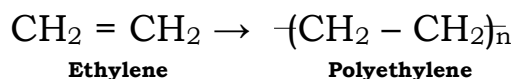


Unit II

POLYMER SCIENCE

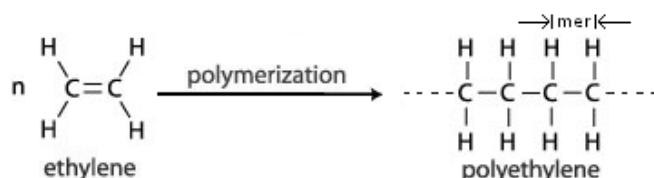
POLYMERS - Introduction

Polymers are large molecules composed of repeated chemical units. The smallest repeating unit is called **monomer** (mono [Single] + mer [part]). The word polymer is derived from the Greek word 'poly' = many; mers = parts. It is generally described in terms of single repeated units such as

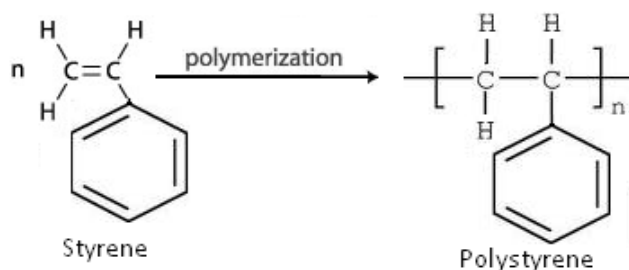


Definition: Polymer is a macromolecule built-up by linking together of a large number of smaller molecules called monomers.

Eg: Polyethylene is a polymer formed by linking together of a large number of ethylene molecules.



The process by which the simple molecules (monomers) are converted into polymers is called **“polymerization”**.



Degree of polymerization

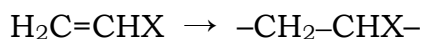
The number of repeating units (n) in a polymer chain is called **degree of polymerization (DP)**.

Eg: If 100 molecules of ethylene polymerize to give the polymer chain, the DP of ethylene is 100.

Functionality

“The number of bonding sites (or) reactive sites or functional groups present in a monomer molecule is called **Functionality**”. For a substance to act as a monomer, it must have at least two reactive sites or bonding sites.

For example, the double bond in vinyl monomers ($\text{CH}_2 = \text{CHX}$) can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.



Monomer	Functionality
Vinyl compounds (C=C)	2
Glycerol (CH ₂ OH-CHOH-CH ₂ OH)	3
Adipic acid (COOH-(CH ₂) ₄ -COOH)	2
Phenol (C ₆ H ₅ OH)	3

Classification of Polymers

Polymers can be classified in several ways.

1. Classification based on the origin or based on source:

a) Natural polymers – They are polymers that occur in nature.

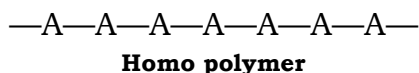
Eg: Starch, cellulose, proteins, nucleic acids, natural rubber, etc.

b) Synthetic polymers – They are polymers that are prepared artificially in the laboratory..

Eg: Polyethylene (PE), Polystyrene (PS), PVC, nylon, terylene, bakelite, etc.

2. Classification based on type of monomers used:

a) Homopolymer – If a polymer consists of identical monomers, it is termed as **homopolymer**.



Eg:

Monomers	Polymers
Vinyl chloride	Polyvinyl chloride (PVC)
Ethylene	Polyethylene (PE)
Styrene	Polystyrene (PS)

b) Copolymer – If a polymer is made up of more than one type of monomers it is called a **copolymer**.

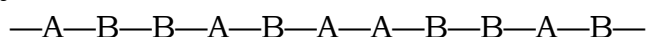


Eg:

Monomeric units	Polymer
Styrene – butadiene	Styrene Butadiene rubber (SBR)
Styrene isoprene	Styrene Isoprene rubber (SIS)

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

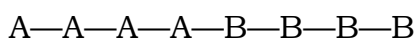
i) Random copolymers – The monomeric units are randomly arranged.



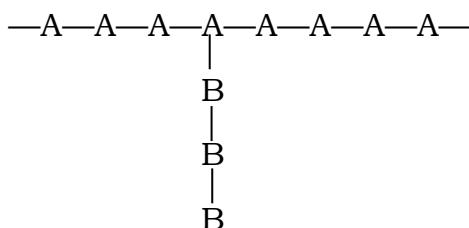
ii) Alternating copolymers – The monomeric units are arranged in an alternating manner.



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.



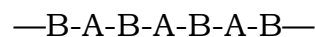
3. Classification based on structure:

a) Linear polymers – in these monomeric units are joined in the form of long straight chains.

Eg: High density polyethylene (HDPE), nylon, polyester, etc.



Linear Homo polymer

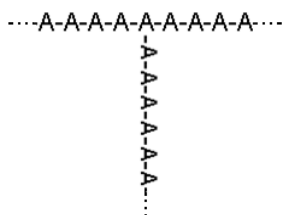


Linear Copolymer

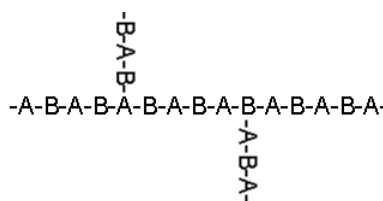
They possess high M.P., density and tensile strength due to close packing of polymer chain.

b) Branched chain polymers – (two-dimensional). These are also linear in nature, but possess some branches along the main chain.

Eg: Low density polyethylene (LDPE), glycogen, etc.



Branched chain homo polymer

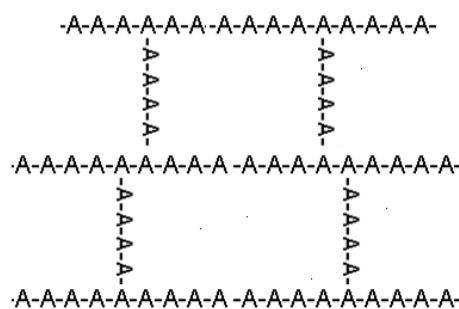


Branched chain copolymer

They possess low M.P., density and tensile strength due to poor packing of polymer chains in presence of branches.

c) Cross-linked polymers – contain monomer molecules connected to each other by only covalent bonds. These are giant molecules in which movement of individual monomeric units is prevented by strong cross-links.

Eg: Bakelite, vulcanized rubber, urea-formaldehyde, etc.



Cross-linked homo polymer

Due to presence of cross link, they are hard, rigid, brittle, and do not melt, but burn on strong heating.

4. Classification based on chain composition:

a) Homochain polymer – Polymers having all carbon atoms along their backbone are called homochain polymers.

Eg: polyethene, PVC, rubber, etc.

b) Heterochain polymer – If the polymeric chain contains a heteroatom, then they are called heterochain polymers.

Eg: nylon (polymeric chain contains nitrogen atom) and terylene (polymeric chain contains oxygen atom)

5. Classification based on mechanism of polymerization:

a) Addition polymers: In these the monomeric molecules bond to each other without the loss of any other atoms. Alkene monomers are the biggest groups of polymers in this class.

Eg: PE, PP, PS, PVC, etc.

b) Condensation polymers: In these usually two different monomers combine with the loss of a small molecule (H_2O , HCl , etc.)

Eg: Polyesters, polyamides (nylon), etc.

6. Classification based on molecular forces:

a) Thermoplastics or thermoplastic polymers: These are linear, long chain polymers which get softened when heated and hardened when cooled. The cycle can be carried out many times without affecting their chemical properties.

Eg: Polyethylene, PP, PVC, teflon, Plexiglass, etc.

b) Thermosets or thermosetting polymers: The polymers which on heating get hardened and once they have solidified, they cannot be softened, i.e., they are permanent setting polymers. Such polymers during heating acquire three-dimensional cross-linked structure with predominantly strong covalent bonds. Thus, a thermosetting polymer once molded cannot be reprocessed.

Eg: Phenol-formaldehyde resin (Bakelite), urea-formaldehyde resin, epoxy resin (araldite), etc.

c) Elastomers or Synthetic rubber: The polymers which undergo a very large elongation when pulled but returns to the original length on release of force are called elastomers. The polymer chains of elastomers are long, coiled and entangled. There are no intermolecular forces except weak Vander Waal's forces.

Eg: Natural rubber, Buna-S, Neoprene rubber, Silicone rubber, etc.

d) Fibres: Fibres are long, thin, and thread-like polymer chains which do not undergo stretching or deformation like elastomers. These long chain molecules are lined up and held together by hydrogen bonding. They have high tensile strength and less elasticity. Fibre forming materials may be synthetic or natural.

Eg: Natural: Wool, Silk, Cotton, Jute, etc.

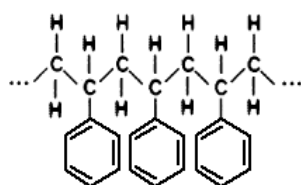
Synthetic: Nylon 6, Nylon 6,6, Terylene, etc.

7. Classification based on Tacticity:

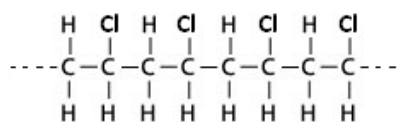
The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The stereochemical arrangement of functional groups on carbon backbone of the polymer is called tacticity of the polymer. This affects the physical properties like crystallinity, rigidity of the polymer. Therefore, tacticity helps to understand at what temperature the polymer melts, solubility in a solvent and its mechanical properties. Depending on the tacticity there are three different types of polymers.

a) Isotactic polymers: Those polymers in which the functional groups are arranged on the same side are called isotactic polymers.

Eg: Polystyrene, PVC



Polystyrene

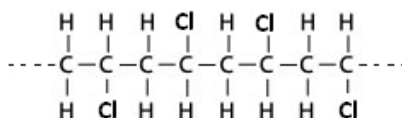


Polyvinyl chloride
(Isotactic)

In this the groups or substituents are arranged in stereochemical fashion. This results in high crystallinity, high M.P. and mechanically strong due to presence of weak interchain forces.

b) Atactic polymers: When there is no regular arrangement of functional groups on the backbone of the polymer chain, those polymers are called atactic polymers.

Eg: PVC, Polypropylene

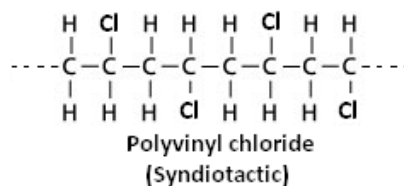
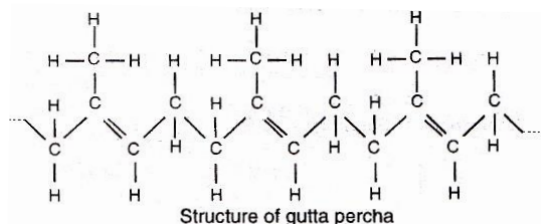


Polyvinyl chloride
(Atactic)

These possess low crystallinity, low M.P. and mechanically weak.

c) Syndiotactic polymers: The polymers with alternate arrangement of functional groups are called syndiotactic polymers.

Eg: Gutta Percha, PVC



8. Classification based on Degree of Polymerization:

a) Oligopolymers – Polymers whose degree of polymerization is less than 600 are called Oligopolymers. These polymers do not possess the engineering properties.

