

HIGH-POLYMERS (UNIT-I)

Introduction:

Polymers are giant molecules produced by the combination of smaller units (polymer is derived from Greek word (poly = many) and (mer = parts or units)).

Hence polymer is giant molecule of high Molecular weight built up by linking together of a large no. of smaller molecules called monomers.

Nature is the first scientist to produce the polymers in its “giant laboratory”.

Ex: Evolution of earth by combination of elements like C, H, O & N.

- Protein is the polymer – synthesized by nature from methane, ethene, ammonia & CO₂
- Some natural polymers are wood, cotton, cellulose.
- Synthetic materials existing in form of polymer are plastics, fibers, gums, laminates, paints etc...

Some polymers have gone to the extent of replacing ailing hearts and other ones sensitive organs.

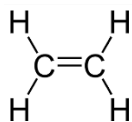
Polymers possess the desirable properties like high strength light wt., good flexibility, special electrical properties resistance chemicals and fabrication into complex shapes in a wide variety of colors.

Naturally occurring macromolecules are cellulose; wood and rubber are very widely used in day today life.

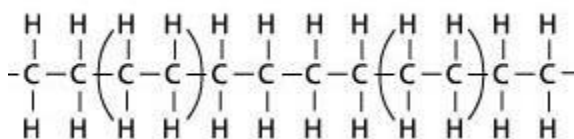
Concept of polymerization:

The polymer (i.e. macromolecules) is the resulting structure comprises of repetition of relatively small molecular fragments referred to as repeating units.

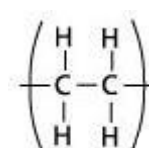
Ex: polythene is made up of interlinking of ethylene



Ethylene monomer



polyethylene



repeating unit

Depending upon degree of polymerization there are 2 types, Degree of polymerization of polythene is 100

- Oligo polymers: - Polymers whose degree of polymerization is less than 600 are called oligo polymers.

These do not possess engg. properties.

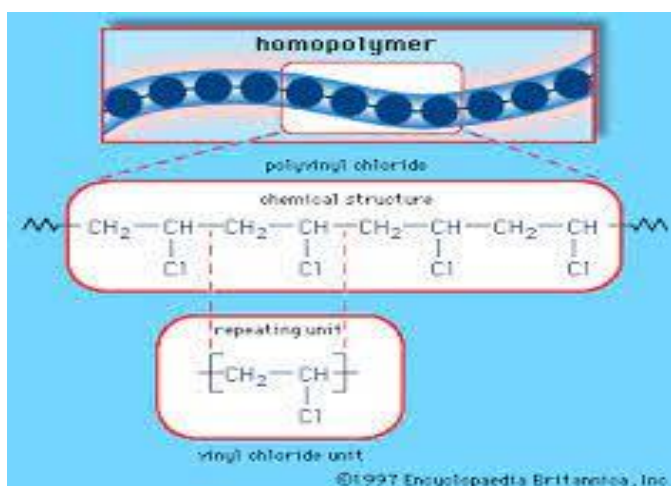
- High Polymers: - Degree of polymerization of polymer is more than 600 they possess desired engg. properties.

Functionality of Monomers:-

For a substance to act as a monomer, it must have at least two reactive sites or bonding sites. No. of reactive or bonding sites in a monomer is called **functionality**.

If x reactive sites are there in a monomer is bi functional – they form linear or straight chain molecules

