catalyst.

• PS is light, transparent, excellent moisture-resistant, electric insulating, resistant to acids, low softening range, brittle, transmits light through curved sections.



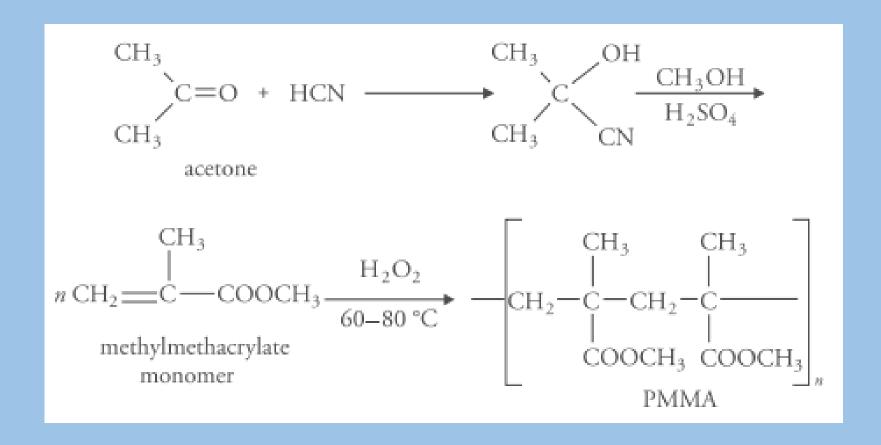
- General purpose polystyrene clear, hard and brittle.
- <u>High Impact Polystyrene</u>: Polystyrene containing a polybutadiene rubber is opaque or translucent rather than transparent.



- Applications of Polystyrene
- 1. Polystyrene is used in making 'throw away' drinking cups, soft drinks, and baby feeding bottles.
- 2. By adding color and filler, it can be used for making toys and household items.
- 3. When gas is blown into Polystyrene liquid, it foams and hardens to form styrofoam which is used for making ice chests and disposable coffee cups.
- 4. Polystyrene is also used as packing material for shipping instruments and appliances, and it is widely used for home insulation.
- 5. Medically it is used for sterilizing test tubes, diagnostic components, and other medical devices.

Polymethylmethacrylate (PMMA)

• It is manufactured by the polymerization of methylmethacrylate monomer in the presence of free radical catalyst hydrogen peroxide at 60–80 °C. The mechanism is as follows:



- Properties:
- It is also known as plexi glass.
- It is colorless, transparent, amorphous and has good strength.
- Although chemically inert, it dissolves in organic solvents such as ketones, chlorinated hydrocarbons and esters.
- Applications:
- Its optical transparency is better than that of glass. Hence, it is an excellent substitute for glass. It is used for the manufacture of contact lens, spectacles and windscreens.
- Because of its good mechanical properties it is used for the manufacture of cockpit canopies, attractive signboards and for decorative purposes.
- It has high weather resistance. It does not turn yellow or crumble when exposed to sunlight. It is used for making transparent windows, aquariums, tail-lights of automobiles, bathtub liners, sinks, cell phone display screens.

Polytetrafluoroethylene (PTFE) (Teflon)

• It is prepared by the polymerization of tetrafluoroethylene at high pressure in the presence of ammonium persulphate as catalyst.

$$CH_2 Cl_2 + 2HF$$

Methylene chloride

$$CHF_2 Cl + HCl$$

Difluorochloro methane

$$2CH F_2 Cl \xrightarrow{-2HCl} CF_2 = CF_2$$

Tetrafluoroethylene (Monomer)

The monomer is polymerised using ammonium persulphate as initiator.

$$n(CF_2 = CF_2) \xrightarrow{\text{High pressure} \atop (NH_4)_2 S_2O_8} (CF_2 - CF_2)_n$$
Teflon

- Properties:
- It is a linear polymer with practically no branching. It has high mechanical strength and is chemically inert.
- Its softening temperature is high (350 °C).
- It does not dissolve in acids, including fuming nitric acid, and is also resistant to the attack of corrosive alkali and organic solvents.
- Applications:
- It is used for making articles like pump valves and pipes where chemical resistance is required.
- It is used for manufacturing insulations for motors, transformers, capacitors, electrical cables, etc.
- It is also used for making gaskets, gas seals, non-sticking stopcocks for burette and for making Teflon coated non-stick utensils.