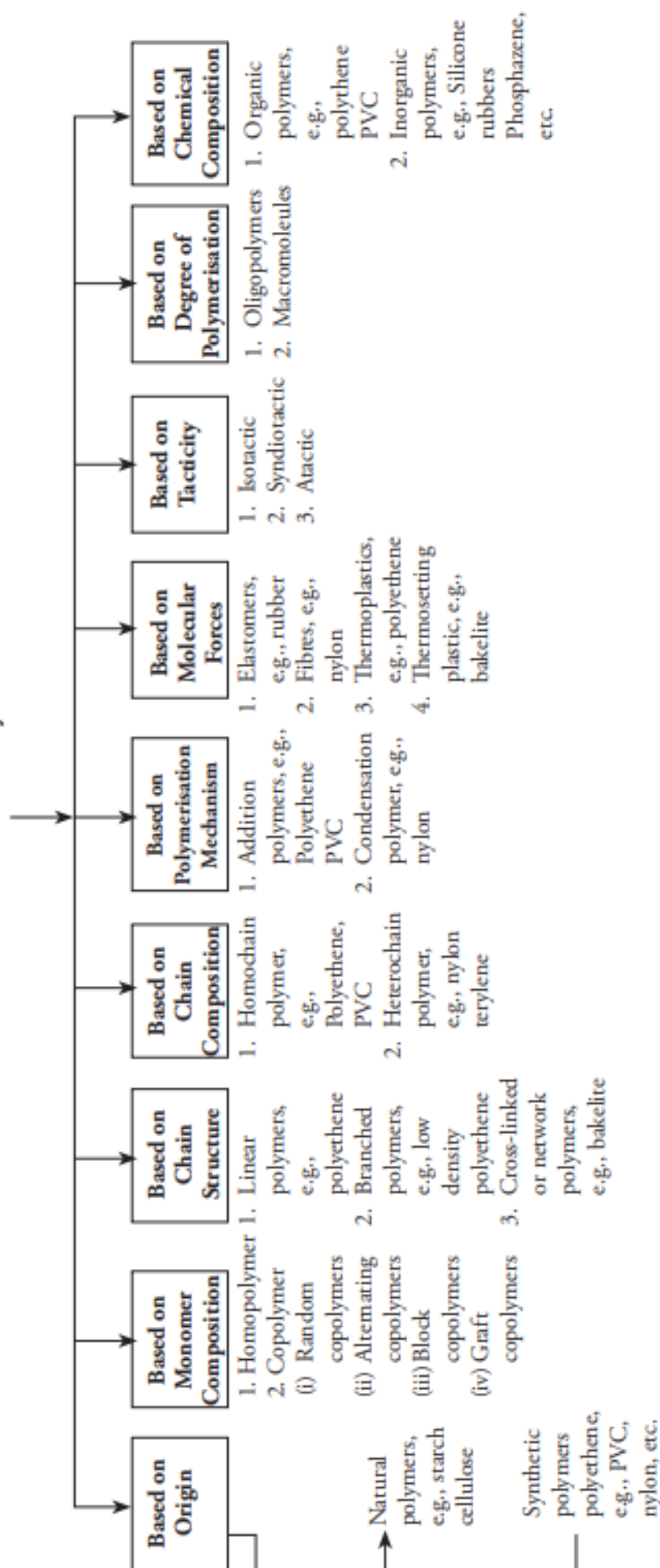
b) High Polymers or Macromolecules – Polymers whose degree of polymerization is more than 600 are called high polymers or macromolecules. These possess the desired engineering properties and widely used.

9. Classification based on Chemical composition:

a) Organic polymers – A polymer whose backbone chain is made mainly of carbon atoms and the side chains consist of oxygen, nitrogen, sulphur, etc.
Eg: polythene, PVC, nylon, etc.

b) Inorganic polymers – These polymers backbone chain is made of elements other than carbon atom.
Eg: silicone rubbers, phosphazene, etc.

Classification of Polymers



Types of polymerizations

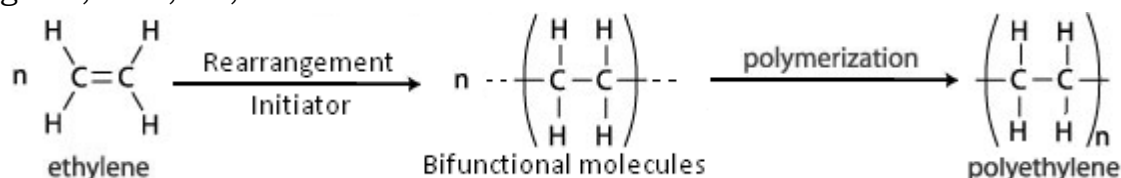
The conversion of a monomer into a polymer is an exothermic process and if heat is not dissipated or properly controlled, explosions may take place. The polymerization reactions are broadly classified into three types.

1. Addition polymerization or Chain polymerization
2. Condensation polymerization or Step growth polymerization and
3. Copolymerization.

• **Addition or Chain polymerization:** The polymerization that takes place by self-addition of the monomer molecules to each other through a chain reaction is called addition polymerization.

- The functionality of monomer is a double bond, and it is bifunctional.
- Polymerization takes place by self-addition of the monomer molecules to each other.
- No by-products like H_2O , CH_3OH etc. are produced.
- The polymer has the same chemical composition as that of monomer.
- The molecular weight of the polymer is the exact multiple of the monomers.
- An initiator is required to start the polymerization reaction.
- The mechanism is carried out in three steps, i.e., initiation, propagation and termination.
- The mechanism is rapid.
- The conversion of a π bond to a σ bond takes place during the polymerization, liberating 20k.cal/mole of energy. (Exothermic reaction).

Eg: PE, PVC, PS, etc.

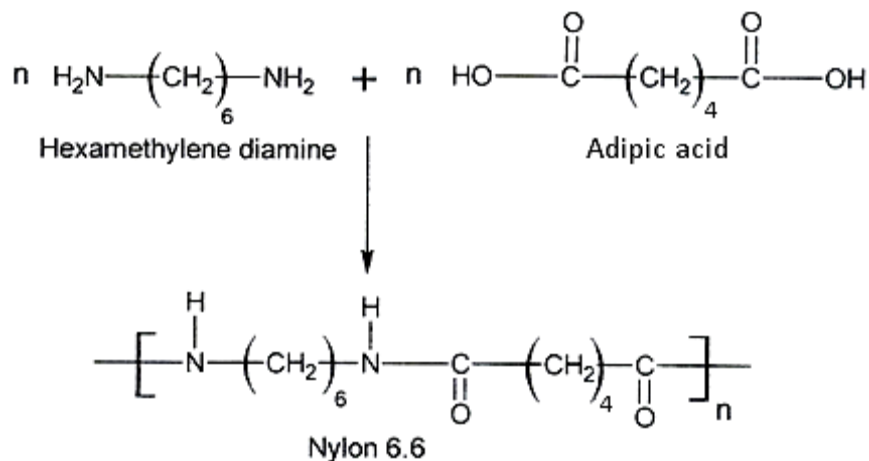


• **Condensation or Step polymerization:** Step polymerization takes place by condensation reactions of functional groups of the monomers and elimination of small molecules like water, HCl , etc.

- The monomers contain functional groups like $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, halides, etc.
- The polymer is built up by a slow stepwise condensation of the functional groups of the monomer.
- The polymers produced are living polymers containing functional groups at the end of the chain.
- The reactions are catalysed by catalysts.
- The functionality of the monomer must be two or more than two. The monomers must be dibasic acids, diols, diamines or triols, etc.
- The polymerization reaction is accompanied by the elimination of by-products like HCl , CH_3OH , H_2O , etc.
- The reactions are not exothermic.

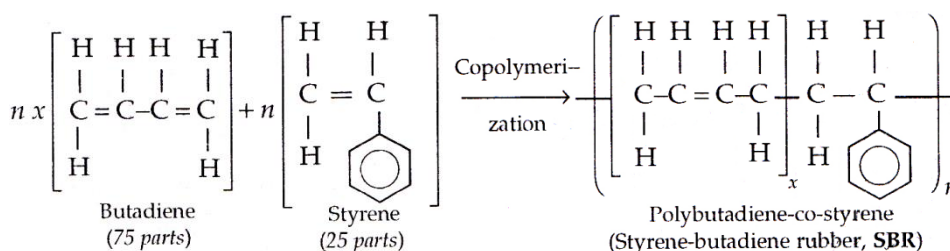
- The molecular weight of the polymer is not the sum of the molecular weights of the monomers.
- It is not a three-step mechanism of initiation, propagation and termination.
Eg: Nylon, Polyester, Bakelite, etc.

Polymerization of a diamine with diacid gives nylon 6,6 (polyamide)



- **Copolymerization:** It is the joint polymerization of two or more species. High molecular weight compounds obtained by copolymerization are called copolymers.

Eg: Butadiene and styrene copolymerize to yield Styrene-butadiene rubber.



Differences between Addition and Condensation polymerization

S.No.	Addition Polymerization	Condensation Polymerization
1.	It is also known as chain growth polymerization	It is also known as step growth polymerization
2.	It takes place only in monomers having multiple bonds	It takes place in monomers having reactive functional groups
3.	No by-products like H ₂ O, CH ₃ OH etc. are produced	By-products like HCl, CH ₃ OH, H ₂ O, etc. are produced
4.	The product obtained by this polymerization is thermoplastic	The product obtained by this method is either thermoplastic or thermosetting
5.	It takes place without elimination of simple molecules	It takes place with the elimination of simple molecules like H ₂ O, HCl, NH ₃ , etc.
6.	The mechanism is rapid	The mechanism is slow

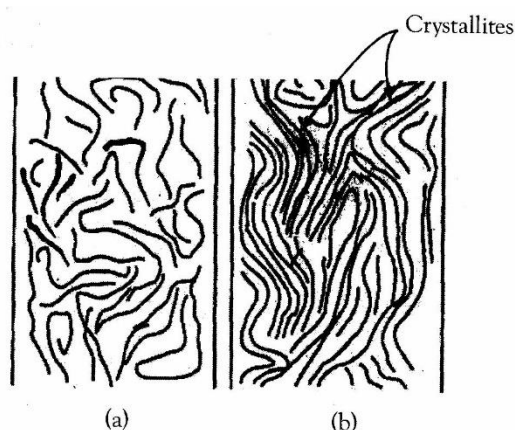
7.	An initiator is required to start the reaction	A catalyst is required for the reaction
8.	The mechanism is exothermic	The mechanism is not exothermic
9.	The mechanism is carried out in 3 steps – initiation, propagation, termination	The mechanism is carried out by slow step wise condensation
10.	The molecular weight of polymers is sum of molecular weights of monomers	The molecular weight of polymers is not the sum of molecular weights of monomers
11.	Ex: PE, PS, PVC, etc.	Ex: Nylon, Polyester, Bakelite

Properties of Polymers

Physical state of polymers

Relative arrangement of polymeric chains with respect to each other may result in an amorphous or crystalline state of a polymer.

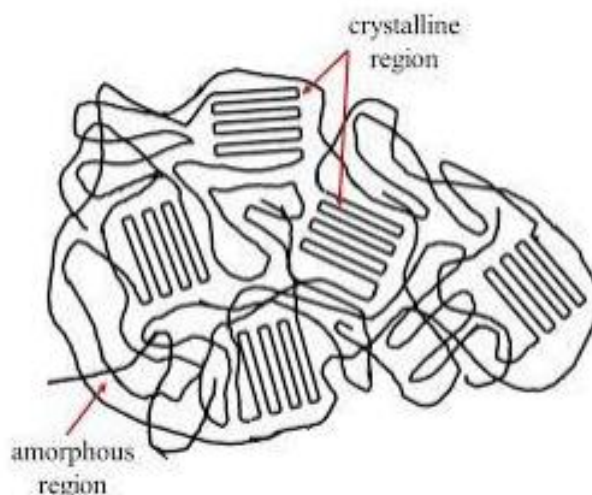
An amorphous state [Fig.(a)] is characterized by a completely random arrangement of molecules; while a crystalline state [Fig.(b)] consists of definite regions of crystallinity (called as crystallites) embedded in an amorphous matrix.



The crystallization tendency of a polymer depends on the ease with which the chains can be aligned in an orderly arrangement. Polymers with a long repeating unit or with a low degree of symmetry do not crystallize easily and therefore generally form amorphous structures. For example, polystyrene, polyvinyl acetate and polymethyl methacrylate (all having bulky side groups attached at random to the main carbon chain) are typically amorphous.