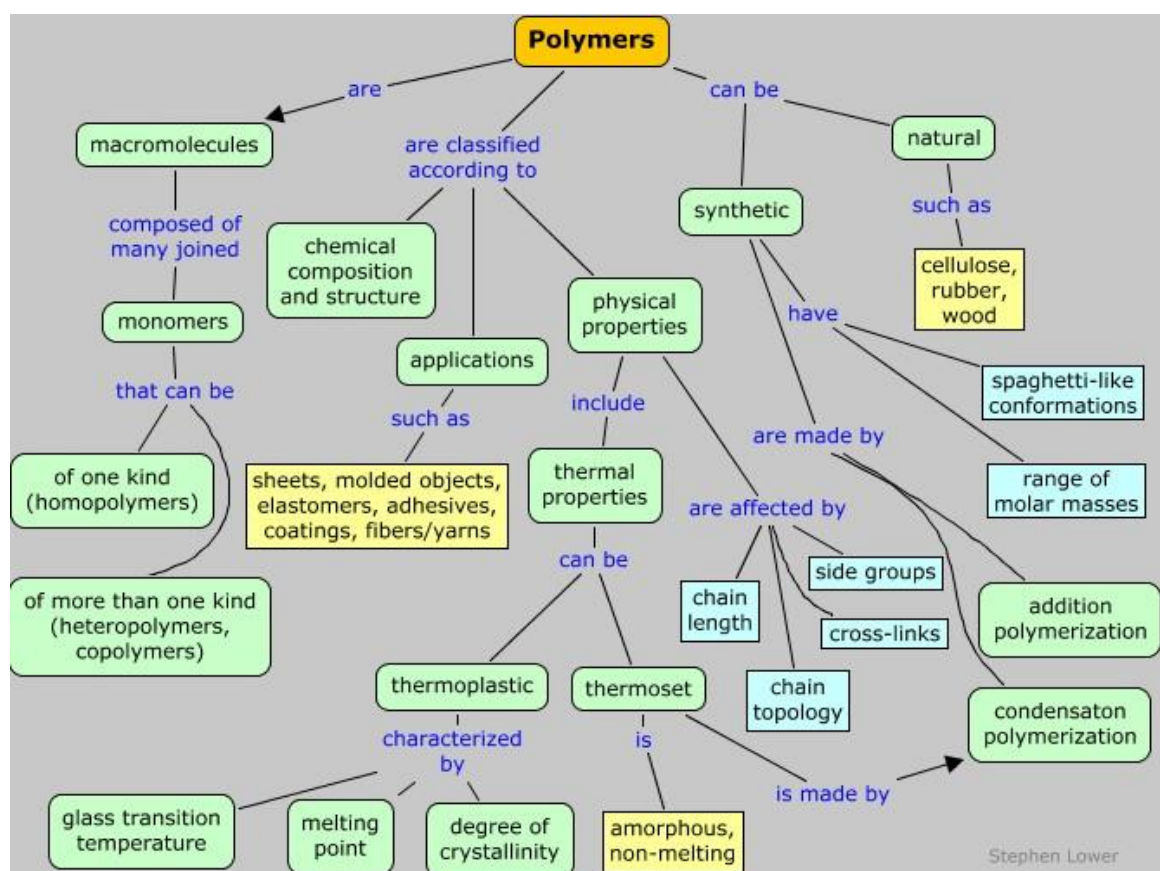
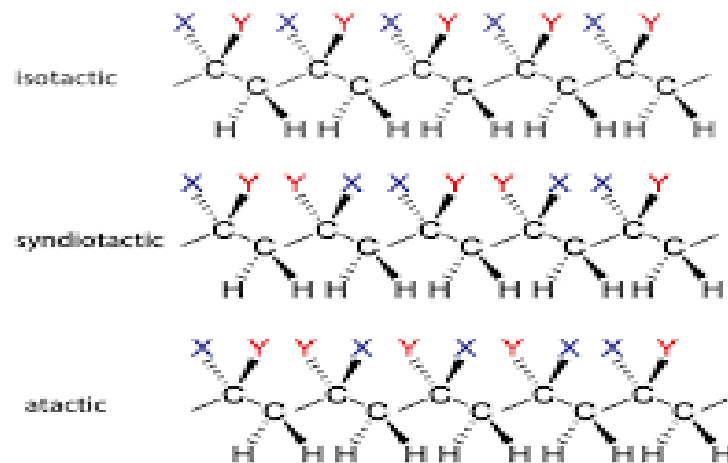
- Depending upon the functionality of monomer units, it is possible to obtain different types structures. In case of a bi functional monomer, two reactive groups attach side by side to each other forming a linear or straight-chain molecule. Linear molecules consist of monomer units linked by primary covalent bonds, but the different chains are held together by secondary van der Waals forces of molecular attraction



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 difference in configuration does affect their physical properties.

- The head-to-tail configuration in which the functional groups are all on the **same side** of the chain is called isotactic polymer
- If the arrangement of functional groups are at **random around the main chain**, it is called atactic polymer e.g. polypropylene
- If the arrangement of functional groups are at **alternating fashion**, it is called syndiotactic polymer e.g. gutta percha.



Q1. What are the types of polymerization? Explain with examples.

Addition (or) chain Polymerization:-

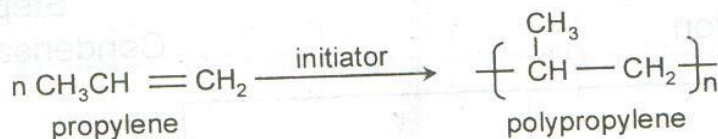
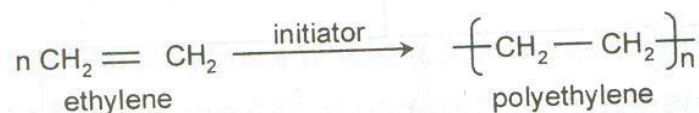
It is a reaction that yields a product which is an exact multiple of the original monomeric molecule.

The monomer contains one or more double bonds and it is bi functional.

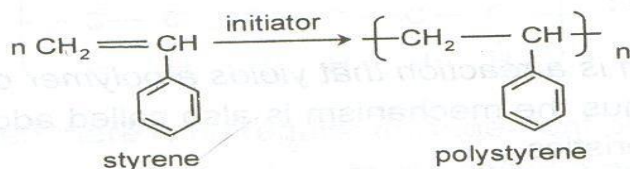
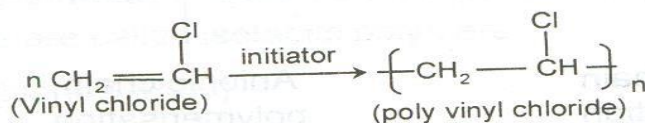
It must be initiated by light, Heat, Pressure (or) a catalyst for breaking down double covalent bonds of a monomer.

Ex: Olefins, Vinyl compounds, Allyl and dienes.