Polyvinyl acetate (PVA)

 It is obtained by heating vinyl acetate in the presence of small amount of benzoyl peroxide.

$$\begin{array}{c}
n \text{ CH}_2 = \text{CH} - \text{COOCH}_3 \\
\text{Vinyl acetate}
\end{array}$$

$$\begin{array}{c}
\text{Polymerisation} \\
\text{CH}_2 - \text{CH} \\
\text{COOCH}_3 \\
\end{array}$$

$$\begin{array}{c}
\text{Polyvinyl acetate (PVA)}
\end{array}$$

- The polymer can be prepared by bulk, emulsion or solution polymerization methods.
- Properties:
- PVA is a solid resin that is insoluble in water but is soluble in aromatic solvents and also in alcohols and esters.
- It is saponified with great difficulty and is not absorbed by the digestive system.
- It is resistant to atmospheric air, water and chemicals.

- Uses:
- It is used in adhesives, lacquers, paints and for large-scale manufacture of gramophone records.
- Polyvinyl acetate adhesives are used for bonding textile to textile, leather to leather, paper to textile, etc.
- Polyvinyl acetate is used as a basic material for chewing gums and surgical dressings.
- On copolymerization with polyvinyl chloride, it is converted into a soft polymer, vinylite, which is used as a surface-coating material for metals.
- Polyvinyl acetate is mainly used for the manufacture of polyvinyl alcohol.

Nylon 6:6 (Polyamide)

- Nylon 6:6 is made of two monomers each containing 6 carbon atoms, hexamethylenediamine and adipic acid, which give nylon 6:6 its name.
- High mechanical strength, rigidity, good stability under heat and/or chemical resistance
- Used in fibres for textiles and carpets and moulded parts,
- In automotive applications-"under the hood" parts such as radiator end tanks, rocker covers, air intake manifolds, and oil pans
- Hinges and ball bearing cages
- Electro-insulating elements, pipes, profiles, various machine parts, zip ties, conveyor belts, hoses, polymer-framed weapons, Parachutes

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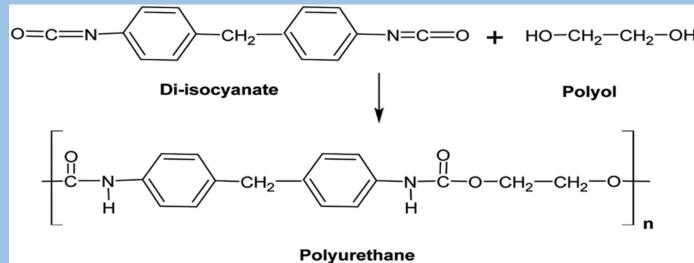
Kevlar

- Exceptionally strong
- Due to many inter-chain bonds. These inter-molecular hydrogen bonds form between the carbonyl groups and NH centers.
- Additional strength –Due to aromatic stacking interactions between adjacent strands.
- Structure consists of relatively rigid molecules which tend to form mostly planar sheet-like structures.
- Armor like helmets, ballistic vests and face-masks, safety clothing for motorcycle and sports like archery, ropes, aerospace industry

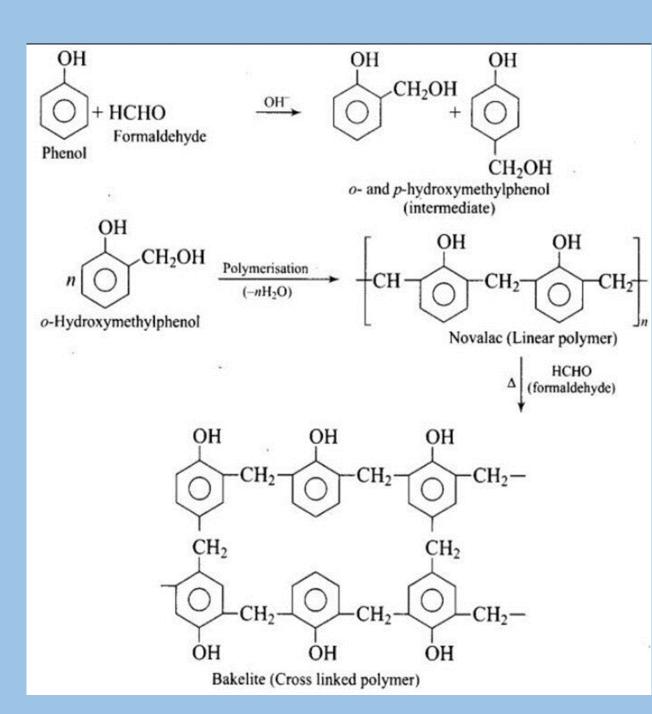
Thermosetting Resins, Polyurethane

Prepared by treating diisocyanate with diol.