Crystallinity

The degree to which the molecules of a polymer are arranged in an ordered pattern with respect to each other is a measure of its crystallinity. In a crystalline solid, the atoms or molecules are arranged in a regular, periodic manner. It is the indication of the amount of crystalline region in the polymer with respect to amorphous content.



Crystallinity has a vital role in determining the hardness, permeability, density, tensile strength, impact resistance, heat capacity and solubility of a polymer. In fact no polymer is 100% crystalline.

Factors effecting Crystallinity

- 1. Molecular weight:** With increase in molecular weight of a polymer, % crystallinity decreases. (Due to large number of entanglement of chains)
- 2. Tacticity:** Geometrical regularity is desired in a polymer to show crystallinity. The irregularity prevents the chains from packing closely to each other. Therefore, Atactic polymers are poorly crystalline, while syndiotactic and isotactic polymers are more crystalline in nature.
- 3. Chain Branching:** Linear polymers have higher crystallinity than branched polymers. Because linear chains can pack well than branched polymer chains. And also, when the number and density of branches are increased, crystallinity will be decreased.
- 4. Presence of side groups:** When the size of the side of the group is increased, it becomes more difficult for that particular polymer to pack tightly and results in the more amorphous polymer.
- 5. Intermolecular forces:** The presence of polar side groups helps to form strong intermolecular interactions. So, polymer chains can come closer and pack tightly. Dispersion forces, dipole-dipole interactions and hydrogen bonds are some examples for intermolecular forces in polymers.
- 6. Chain composition:** Homopolymers are highly crystalline whereas the properties of the copolymers depend on the monomers and their configuration. Alternating copolymers are more crystalline than Block, Random and Graft Copolymers.
- 7. Rate of cooling:** When the cooling rate is high, polymer molecules have no time to organize orderly. So, crystallinity becomes low. Slower cooling promotes crystal formation and growth.
- 8. Plasticizers:** Plasticizers are the low molecular weight additives which are used for keeping polymer chains separated from each other. So, adding a plasticizer reduces crystallinity.

Crystallinity affects the following properties of the polymer:

With increase in % of crystallinity,

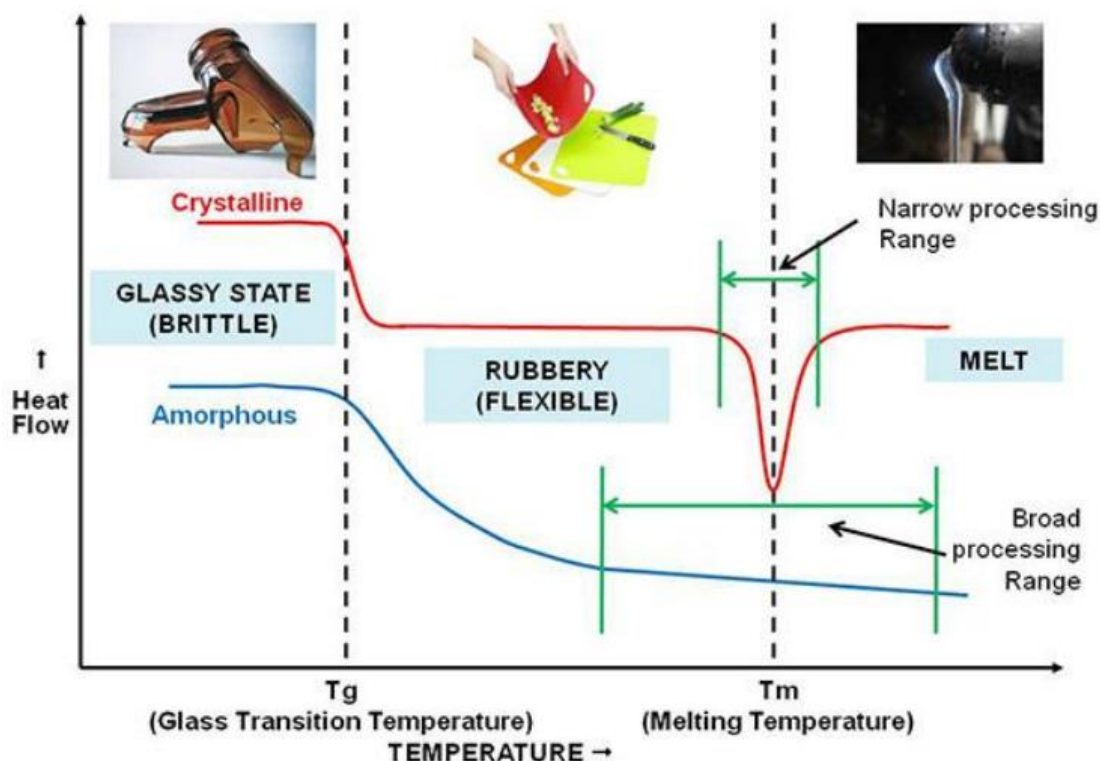
- Strength and stiffness of polymer increases, but brittleness also increases,
- Solubility and permeability of polymer decreases,
- Density and melting point of polymer increases,
- Opacity of the polymer also increases.

Thermal behaviour of polymers

Glass Transition Temperature

Glass transition temperature (T_g) is the temperature at which amorphous polymers undergo a transition from the glassy state to the rubbery state. It is represented by T_g .

Glassy state is hard and brittle state of material which consists of short-range vibrational and rotational motion of atoms in polymer chain, while Rubbery state is soft and flexible state of material which is a long-range rotational motion of polymer chain segments.



Some polymers are used above their glass transition temperature, and some are used below.

- Hard plastics like polystyrene and poly methyl methacrylate are used below their glass transition temperature; that is in their glassy state. Their T_g 's are well above room temperature.

- Elastomers like polyisoprene and polyisobutylene are used above their T_g 's, that is in the rubbery state, where they are soft & flexible.

Factors effecting Glass transition temperature (T_g)

- 1. Chain flexibility:** As T_g depends on the ability of a chain to undergo internal rotations, chain flexibility to be associated with low glass transitions.
E.g., Polymers that contain $-\text{CH}_2-\text{CH}_2-$ sequences and ether linkages in the main chain have relatively easy internal rotations and therefore low T_g values.
- 2. Steric effects:** The presence of bulky side groups hinders rotation of the backbone atoms due to steric hindrance, and therefore results in an increase in T_g . The magnitude of this effect depends on the size of the side groups.
- 3. Effect of Intermolecular Forces:** The presence of polar side groups leads to strong intermolecular attractive interactions between chains which hinders molecular motion thus causing an increase in Glass transition temperature.
- 4. Copolymerization:** It is possible to alter the glass transition of a homo polymer by copolymerisation with a second monomer.
If the two homo polymers prepared from the monomers have different T_g s, then it is reasonable to expect that their random copolymer should have a glass transition which is intermediate between the T_g s of the homo polymers.
- 5. Cross-linking & Crystallinity:** Both cross-linking and crystallinity cause an increase of the glass transition temperature.
The presence of covalent bonding between chains reduces molecular freedom and thus the free volume.
Similarly, the presence of crystalline regions in a semicrystalline material restricts the mobility of the disordered amorphous regions.
- 6. Plasticizer:** By the addition of plasticizers to the polymer, it becomes flexible. So T_g is reduced.

PLASTICS – Introduction

The word plastic is derived from the Greek word *plastikos* (= capable of being shaped or moulded). In a broad sense, a plastic refers to a material which exhibits plasticity, i.e. the ability to get deformed or to undergo change of shape under pressure. However, the term plastic generally refers to organic materials of high molecular weight that can be moulded to any desired shape when subjected to pressure and temperature in the presence of a catalyst.

Types of plastics

From engineering point of view plastics can be classified into two types. They are

1. Thermoplastics
2. Thermosettings

- 1. Thermoplastics:** The polymers which become soft on heating and hard on cooling are called thermoplastics. The cycle can be carried out many times without affecting their chemical properties. These have either linear or branched structure and can be amorphous or semi-crystalline materials. Neighbouring

polymeric chains are held together by weak Vander Waal's forces and hence do not have any cross-links.

Eg: Polyethylene, Polystyrene, Polypropylene, nylon, Teflon, PVC, polyester, etc.

2. Thermosettings: The polymers which on heating get hardened and once they have solidified, they cannot be softened, i.e., they are permanent setting polymers. Such polymers during heating acquire three-dimensional cross-linked structure with predominantly strong covalent bonds. Thus, a thermosetting polymer once moulded cannot be reprocessed.

Eg: Bakelite, urea-formaldehyde resin, epoxy resin, vulcanized rubber, etc.

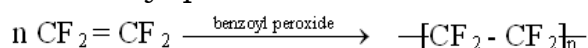
Differences between thermoplastics and thermosettings

S.No.	Thermoplastics	Thermosettings
1.	They are the products of addition polymerizations.	These are the products of condensation polymerization.
2.	They have either linear or branched structures.	They have three-dimensional cross-linked network structures.
3.	They soften on heating and stiffen on cooling.	They do not soften on heating.
4.	Adjacent polymer chains are held by either Vander Waal's forces or by dipole-dipole forces or H-bonding.	Adjacent polymer chains are held together by strong covalent bonds called cross-links.
5.	Soluble in organic solvents.	Insoluble in organic solvents.
6.	They are soft, weak and less brittle.	They are hard, strong and more brittle.
7.	They can be remoulded, reshaped and reused.	They cannot be remoulded and hence cannot be reused.
8.	They can be reclaimed from waste i.e., they can be recycled.	They cannot be reclaimed from waste and hence cannot be recycled.
9.	Eg: PE, PS, PVC, etc.	Eg: Bakelite, Urea-formaldehyde resin, vulcanized rubber, etc.

Individual Polymers

1. Teflon or Poly tetra fluoro ethylene (PTFE) or Fluon: $\text{---}[\text{CF}_2 - \text{CF}_2]_n\text{---}$

Preparation: Teflon is obtained by the chain polymerization of tetra fluoro ethylene in presence of benzoyl peroxide as an initiator.



Properties:

Due to the presence of highly electronegative fluorine atoms, TEFLON has got

- High melting point.
- Exceptionally high chemical resistance.
- High density 2.1 – 2.3 gm/cc.
- It is very strong, hard polymer that can be machined to drilling, punching, etc.
- Teflon is a very good electrical insulator.

- It possesses very good abrasion resistance.

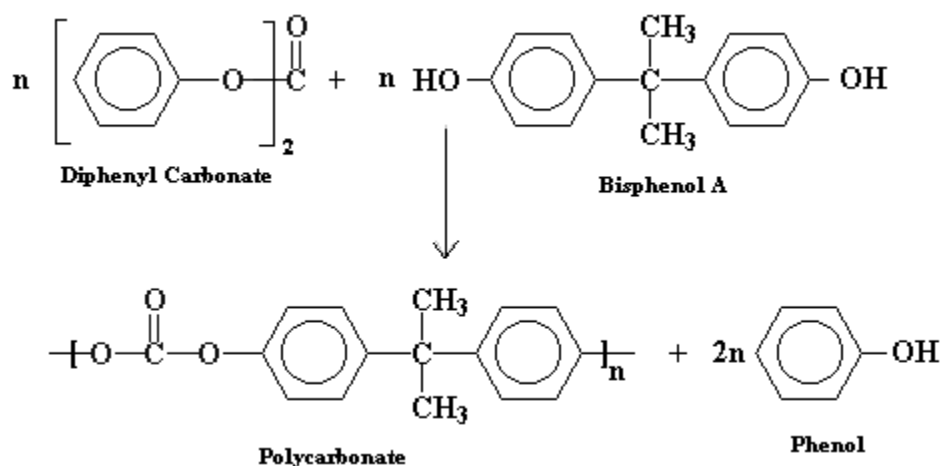
Applications:

- It is used as non-stick coating for pans and other cookware.
- Teflon is a very good insulating material for motors, transformers, cables, wires, fittings, etc.
- It is used for making gaskets, pump parts, tank linings, tubing, etc.
- Due to its extreme chemical resistance, it is used for making chemical carry pipes.
- Non-lubricating bearings and non – stick stop cock for burettes are made from teflon.
- It is also used for coating as impregnating glass fibre, asbestos fibres.