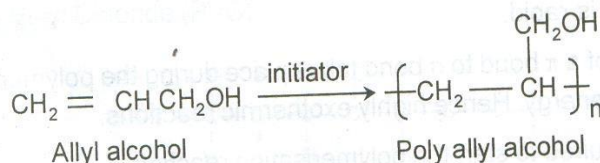
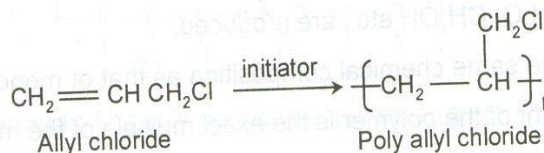
Olefins:-



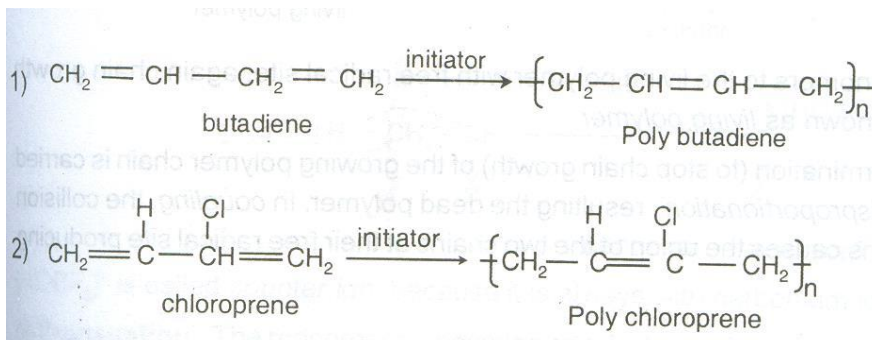
Vinyl compounds:-



- Allyl compounds:-



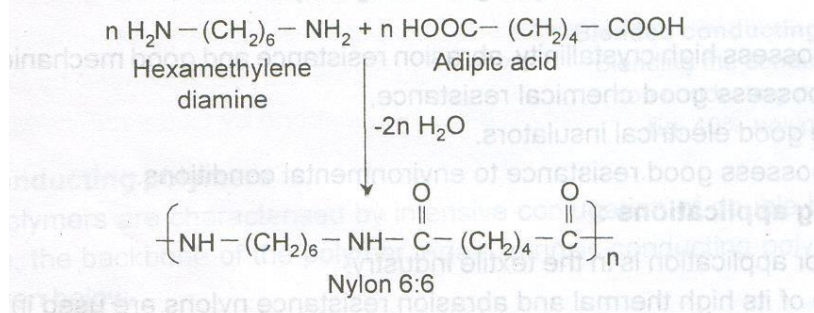
- Diene compounds:-



II. Condensation (or) step polymerisation: -

It involves the reaction occurring b/w polar gps containing monomers with formation of polymer and elimination of small molecules like water, etc.

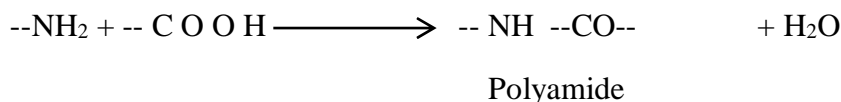
Ex: Nylon 6,6 : -Hexamethylene diamine and adipic acid condense to form nylon 6:6



The types of functional groups, which are most important in condensation reactions, are



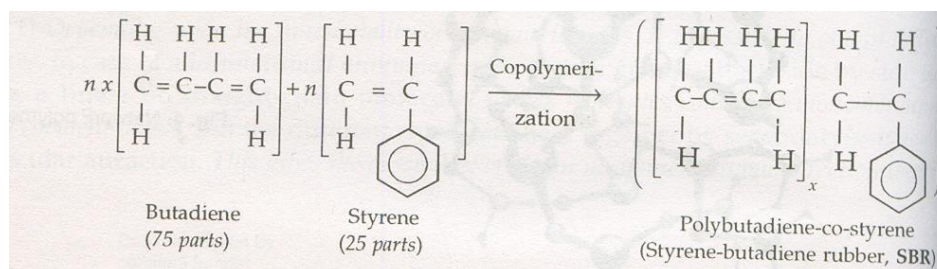
Ex: polyethylene terephthalate(terylene)



Ex: spandex fibre

III copolymerization : - (it is also addition polymerization high M.wt compounds obtained by copolymerization, are called copolymers.

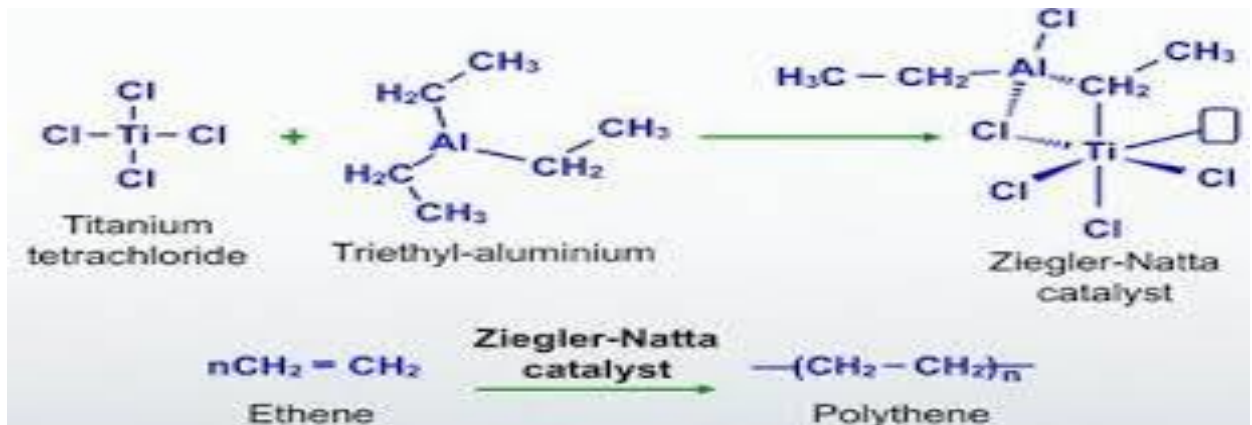
2 diff. monomer units combine to form polymer