- Resilient, flexible and durable.
- Affordable, safe and sustainable.
- Uses:
- Building insulation.
- Refrigerators and freezers.
- Furniture and bedding.
- Footwear.
- Automotive.
- Coatings and adhesives.



- Bakelite: Phenolic resins (thermosetting)
- Prepared by condensing phenol with formaldehyde in presence of acidic /alkaline catalyst → o- and p- hydroxy methyl phenol → linear polymer Novolac
- During moulding, hexamethylene tetramine is added → cross-linked Bakelite



- Properties:
- It can be moulded very quickly, which decreases production time.
- Mouldings are smooth, retain their shape and are resistant to heat, scratches, and destructive solvents.
- It is resistant to electricity.
- It is not flexible.
- It is rigid, hard, scratch-resistant.
- It may swell slightly under conditions of extreme humidity
- When rubbed or burnt, it has a distinctive, acrid, sickly-sweet or fishy odour.

USES

- Electrical insulator parts, like switches, plugs, boards, etc.
- Moulded articles like telephone parts, cabinets for T.V., radio etc.
- As adhesives, paints, varnishes, resins for water-treatment

Silicone resins They are inorganic polymers containing alternate silicon—oxygen structure. Organic radicals are attached to the silicon atoms.

$$\begin{array}{c|cccc}
R & R & R & R \\
 & & & & \\
R & & & \\
R & & & \\
R & & & & \\
R & &$$

where R = alkyl or phenyl radical.

Preparation

(i) By the reactions of alkyl halide with silicon.

$$CH_3Cl + Si \longrightarrow CH_3SiCl_3$$
; $(CH_3)_2SiCl_2$
(methyl chloride) (silicon)

(ii) Reaction of silicon halide with Grignard's reagent

Mixture of organosilicon chlorides is obtained, which is separated by fractional distillation and polymerised by controlled hydrolyis.

- Properties
- Silicones are water repellent and chemically inert.
- They are resistant to oxidation, thermal decomposition and attack by organic reagents.
- They are also good electrical insulators and antifoaming agents.
- Uses
- Their viscosities do not change with temperature; hence, they are used for making all weather lubricants.
- They are used for coating papers, textiles and wools to make them waterproof.
- They are used as antifoaming agents in industries.
- Silicones are also added to paint for resisting dampness and for waterproofing.
- Owing to their water-repellant nature and high dielectric constant, they also find use in electrical condensers.

Polymer composites

- They are mixtures of two materials that result in synergistic properties.
- Most polymer composites consist of:
 - Continuous phase or matrix which is typically the resin or polymer phase Discontinuous phase with is typically a reinforcement (such as glass or carbon fibers, silica fillers, etc.)
- They can be made with either thermoset and thermoplastic resin matrices.
- Composites can be categorized into two main types; advanced composites and engineering composites.
- The main differences between the advanced and engineering composites is typically cost and performance.
- The beauty of the composite approach is to be able to tailor the performance to the required cost targets.
- High performance aerospace composites deliver very high performance (good fracture toughness and fatigue resistance, high modulus, low weight) but are expensive from a raw materials perspective (carbon fiber or Kevlar fibers along with high performance matrix resins) and complex parts require a sophisticated manufacturing processes such as autoclave or resin infusion.

- Advantages
- Lightweight (potentially very high strength-to-weight ratio)
- High modulus and glass transition temperatures
- Ability to tailor properties for a wide range of applications
- Good fatigue resistance
- Easy to mould and bond to a variety of substrates or other composites
- Low thermal expansion (along with ability to tailor the CTE in the X, Y, and Z direction)
- Tailorable electrical properties
 - Insulating composites with non-conductive fillers such as glass fibers and silica fillers
 - Conductive composites using silver flake or powders

DISADVANTAGES:

- Advanced composites have a high cost of raw materials
- Complex manufacturing processes are typically required to ensure low voids and porosity
- Long development times
- Low ductility
- Damage susceptibility and the potential for hidden damage (hard to inspect)
- Need careful resin selection to minimize moisture and solvent attack