2. Polycarbonates (PC) (Lexan, Merlon):

Polycarbonates are commonly known by the trademarked name Lexan. They received their name because they are polymers containing carbonate groups (-O-(C=O)-O-). Most polycarbonates of commercial interest are derived from rigid monomers.

Preparation: Polycarbonates are prepared by the interaction of diphenyl carbonate with bisphenol-A.



Properties:

- They are characterized by high impact and tensile strength over a wide range of temperature.
- They are soluble in organic solvents and alkalis.
- They have high transparency and stiffness.
- Good dimensional stability.
- Flame retardancy and excellent fire performance
- Biologically inert and readily recyclable

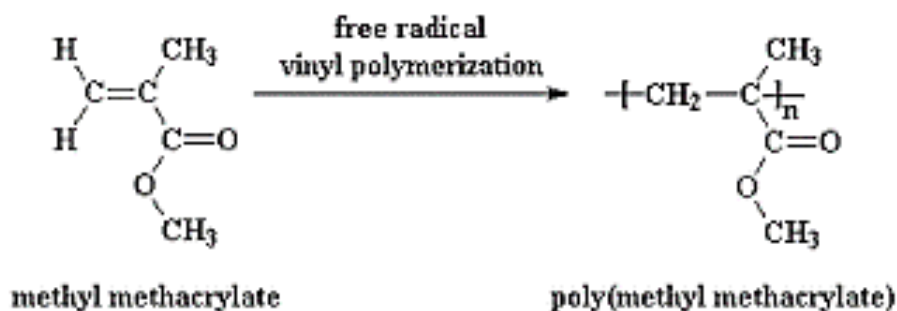
Applications:

- For preparing moulded domestic ware,
- housing for apparatus, and
- electrical insulator in electronics and electrical industries.
- used in cameras (lens holders, shutter assembly etc)
- CD's, DVD's, Cell phones, laptops

- Automobile headlights

3. Poly methyl methacrylate (PMMA) or Plexiglass or Lucite

Preparation: It is prepared by polymerization of methyl methacrylate in the presence of acetyl peroxide or hydrogen peroxide as catalyst.



Properties:

- Amorphous, colourless, transparent thermoplastic with high optical transparency.
- Presence of methyl groups restrict the chain flexibility. So, it is hard and has higher T_g .
- Polar compound, hence, does not have electrical insulation properties comparable with PE.
- Excellent weather ability
- Compared to glass, PMMA weighs only one-third, can be readily moulded to desired shape.
- Low chemical resistance to hot acids and alkalis and low scratch resistance.
- Scratches on it can be easily removed by rubbing it with a cloth moistened with acetone.

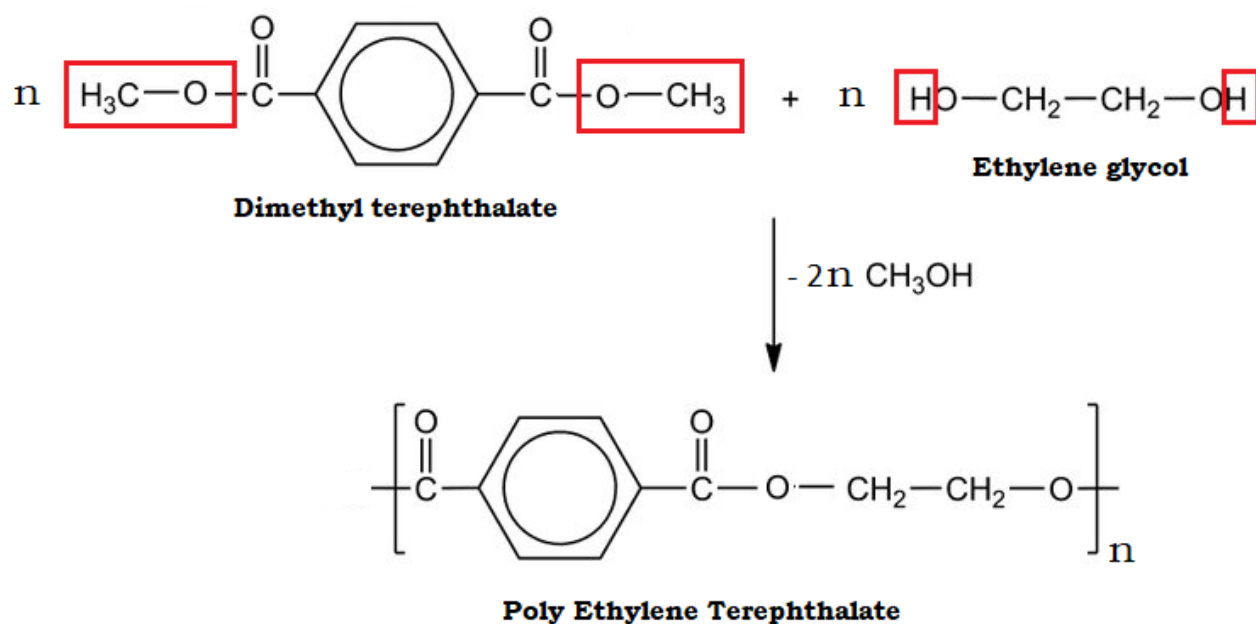
Applications:

- Display signs both illuminated and non-illuminated for internal and external use.
- Light fittings for streetlamp housing, ceiling lighting for school rooms, railway stations, factories.
- Familiar bubble body of many helicopters.
- Motor-cycle windscreen.
- Wash basins.
- Dome-shaped covers of solar collectors (solar heaters)
- Optical fibres.
- For making lenses, artificial eyes, dentures, etc.

4. Polyethylene Terephthalate (PET) or Terylene or Dacron:

PET is a thermoplastic polyester resin. It is mostly used to create clothing labels under the name “polyester”, and synthetic fibres and plastic bottles.

Preparation: PET resins are produced commercially from ethylene glycol (EG) and either dimethyl Terephthalate (DMT) or terephthalic acid (TPA) by condensation polymerization with loss of methanol or water molecule.



Properties:

- Because of the symmetrical structure and presence of numerous polar groups, the polyester is a good fibre forming material.
- It's Glass transition temperature and melting point are 80°C and 265°C
- PET fibres have high stretch-resistance, high crease and wrinkle-resistant.
- It is insoluble in most organic solvents.
- It is resistant to mineral and organic acids but is less resistant to alkalis.

Applications

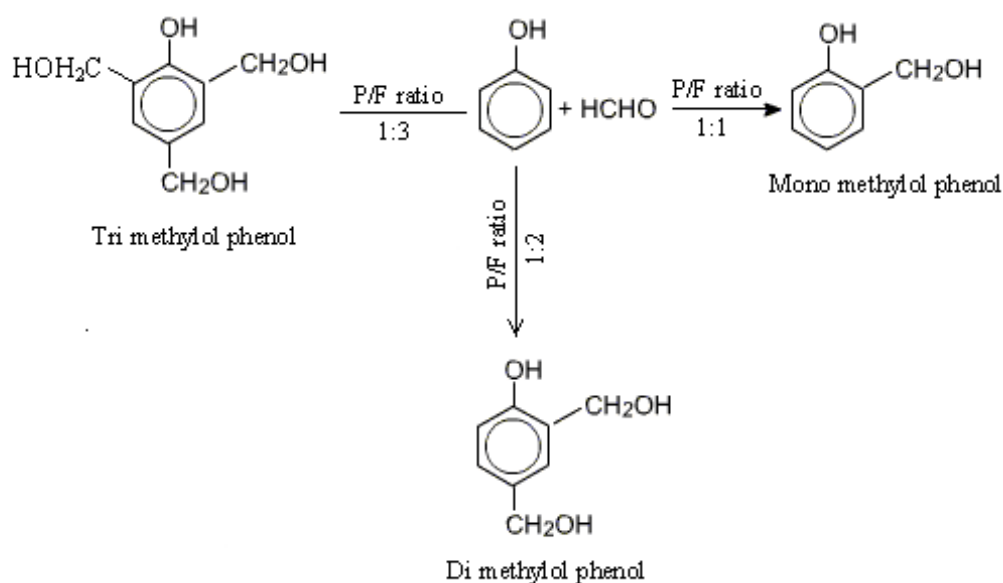
- Used for making synthetic fibres like Terylene, Dacron etc.,
- It is mainly used in making plastic bottles, sheets, ropes, nets and sails.
- To make transparencies for overhead projectors.
- Used for preparation of magnetic recording tapes.
- For making electrical insulation materials.
- For making storage containers for carbonated beverages.
- Materials for microwaves and conventional ovens

5. Bakelite or Phenol-formaldehyde resin:

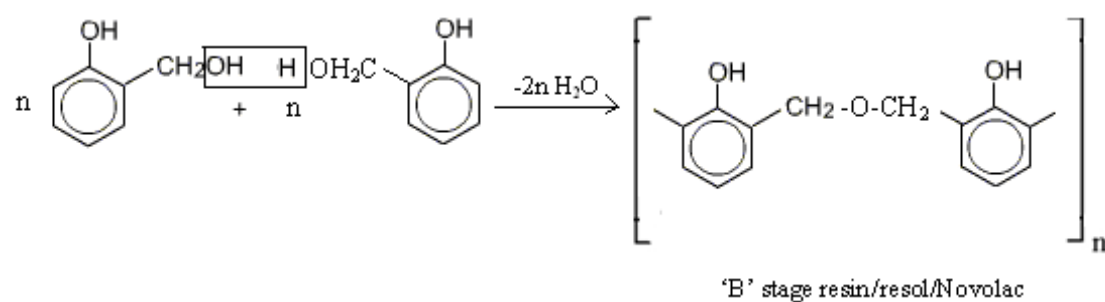
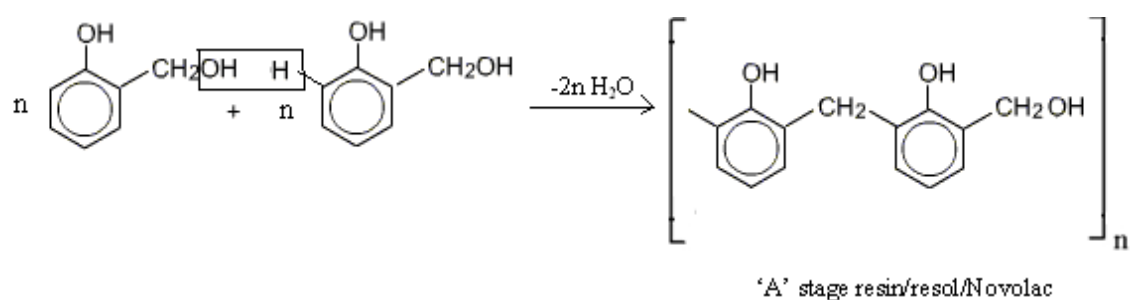
Bakelite is an important thermoset resin (World's first synthetic resin) named after the scientist Bakeland, who synthesized this resin in the year 1909.

Preparation: It is prepared by the step polymerization of phenol with formaldehyde in the presence of an acid or alkali as a catalyst. The polymerization takes place in three stages.