Polymerization like in addition and it requires special catalyst)

Co – ordination Polymerization (or) Ziegler – Natta polymerization

Ziegler & Natta proposed that presence of combination of transition metal halides like TiCl_4 , ZnBr_3 ... with an organometallic compound like $(\text{C}_2\text{H}_5)_3\text{Al}$ (or) $(\text{CH}_3)_3\text{Al}$ polymerization can be carried out. It explains the stereo specific type of polymerization. Coordination polymerization is carried out in presence of Ziegler-Natta catalysts. The most commonly used Ziegler-Natta catalyst is a combination of triethyl aluminium and titanium tetrachloride. The mechanism can be explained by taking the example of polyethene. The ethene monomer first approaches towards the catalyst surface (Ti) and forms a π -complex. Then, it partially uses its π -es and also interacts with the alkyl group, yielding a transition state. Ultimately Ti-alkyl bond breaks resulting in the formation of Ti-monomer and alkyl- monomer bonds, i.e., the monomer induces itself in between Ti and the alkyl group. The mechanism can be shown as:



1. It is used for preparation of branch free polymer. Since, the chain stands already terminated, as the monomer units are added in between the catalyst surface and the alkyl group already present, there is no possibility of branch formation and the polymer formed will be 100% branch free.

It is used for preparation of highly stereo-regular polymer

POYMER STRUCTURE ON PROPERTIES:

- In straight-chain and branched-chain polymers, the individual chains are held together by weak intermolecular force of attraction, the strength of which increases with the chain length or molecular weight
- Thermoplastic materials deformed to plastic stage on application of heat or pressure
- It contains elastic character (Snarls in normal unstretched condition); Aignment of chains in stretched condition.
- Polymers containing polar groups ike $-\text{OH}$, $-\text{COOH}$ are uaually dissolved in poar solvents like water, alcohols and ketones. Non-polar groups like $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ are swollen or even dissolved in non-polar solvents like benzene, toluene, petrol
- Effect of heat on poymers
- (i) Amorphous polymers

GLASS→RUBBER→GUM→LIQUID

(b) Crystalline polymers

CRYSTIINE AND GLASS REGIONS→FEXIBETHERMOPLASTIC→LIQUID

Mechanical properties of polymers: The length and type of polymer chain also affect the strength of the polymer. Strength can be estimated with the help of stress-strain test. As the applied force increases, the amount of stretch is a measure

of the strain. Typical stress-strain curves for different types of polymer is shown in Fig.

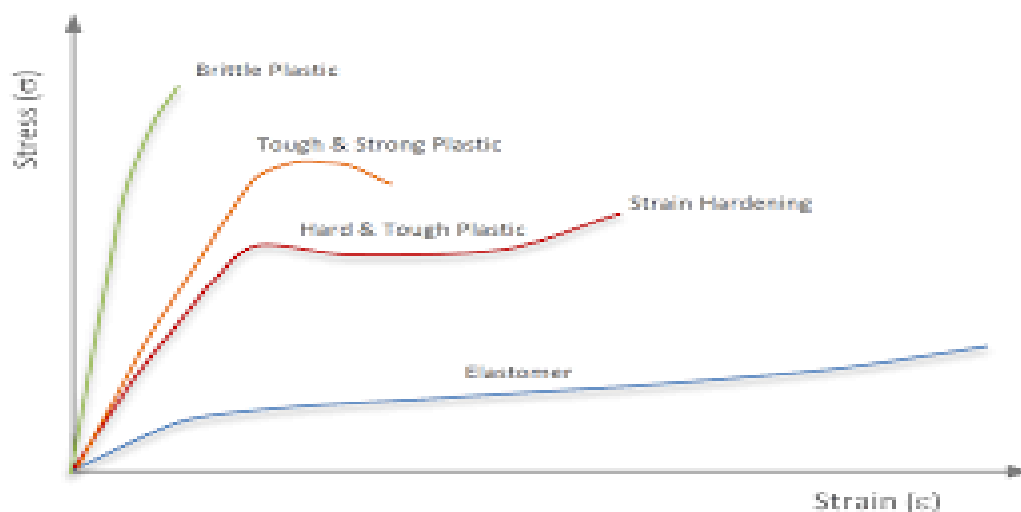


Fig: Four types of stress-strain curves illustrating how polymer of different types behave. The lines end where the sample breaks

Q2. What is a plastic? Explain the differences between thermoset and thermoplastic materials. Give examples.

Plastics are polymers characterized by property of plasticity (permanent deformation in structure on applying some stress / force) and moulded to desired shape upon subjected to heat and press in presence of catalyst.

Resin : - It's the product of polymerization and form the major part of plastics.

Condensation polymerization	Additional polymerization
It is also known as step growth polymerization	It is also known as chain growth polymerization
It takes place in monomers having reactive functional groups	It takes place only in monomers having multiple bonds
It takes place with elimination of simple molecule like H_2O , NH_3 , HCl etc.,	It takes place without elimination of simple molecule
Repeat units of monomers are different	Repeat units & monomers are same
The polymer is formed in gradual steps	Reaction is fast and polymer is formed at once
The molecular mass of polymer increases throughout the reaction	There is very little change in the molecular mass throughout the reaction
Product obtained may be thermosetting/thermoplastic	Product obtained are thermoplastic
E.g.:- Bakelite, polyester, polyamides etc.,	E.g.:- Polyethylene, PVC, poly styrene

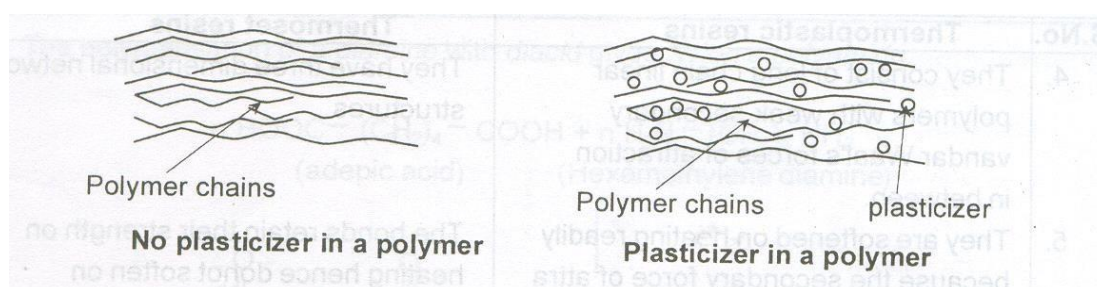
	Thermoplastic resins (or) Polymers	Thermosetting resins (or) Polymers
1	These are produced by additional polymerization	These are produced by condensation polymerization
2	The resins are made of long chains attached by weak Vander Waal's force of attraction.	The resins have three dimensional network structure connected bonds
3	On heating they soften and on cooling become stiff chemical nature won't change	On heating they become stiff & hard. No change on cooling. Chemical nature changes
4	They can be remoulded	They cannot be remoulded because once set means they are permanently set
5	Scrap (waste product) can be used	Scrap cannot be used
6	The resins are soft, weak and less brittle	The resins are usually hard, strong tough & more brittle
7	These are easily soluble in some organic substances E.g.:- PVC, polyethylene etc.,	Resins are not soluble in organic solvents E.g.:- Nylon, Bakelite etc.,
8	Contain long chain polymer with no cross linkage	They have 3D network structure

Q3. How compounding of plastics is done?

Compounding of plastics: - Polymer Resin is mixed with 4 to 10 ingredients during fabrication to impart useful properties to the finished article, this is called compounding of plastics

- **Resin:** - it's a binder which holds the diff. constituents together. Thermoset resins are supplied as linear polymers of comparatively low M.wt. This is converted to cross link infusible from during moulding.
- That is added to resins to increase their plasticity and flexibility.
- They neutralize the intermolecular forces of attraction b/w polymer chains.
- They impart greater freedom of movement b/w the polymeric molecules

Plasticizers decrease the strength and chemical resistance. Commonly used plasticizers are vegetable oils, camphor, esters of stearic acid ... tricresyl phosphate and trivinyl phosphate.



- **Fillers:** - They are added to give final plastic better hardness, tensile strength, opacity and brittleness.
- They reduce cost of polymers

- Some special type of fillers are added to impart special properties to polymers like Ba salts make polymers impermeable to x-rays and Asbestos provides heat & Corrosion resistance to polymers

Percentage of fillers is up to 50% of total moulding mix commonly used fillers are wood flour, gypsum saw dust, marble flour, paper pulp, cotton fibres and metallic oxides like ZnO & PbO.

3. Lubricants: - a. waxes oils stearates and soaps are employed to make the moulding of plastic easier

b. They prevent plastic material from sticking to the fabrication equipment.

4. Catalysts or Accelerators:-

They accelerate the polymerization of fusible resin during molding operation into cross linked infusible form for thermosetting resins.

Commonly used catalysts for compounding of thermosetting resins are benzoyl peroxide, H_2O_2 acetyl H_2SO_4 , metals like Ag, Cu & lead, metal oxide like ZnO.

5. Stabilizers: -

They improve thermal stability during polymerization.

- During moulding heat stabilizers are used

Ex: opaque moulding compounds like salts of lead, lead chromate, litharge, red lead, lead silicate and lead naphthalene.

Transparent moulding compounds like stearates of lead, Cd and Ba.

6. Colouring Materials: -

- Colouring is of high importance in high polymer articles.
- Colouring materials impart esthetic sense and appeal to plastics.
- Organic dyestuffs and opaque inorganic pigments are commonly used as colouring materials.

Summary of compounding of plastics

- Resin forms body of the plastics and binder for diff ingredients.

Ex: Thermoplastic & Thermoset resin.

- Plasticizer gives plasticity and flexibility.

Ex: Oils, water, tricresyl and triamyl compounds.

- Fillers | reinforced fillers give hardness, tensile strength, opacity, finish workability to plastics, reduces the cost.

Ex: Ba salts, quartz, mica, ZnO, PbO, Al, Cu, Pb.

- Lubricants makes moulding easier gives flawless gloss finish to plastics.

Ex: waxes, oils, stearates and oleates.

- Catalysts | accelerators accelerates the cross linking of thermosetting resin.

Ex: H_2O_2 , Cu, Ag, Pb.