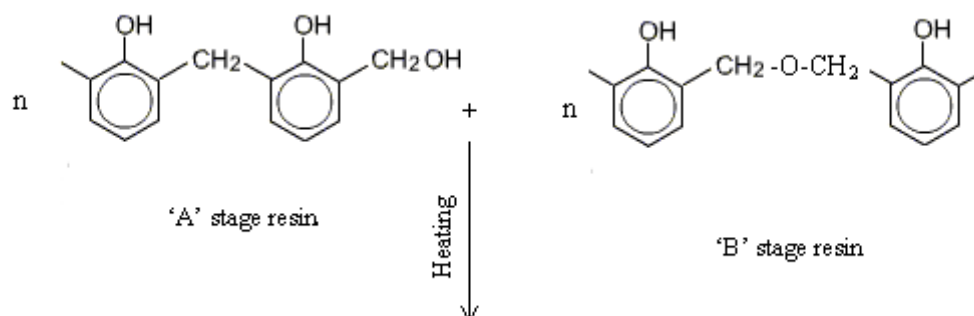
I Stage: Phenol is made to react with formaldehyde in presence of acid/alkali to produce non-polymeric mono, di and tri methylol phenols depending on the phenol formaldehyde ratio (P/F ratio).

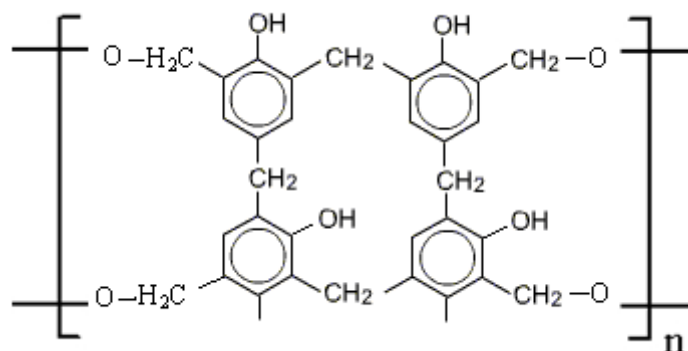


II Stage: The mono, di and tri methylol phenols are heated to produce two types of straight chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.



III Stage: This stage of preparation includes heating of 'A' stage resin and 'B' stage resin together, which develops cross linkages and Bakelite plastic resin is produced.





Bakelite

Properties:

- Bakelite plastic resin is hard, rigid, and strong.
- It is a scratch resistant and water-resistant polymer.
- It has good chemical resistance, resistant to acids, salts and many organic solvents, but it is attacked by alkalis due to the presence of $-\text{OH}$ group.
- It is a good anion exchanging resin, exchanges $-\text{OH}$ group with any other anion.
- Bakelite is an excellent electrical insulator.
- It is a very good adhesive.
- It has very good corrosion resistance, resistant to atmospheric conditions like O_2 , CO_2 , moisture, light, UV radiation, etc.

Applications:

Bakelite is used widely–

- For making electrical insulator parts like switches, switch boards, heater handles, etc.
- For making handles for cookers and saucepans.
- For making moulded articles like telephone parts, cabinets for radio and television.
- For making tarpaulins, wood laminates and glass laminates.
- As an anion exchanger in water purification by ion exchange method in boilers.
- As an adhesive for grinding wheels, etc.
- In paints and varnishes.
- For making bearings used in propellers shafts, paper industry and rolling mills.

Moulding or Fabrication of plastics

Giving desired shape to plastic material with the help of mould at desired temperature and pressure is called moulding or fabrication. Depending on the type of resin whether thermoplastic or thermoset, there are different methods of fabrication.

- Compression
- Extrusion
- Blowing
- Thermoforming

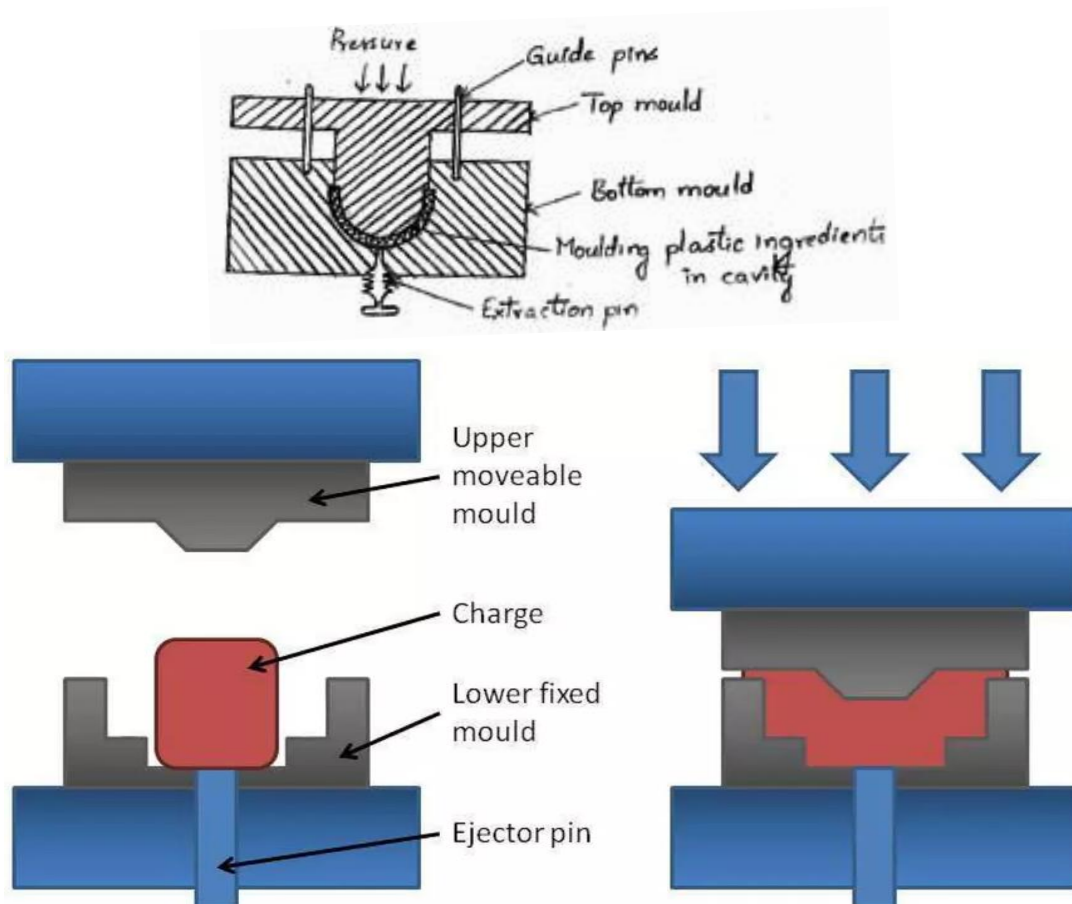
- Injection
- Transfer

Compression moulding

It is the oldest mass production process for polymer products. It is used in fabrication of both thermoplastics and thermosets.

Process:

In this process, initially, a synthetic plastic material with added fillers and ingredients is placed between the mould and heated (130-180°C) under pressure (100-500Kg/cm²). The plastic material is converted into fluidized plastic in the mould and gets moulded into the required shape after curing. Curing is done by cooling in thermoplastics whereas heating in thermosetting plastics. Hence the required moulded article is taken from the opening of the moulded parts.



Advantages:

- The initial setup cost is low.
- It gives good surface finish.
- The material loss is less.
- Low mould maintenance.
- Product has low residual stress.

Disadvantages:

- It is not economical for making a small number of parts.

- Sometimes secondary processing of product is required.
- Greater waste
- It has slower processing times.

Applications: It is used in fabrication of –

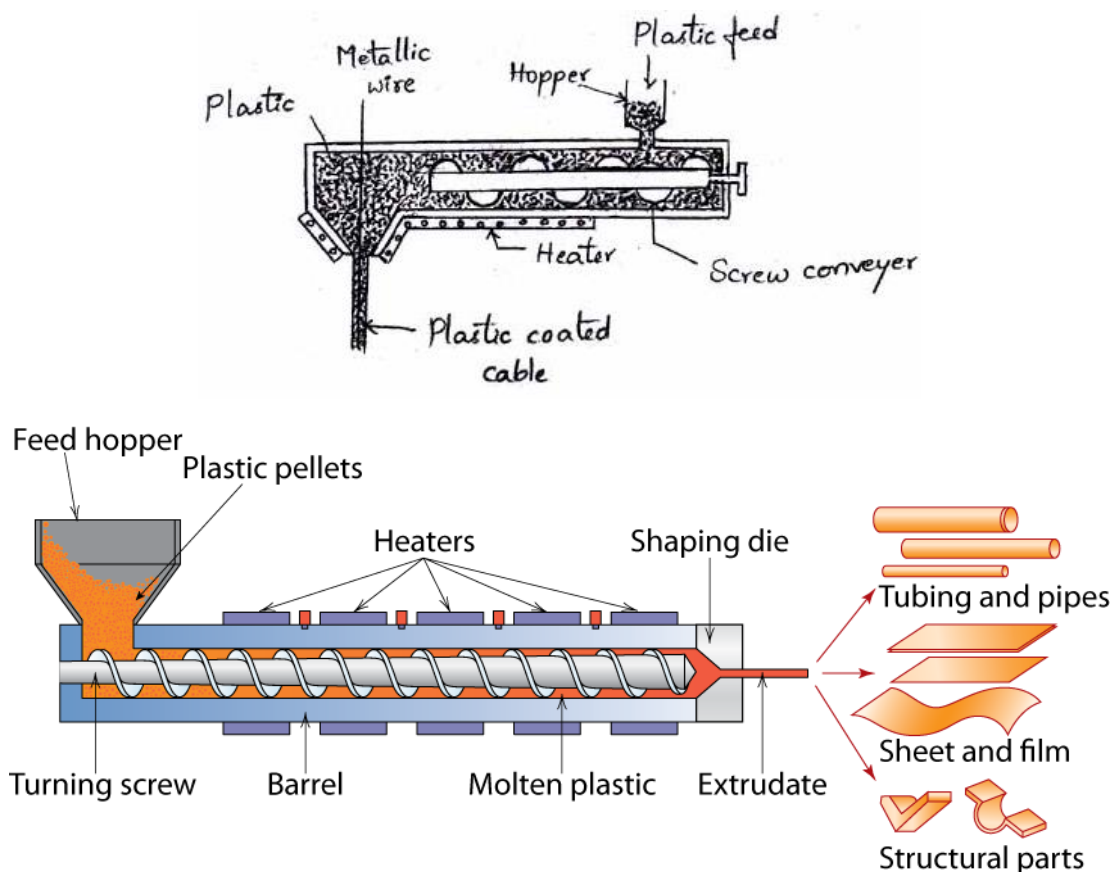
- Thermoset products like electrical plugs and sockets, switches, etc.
- Thermoplastic products like buttons, gramophone records, etc.
- Rubber products like O-ring seals, springs, anti-vibration mounting pad, etc.

Extrusion moulding

It is used for moulding of thermoplastic materials into articles of uniform cross-section like tubes, rods, sheets, wires, cables, etc.

Process:

The thermoplastic ingredients are fed into the barrel with the help of a hopper. The feed is heated with the help of heaters to plastic state and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to be fabricated. The extruded article gets cooled due to atmospheric exposure or artificially by air jets. A long conveyor carries away the cooled product continuously.



Advantages:

- Products can be produced quickly and at a high volume, ensuring cost-efficiency and speed.
- Low-cost relative to other moulding processes.
- Better flexibility in manufacturing products.

- Many types of raw materials can be used.
- Continuous operation
- Good mechanical properties obtained in cold extrusion.
- Post-extrusion manipulations (as plastic remains hot when it leaves the extruder) are possible.
- Surface finish obtained is good.

Disadvantages:

- It limits on the kinds of products it can manufacture (products of uniform cross-section only manufactured).
- It can be used only for linear polymers.
- When hot plastic exits the extruder, it frequently expands.