- Stabilizers increase thermal stability during fabrication

Ex: Pb salts, Ca & Ba

- Colouring materials gives esthetic sense and appeal to plastics.

Ex: organic dyes & opaque inorganic pigments

Moulding of plastics into articles

To give suitable shape to plastic several methods of fabrications are in used.

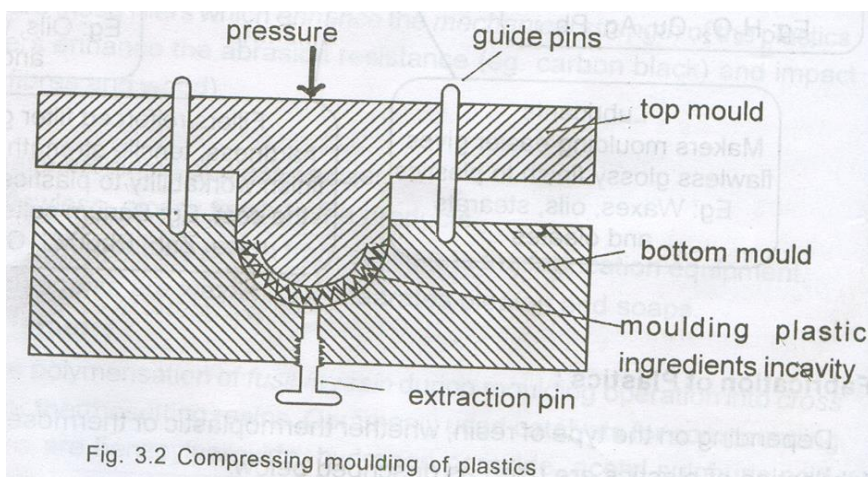
The method chosen depend upon type of plastics (i.e. thermo or thermosetting plastics) and shape of finished product commonly used methods are given below.

Q4. Explain different types of moulding techniques involved in preparation of plastics.

Compression Moulding: -

This is applicable to both thermoplastic and thermosetting resin. A known quantity of compounded plastic resin is filled in the cavity present in the bottom mould. Top mould and bottom mould are capable of being moved relative to each other when heat and press are applied according to specifications the cavities get filled with fluidized plastic.

The two mould (top & bottom in fig.) are closed tightly and curing (time given to polymer to set in the mould) is clone either by heating in case of thermoplastic resins



case of thermoplastic resins

After curing the moulded article is taken out by opening the mould.

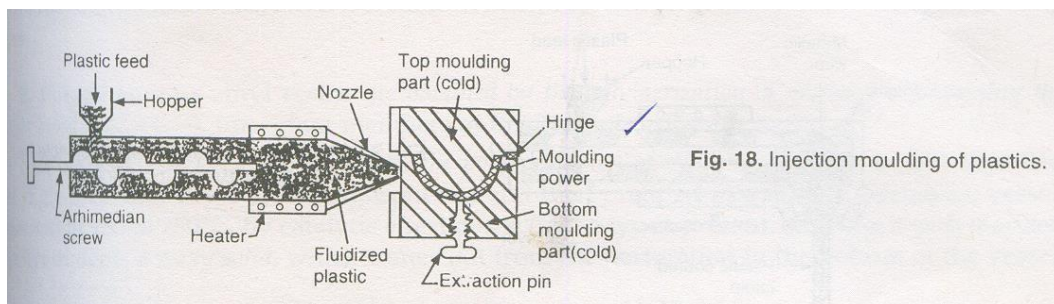
Uses: the process is used for manufacturing of cylinders and gear handles.

Injection moulding: - (Applicable to thermoplastic resins)

The moulding plastic powder is fed into heated cylinder from a hopper is fed into heated cylinder from where it is injected at a controlled rate into tightly locked mould by means of screw arrangement or by piston the mould is kept cold to allow hot plastic to cure and become rigid.

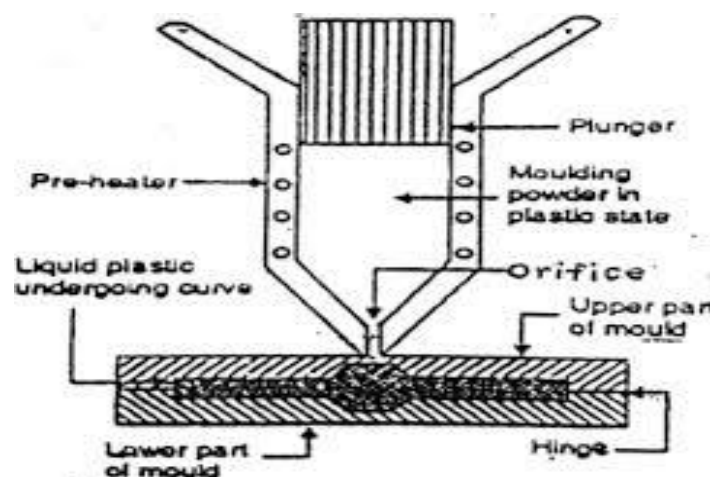
When material have been cured sufficiently half of the mould is opened to allow the injection of finished article without any deformation. Heating is done by oil or electricity.

Advantages : - Mainly useful for moulding of thermo plastics because of high speed production, low mould cost, very low cost of material and low finished cost.