Applications:

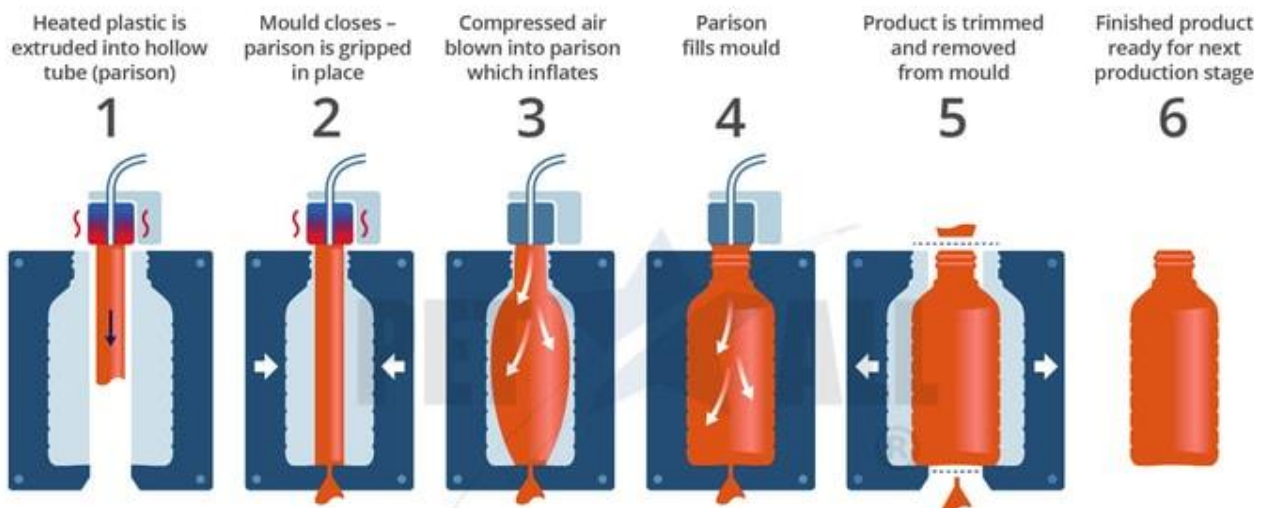
- It is used in manufacturing of tubes, electric cables, optical fibres, pipes etc., by hot extrusion.
- Collapsible tubes, gear blanks, aluminium cans, cylinders are some of the items produced by cold extrusion.
- PVC window frames, curtain rails, window screens, doors, flat and corrugated sheeting (e.g., roofing), etc., are prepared by profile extrusion.
- It is also used for preparing sheets for thermoforming.

Blow moulding

It is used for producing hollow articles like bottles and hollow toys. Thermoplastic articles such as PE, polycarbonate, PVC, nylon, and styrene are blow-moulded.

Process:

In this process a hot, softened thermoplastic tube called 'parison' is properly placed inside the two-piece hollow mould. The split mould is then closed, sealing the bottom. This joint is usually seen at the bottom of the plastic bottles. Air is then blown in the hot parison. It is inflated and acquires the shape of the mould. The mould is allowed to cool, and the rigid thermoplastic article formed is removed by opening the mould.



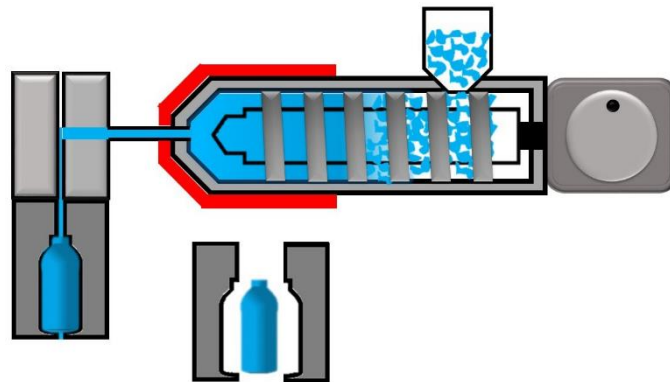
Types of Blow moulding

In general, there are three main types of blow moulding:

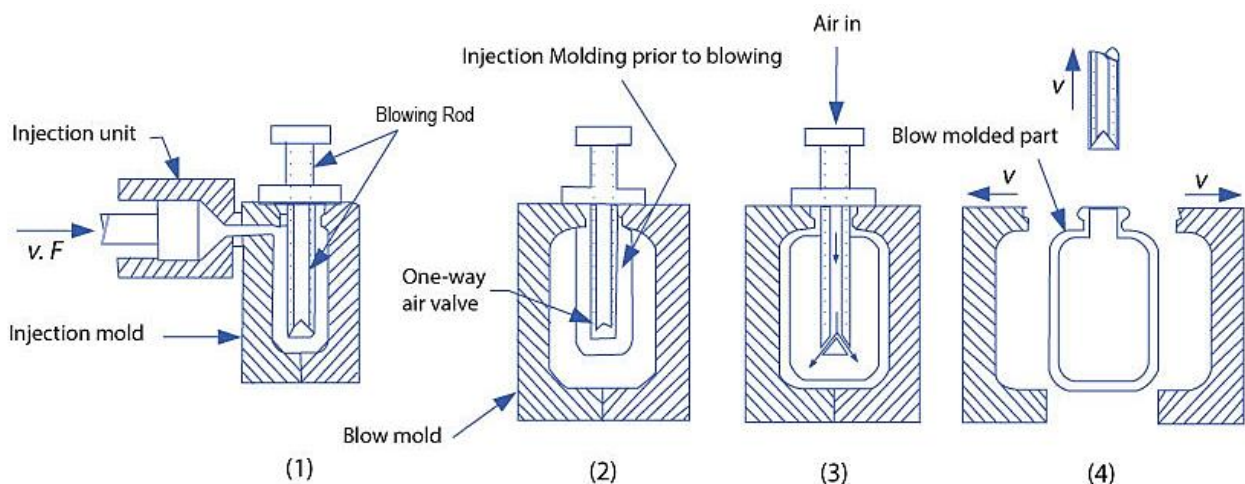
- Extrusion blow moulding
- Injection blow moulding
- Stretch blow moulding.

All the types have one primary difference that is making of parison by extrusion, injection and stretching.

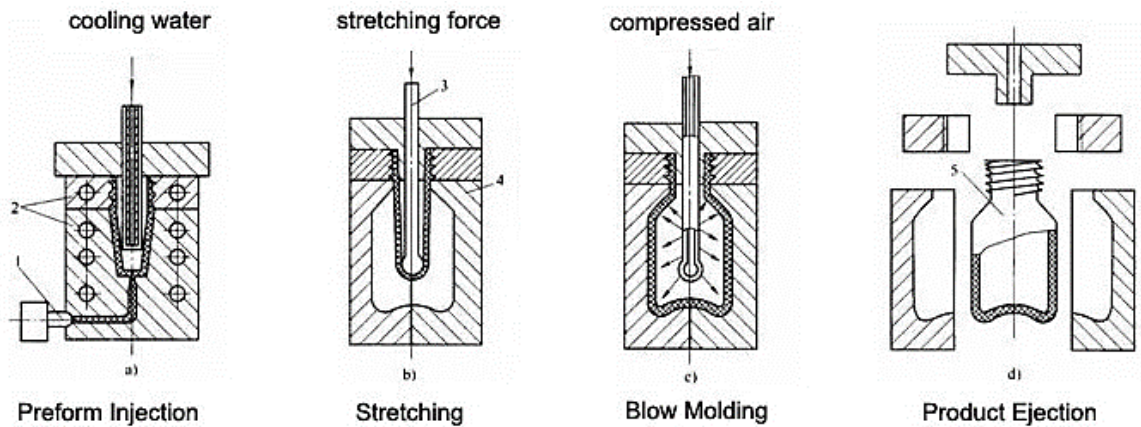
Extrusion blow moulding: In the extrusion blow moulding process, plastic is melted and extruded into a hollow tube (a plastic parison). The extruded parison is cut off and moved to the mould and clamped there. The mould closes and parison is blown to shape. The blown bottle is cooled and then ejected.



Injection blow moulding: In the injection blow moulding process, the molten plastic is injected into a mould to form a plastic tube called parison. The parison is moved to the mould, blown into shape, cooled, and then ejected.



Stretch blow moulding: Stretch blow moulding is the common method for producing soda bottles. The process begins with an injection moulded preform. The preform is typically pre-heated then stretched in the axial direction and blown into its final shape by a stretch blow holding machine. The blown article is cooled and ejected.



Advantages:

- Low tooling costs.
- Fast production rates.
- Ability to mould complex parts.
- Little scrap generated.
- Large hollow shape can be produced.
- Produced parts can be recycled.

Disadvantages:

- Limited to hollow parts.
- Thick parts cannot be manufactured.
- Higher scrap rate.
- Limited wall thickness control.
- It is highly dependent on petroleum.
- It creates a huge impact on the environment.

Applications:

- Thermoplastic materials like Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE), Polyethylene Terephthalate (PET), Polypropylene (PP), Polyvinyl Chloride (PVC) etc., can be processed by this method.
- Hollow products like bottles, containers, jars, jerry cans and automotive fuel tanks, dust bins, drums, oil storage containers, petrol tanks for cars, hollow spheres, toys, etc.

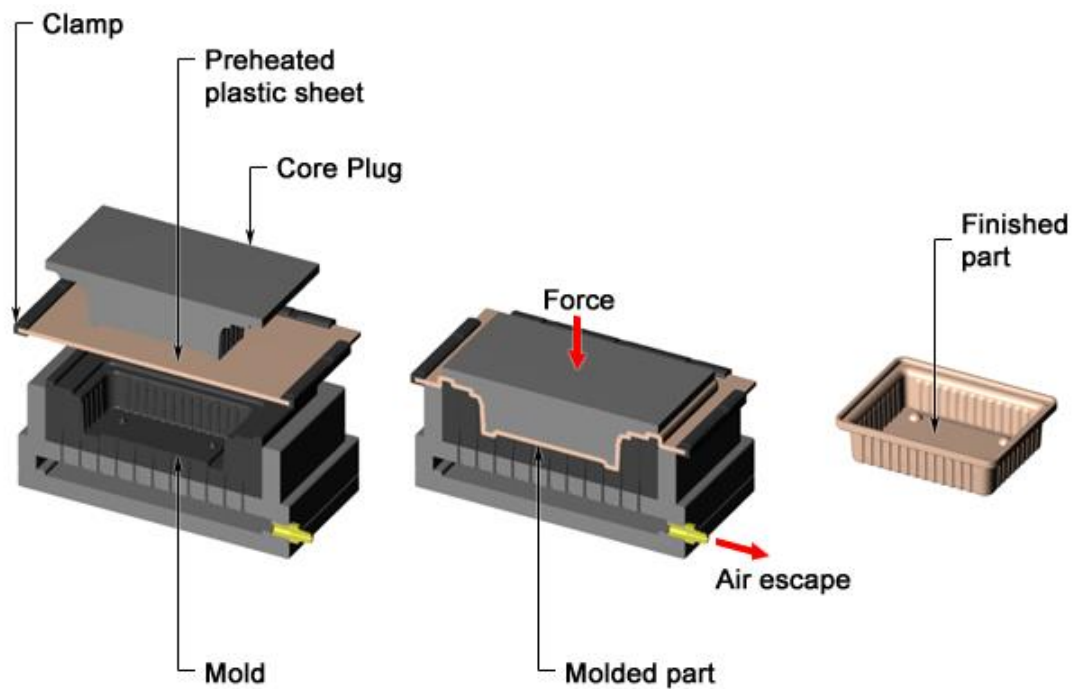
Thermoforming Process

It is the combination of extrusion with compression moulding. Materials like PS, PVC, PMMA, PC, HDPE, PP, etc., can be processed by this method.

Process:

Thermoplastic resin is extruded in the form of a sheet and heated to its softening temperature. The warm flexible sheet is compressed between the two moulds. On cooling, the shaped article, becomes rigid. It is then removed from the mould.

Compression of the moulding can be done by applying anyone of the following - vacuum (vacuum thermoforming), pressure (pressure thermoforming) and mechanical forces (mechanical thermoforming).