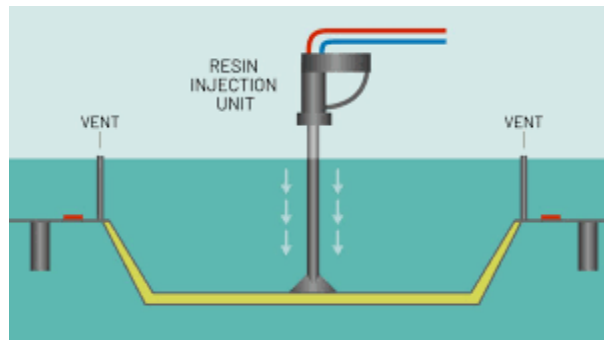


Limitations: - large no. of cavities can't be filled simultaneously. So there is limitation of design articles to be moulded.

Transferrmoulding: Is a method, which uses the principal of injection moulding for thermo setting materials. In this (Fig) the moulding powder is a heated in a chamber, maintained at the minimum temperature at which the moulding powder just begins to become plastic. This plastic material is then injected through an oriffic into the mould by a plunger, working at a high pressure. Due to the very great friction developed at the oriffic, the temperature of the material, at the time of ejection from the orifice, rises to such an extent that the mouding powder becomes almost liquid, and consequently, it flows quickly into the mould, which is being heated up to the curing temperature required for setting. The moulded article is then ejected mechanically.

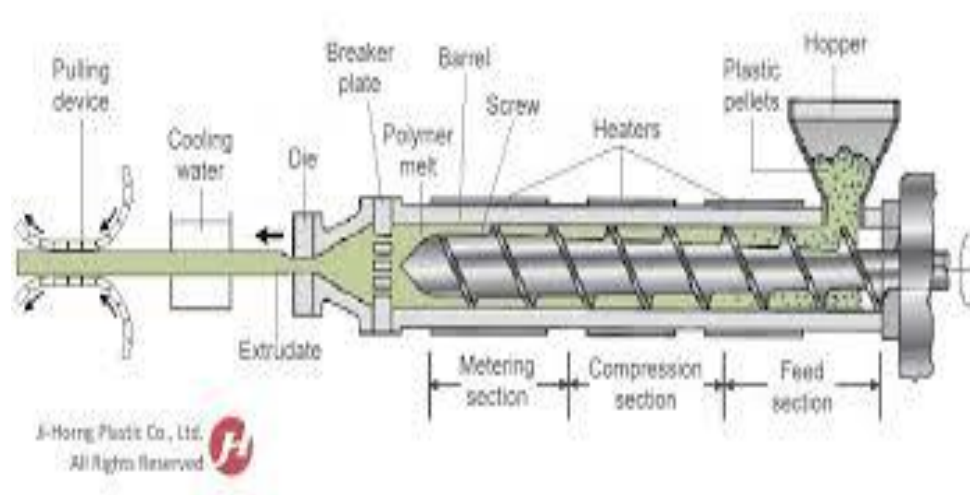


Fig; Transfer moulding of plastic



Fig; Transfer moulding of plastic

Extrusion moulding: Is used mainly for continuous moulding of thermo plastic materials into articles of uniform cross-section like tubes, rods, strips, insulated electric cables. The thermoplastic ingredients are heated to plastic condition and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to be manufactured. Here the plastic mass gets cooled, due to the atmospheric exposure. A long conveyor carries away continuously the cooled product



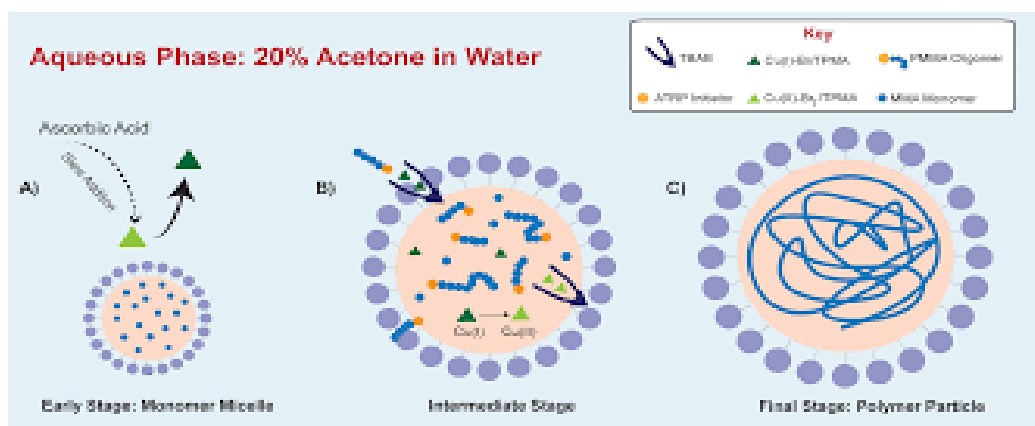
Fig; Moulding of insulated electric cable by vertical extrusion method

Emulsion polymerization;

The monomers are dispersed as fine droplets (10^{-5} to 10^{-6})mm in a large amount of water and then emulsified by the addition of soap, or detergent or protective colloids (casein, gum, gelatin, dextrin) .redox type of initiators are added. Persulphate (SO_4^-) free radicals are used. These ion radicals or micelles form polymerization occurs. Finally, the emulsion is used as adhesive, surface coating or textile finishing. This method is widely used to prepare vinyl polymers like PVC, PVA, etc.