Advantages:

- Design flexibility
- Low initial setup costs
- Low production cost
- Less thermal stresses
- Good dimensional stability

Disadvantages:

- Poor surface finish.
- Parts may have non-uniform thickness.
- All parts need to be trimmed.
- Limited materials can be made.

Applications:

- It is useful for the fabricating 3D articles, Automotive parts, Submarine hulls, Food packaging items, Disposable cups, glasses, ice cream cups, plastic trays for cookies and candy, Aircraft windscreens, Vehicle doors, etc.

Fibre-Reinforced Plastics (FRPs)

The combination of polymeric substance with solid fillers is called reinforced plastic. The filler acts as reinforcing material, while the polymer links the filler particles. Polymer composites consist of two or more phases, one of which is a dispersed phase (fibres, particles, flakes, etc.) in a continuous matrix phase (polymer/plastic).

Fibre reinforced plastics are produced by reinforcing a plastic matrix with a high strength fibre material such as glass, graphite, alumina, carbon, boron, beryllium, and aromatic polyamide (aramid). Natural fibres such as sisal, asbestos are also used for reinforcement. Depending on the desired properties of the final reinforced

composite, the nature of the fibre used is decided. FRPs find extensive use in space crafts, aeroplanes, boat-hulls, acid-storage tanks, motor cars and even buildings.

The main advantages of FRPs:

- Light weight- easy to handle and transport.
- High strength to weight ratio.
- Corrosion resistant-will not corrode.
- Better toughness, impact and thermal shock-resistance.
- Lower electrical conductivity.
- Better creep and fatigue strength.
- Higher specific stiffness.
- Cheaply and easily fabricable.
- Lower thermal expansion.

Types of Fibre-Reinforced Plastics

FRP's are classified into three types based on the type of reinforced material used. They are:

1. Glass fibre reinforced plastics
2. Carbon fibre reinforced plastics
3. Aramid fibre reinforced plastics

1. Glass fibre-reinforced plastics (GFRP's)

Glass fibre is the most extensively used reinforced fibre because of durability, acid proof, waterproof and fireproof nature of glass. Glass fibres are basically made by mixing silica, sand, limestone, folic acid, and other minor ingredients. The mix is heated until it melts at about 1260°C. The molten glass is then allowed to flow through fine holes in a platinum plate. The glass strands are cooled, gathered, and wound.

Glass is drawn into threads or fibres in the form of filaments fine than cotton or silk thread. Then the filaments are woven in the form of mats. The fibre material is suitably bonded with plastic materials to be reinforced. The common plastic resins used are polyesters, epoxies, silicones, melamine, vinyl derivatives and polyamides.

Properties:

- Lower densities.
- High tensile strengths.
- High impact resistance.
- Excellent chemical resistance and
- Corrosion resistance.

Disadvantages:

- Limited-service temperatures because most polymeric matrices begin to deteriorate or flow at high temperatures.
- These materials do not possess the desired stiffness and rigidity, particularly in their applications as structural components.

Applications: Some typical applications of these materials are in-

- Automotive parts
- Boat hulls
- Storage tanks
- Industrial flooring
- Plastic pipes
- Transportation industries to reduce vehicle weight and boost fuel efficiency.

2. Carbon fibre-reinforced plastics (CFRP's)

Carbon fibres are used as reinforcement in a polymer matrix. Carbon fibres do not absorb water and are resistant to many chemical solutions. They withstand fatigue excellently; do not stress corrode and do not show any creep or relaxation.

Properties:

- Alkali resistance
- Resistance to corrosion
- Low thermal conductivity
- High mechanical strength
- High fatigue resistance

Disadvantages:

Carbon fibre is electrically conductive and therefore might give galvanic corrosion in direct contact with steel.

Applications: Some typical applications of these materials are in-

- Space vehicles, satellites
- Sports equipment
- High speed reciprocating parts for industrial machinery
- High temperature machinery
- Structural components requiring high specific stiffness and strength.

3. Aramid fibre-reinforced plastics (AFRP's)

Aramid is the short form for aromatic polyamide. Aramid fibres are usually used as fibre reinforcement for polymer matrix composites.

E.g., Kevlar and Nomex are extremely tough and resistant materials, which find use in bullet-proof vests, fire-resistant clothing and puncture resistant bicycle tyres.

These can be further classified into following two categories:

- a.) Short Aramid fibre reinforced plastics
- b.) Long Aramid fibre reinforced plastics

a.) Short Aramid fibre reinforced plastics:

Properties: They give effective reinforcement due to their-

- High surface area
- Strength
- Heat stability
- Inherent toughness and

- High wear resistance

Applications:

- Used in Automotive brakes and clutches.

b.) Long Aramid fiber reinforced plastics:

Properties:

- Metal-like ductile
- High compressive strength as they are capable of absorbing energy.
- High Temperature range (-200 to 200°C)

Applications:

- Used in helicopter industry in making rotor blades, motor housing, etc.

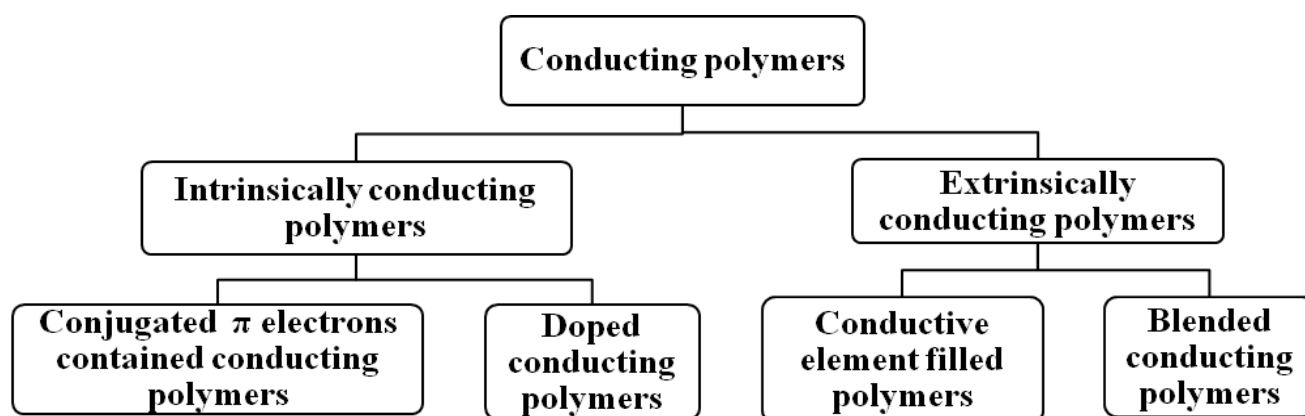
Conducting polymers

A polymer which can conduct electricity is termed as conducting polymer. Most polymeric materials are poor conductors of electricity, because of the non-availability of free electrons in the conduction process.

Within the past several years, polymeric materials have been synthesized which possess electrical conductivities similar to that of metallic conductors. Such polymers are called conducting polymers.

Eg: Polyacetylene, polypyrrole, polyaniline, polynaphthalene, polyquinoline, etc.

Conducting polymers can be classified into following types:



1. Intrinsically conducting polymers (ICP)

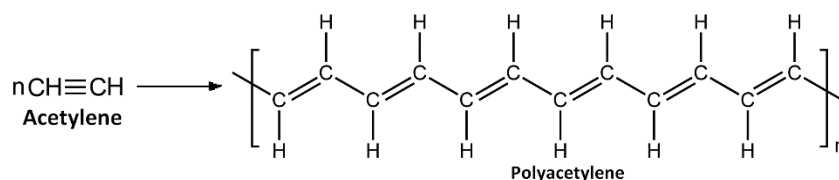
These polymers have extensive conjugation in the backbone, which is responsible for conductance. These can be further classified as two classes. They are as follows:

a.) Conducting polymers having conjugated π electrons in the backbone:

These polymers contain conjugated π electrons in the backbone, which increases their conductivity to a large extent. This is because, overlapping of conjugated π electrons over the entire backbone results in the formation of valence as well as conduction bands.

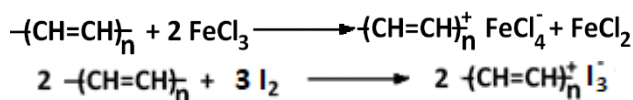
The electrical conductance could occur only after thermal or photolytic activation.

E.g., Polyacetylene, Polypyrrole, Polyaniline, etc.

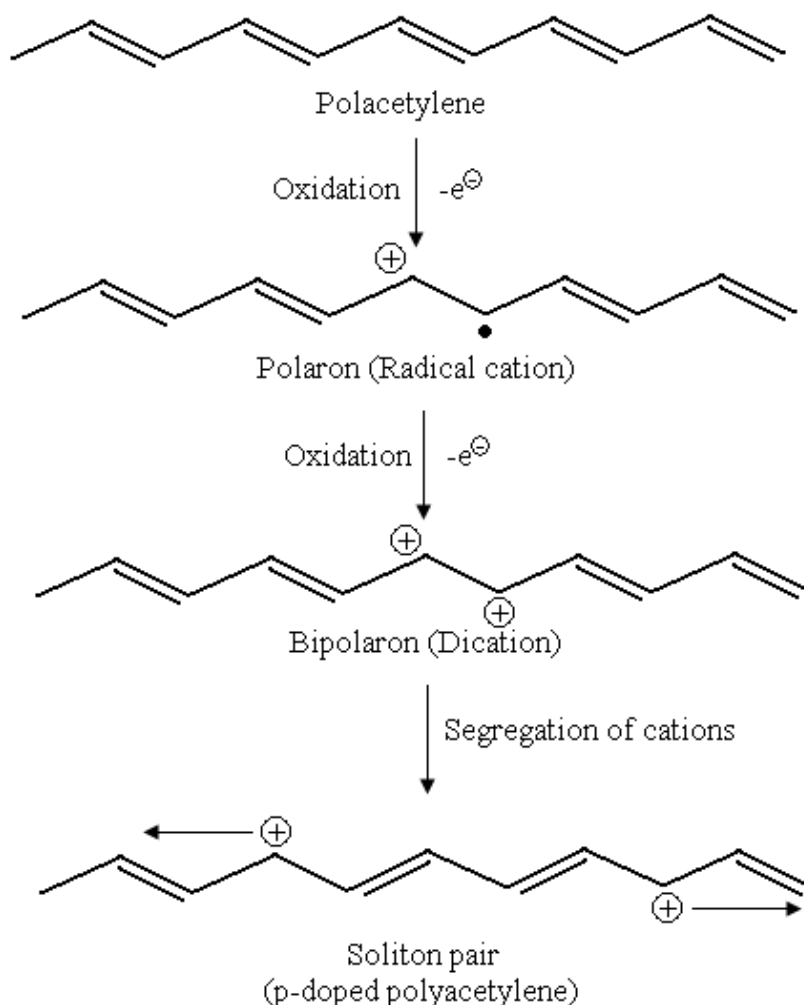


b.) Doped conducting polymers: It is obtained by exposing a polymer to a charged transfer agent in either gas phase or in solution. ICP possess low conductivity, but these possess low ionization potential and high electron affinities, so these can be easily oxidized or reduced. Consequently, the conductivity of ICP can be increased by creating either +ve or -ve charges on the polymer backbone by oxidation or reduction. This technique is called doping which is of two types:

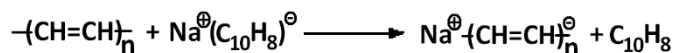
p-doping: It is done by oxidation process. Conducting polymers having conjugation is treated with Lewis acids or with iodine vapour or iodine molecule.



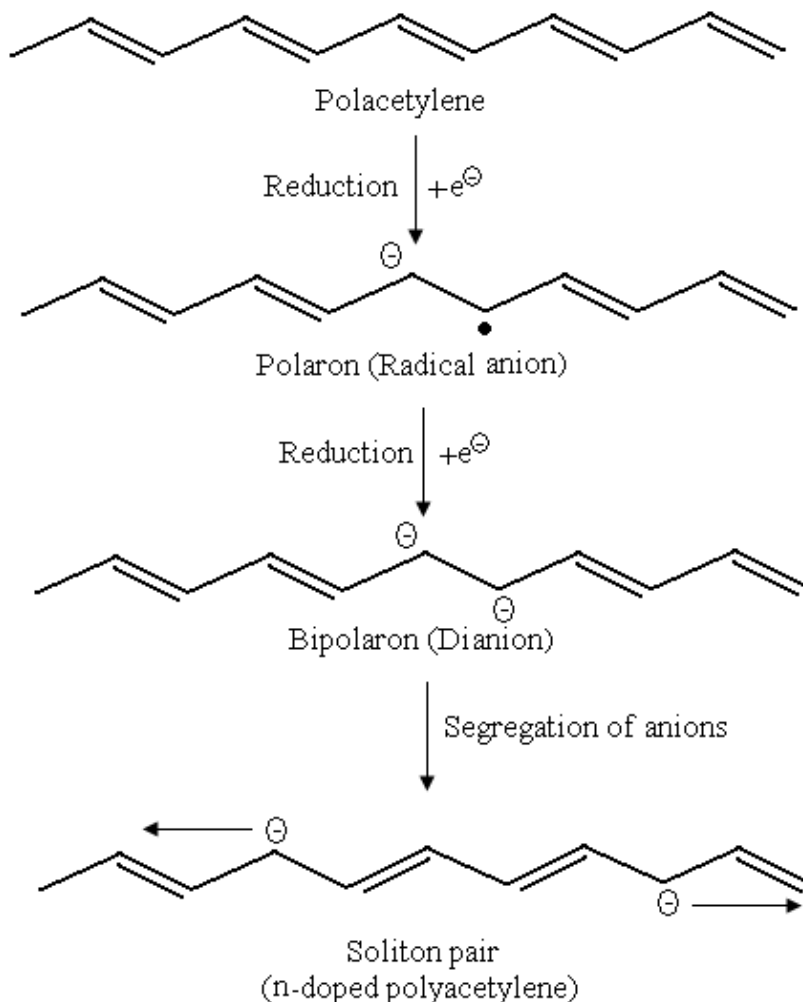
Oxidation process leads to the formation of delocalized radical ion called polaron. p-doping of polyacetylene gives a Polaron, a bipolaron and a soliton pair. This can be explained on the basis of the following equations:



n-doping: It is done by reduction process. For this conductance, polymers having conjugation is treated with Lewis base like sodium naphthalide.



The formed radicals yield to carry negative charge for conductance. This type of doping also gives a polaron, bipolaron and a soliton pair.



2. Extrinsicly conducting polymers (ECP)

These polymers possess their conductivity due to the presence of externally added ingredients in them. These can be of the following types:

a.) Conductive element filled polymers: The polymer acts as the binder to hold the conducting element (such as carbon black, metallic fibres, metallic oxides, etc.) together in the solid entity.

Minimum concentration of conductive filler, which should be added so that polymer starts conducting, is known as percolation threshold. Because at this concentration of filler, a conducting path is formed in polymeric material. Generally, Carbon-black is used as a filler which has very high surface area, more porosity and more of filamentous properties.

b.) Blended conducting polymers: These polymers can be obtained by blending a conventional polymer with a conducting polymer. Such polymers possess better physical, chemical, electrical, and mechanical properties and they can be easily processed.

E.g., up to 40% of polypyrrole will have little effect on tensile strength and also give a much higher impact strength than obtained with carbon-black filled compound.

Applications:

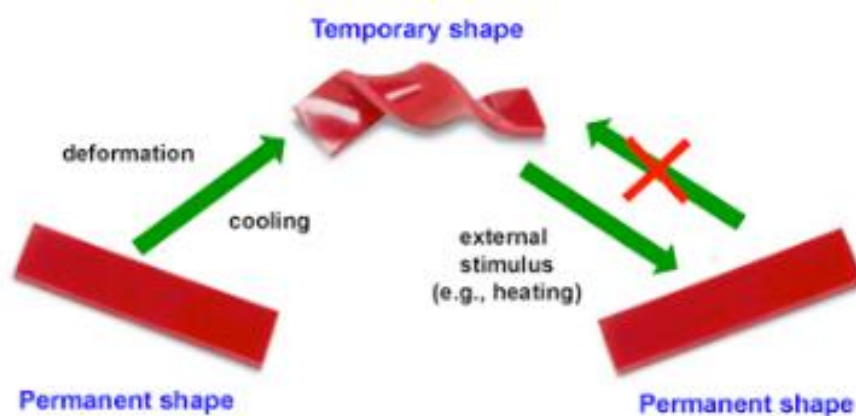
There are several utilities of conducting polymer due to their better physical, chemical, mechanical properties, light weight and easy to process. Some of them are-

- To make electromagnetic screening materials.
- In electronic devices such as transistors and diodes.
- Making of solar cells.
- Drug delivery system for human body.
- In the manufacture of non-linear optical materials, optical filters and electro chromic displays.
- Used in molecular wires and molecular switches.
- To make rechargeable light weight batteries.
- In making of analytical sensors for pH, O₂, NO_x, SO₂, NH₃ and glucose.
- Making of ion-exchangers.

Shape memory polymers (SMPs)

SMPs are considered as smart materials as they have ability to return from a deformed state (temporary shape) to original (permanent shape) through external stimuli (activation mode).

Ex: PTFE, PLA, EVA, PEG.



Features/properties of SMPs

- Rubbery in nature, composed of long, entangled-polymer chains and these chains gets stretched under tension to accommodate the deformation.
- High elastic deformation (strain up to 200% in most of the materials).
- Low cost, low density, biocompatibility, and biodegradability.
- SMPs are capable of recovering fully under low deformation level.
- If these are cooled below their glass transition temperature and deformed by external forces.

- Once the external forces are removed it will return to its previous unreformed state.
- When the temperature is greater than “Glass transition temperature” (T_g), the material enters the soft rubber phase and becomes easily definable.

Working Principle of SMPs

- In shape memory polymers, typical shape recovery process begins at a temperature above T_g .
- At this temperature, the polymer is in a rubbery elastic state.
- The polymer is then deformed with an applied stress which creates a strain in the polymer.
- When cooled below T_g , the material autonomously returns to the original shape (shape recovery characteristic).
- This property of the material which repeatedly returns to its original shape is called “shape memory”

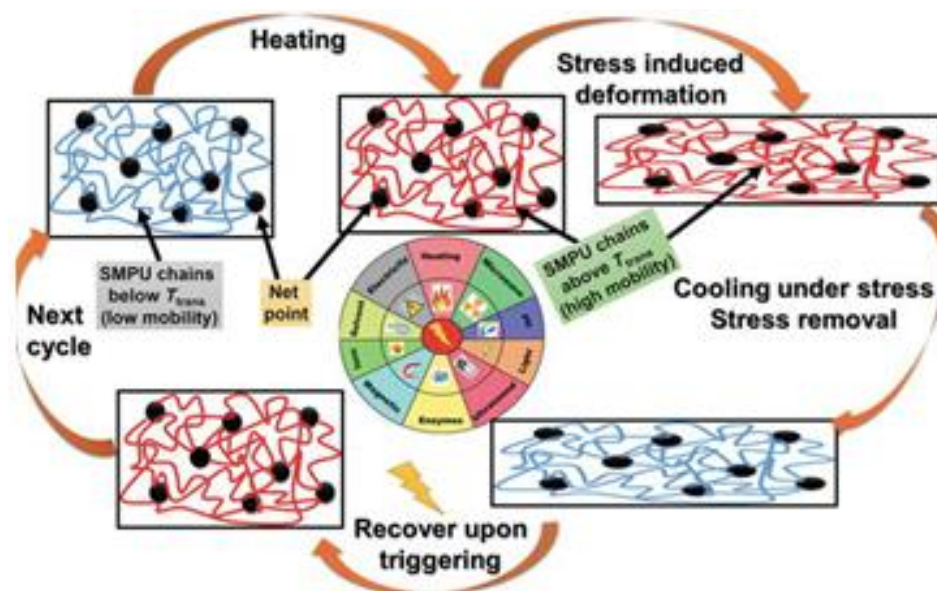
Semicrystalline polymers possess SME as they occur in both states (crystalline & amorphous) at the same time within specific temperature, usually room temp.

It has 3 stages of working

Programmable – By applying heat and deformation stress the polymer will be converted to deformed state and this deformed state is fixed by removing stress at cooling.

Storage – temporary shape of the polymer

Recovery – By applying external stimuli, they are deformed to permanent shape called as recovery state.



Classification of Shape Memory based on their mode of activation

SMPs are classified based on their mode of activation as thermo-responsive, light responsive, electrically, magnetically induced and water induced).

Most common is thermo-responsive.

Thermo-responsive shape memory polymers

The shape memory polymers which change in shape with the change of temperature are called thermo-responsive shape memory polymers. By far these are the most common shape memory polymers.

The following is a list of some of the consumables for Thermoresponsive polymers:

- Poly (N-alkyl acrylamide);
- Poly (N-vinyl caprolactam) [PVC];
- Poly (N-ethyl oxazalone) [PET Ox];
- Poly (methyl vinyl ether) [PMVE];
- Poly (acrylic acid-co-acrylamide);
- Elastin-like oligo- and polypeptides.

Electrical heating induced shape memory polymers

The shape memory polymers are generally nonconductive. So, they are made conductive by blending with carbon nano powders. The electric current is converted into heat. They recover the original shape when an electric current is passed through the shape memory polymers.

Light induced shape memory polymers

The shape memory polymers which are to be activated by light should have some photosensitive groups which act as molecular switches. The shape memory polymers are stretched and illuminated by a light of wavelength greater than a fixed wavelength and the photosensitive groups form cross links.

Magnetically induced shape memory polymers

Non-contact triggering of shape changes in polymers has been realized by incorporating magnetic nanoparticles in shape memory polymers and inductive heating of these compounds in alternating magnetic fields.

Water activated shape memory polymers

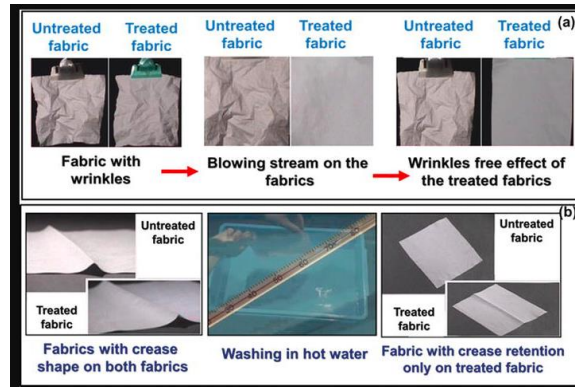
The activation of the polymer can be achieved by immersion in water. A shape memory polymer which has the permanent shape of a straight rod is programmed into a Z shape. The left part of the polymer is dipped into water and the right part is not dipped. There is a reduction of the glass transition temperature for the left part and it gets activated i.e., gets back to its original form with the help of the room temperature water itself.

Applications

Textiles

- Smart breathable garments that can regulate heat & moisture to the wearer's body.
- Wrinkle free, anti-shrinkable, crease retention fabrics.

- Wearable electronic devices



Industry

- Automotive seat belts – absorb kinetic energy increasing safety.
- Self-tightening tubes – to avoid leakage
- Packaging – perfect to the size & shape of product
- Damping elements
- Temperature sensors, MEMS (Micro-electronic mechanical systems)

Biomedical

- Implantable biomedical devices
- Orthodontics – metal wires replaced with SMP's.
- Bandages – adapt perfectly to patient skin.
- Sutures – Self shrinking.
- Intravenous needles
- Drug delivery

Packaging

- Perfect size & shape of the product

Rewritable digital storage devices