EMULSION POLYMERIZATION

- The emulsion of monomer in water is stabilized by a surfactant.
- A surfactant has a hydrophilic and hydrophobic end in its structure.
- When it is put into a water, the surfactant molecules gather together into aggregates called micelles.
- The hydrocarbon tails (hydrophobic) orient inwards & heads (hydrophilic) orient outwards into water.
- The monomer molecules diffuse from monomer droplets to water & from water to the hydrocarbon centre of micelles.



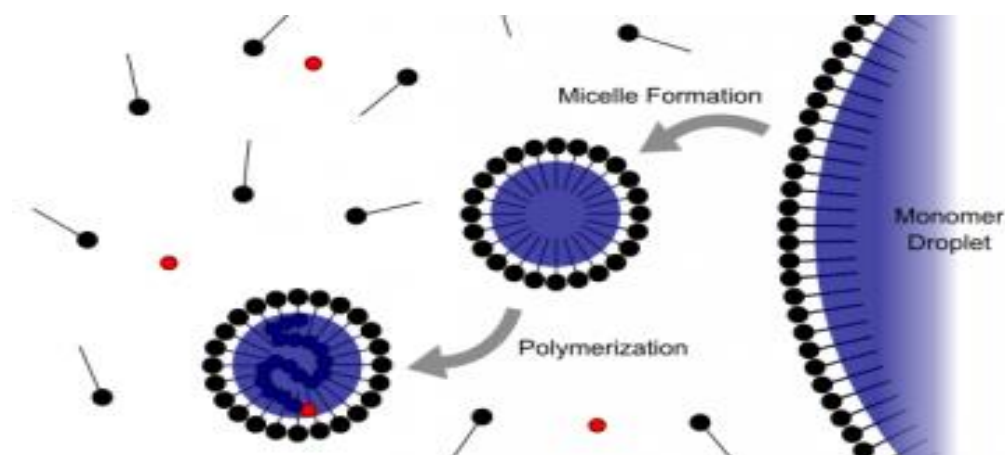
Fig; Emulsion polymerization

Suspension polymerization;

The monomer is dispersed as relatively large droplets (0.1 to 1 mm particle size) in water. It is kept in mechanical agitation. The catalyst is then added and initiation takes place. At this stage, suspension is stabilized by addition of a small amount of suspension stabilizer (e.g., kaolin, magnesium silicate, aluminum hydroxide). When the reaction is complete, the reaction products are washed, dried, and used. Prepared in this method is PVC & PS.

SUSPENSION POLYMERIZATION

- Liquid or dissolved *monomer suspended in liquid* phase like water.
- *Initiators used are monomer soluble* e.g. dibenzoyl peroxide.
- Thus, polymer is produced in heterogeneous medium.
- Initiator
- The size of monomer droplets is *50-200 μm* in diameter.
- The dispersion is maintained by continuous agitation and *the droplets are prevented to coalesce* (unite or merge) by *adding small quantity of stabilizers*.

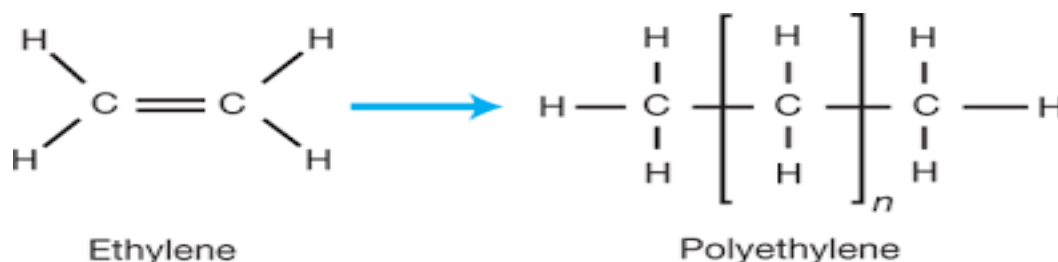


Fig; Suspension polymerization

Q5. How is HDPE prepared? Write its properties and applications.

Polyethene:

Polyethene is a homo-polymer and its monomer unit is ethene (ethylene). It is the most common and with simplest structure among all plastics. The reaction for preparation of polyethene can be shown as:



Polyethene is broadly of two types:

- i). Low Density Polyethene (LDPE)
- ii). High Density Polyethene (HDPE)

i) **Low Density Polyethene (LDPE):** As the name itself indicates, it is a polymer of very low density. It is prepared via free radical mechanism at a temperature of 80 to 350° C under high pressure (1000 to 3000 atm) in presence of a oxygen or a peroxide (Benzoyl peroxide) as **initiator**, wherein extensive branch formation takes place and the density of the resultant polymer is very low in the range of 0.910–0.940 g/cm³.

Properties:

- It is a waxy translucent material, exhibits high impact strength, low brittleness temperature, film transparency and outstanding electrical insulating properties.
- It is chemically inert and has good resistance to acids and alkalis. However, it swells in and is permeable to oils.
- It melts in temperature range of 107-120°C. Its Tg (Glass Transition) value is -120°C.
- It is flexible over a wide temperature range.

Applications: It is used in making packaging materials for food, garments, etc. It is used in production of squeeze bottles, coatings, wrappings, etc. It is also used in cable and wire insulations.

i) *High Density Polyethene (HDPE)*: It is a linear polymer with little or no branching. It is prepared via ionic mechanisms at a low temperature of 60 to 70° C and very low pressure (6 to 7 atm), wherein little or no branch formation takes place and the density of the resultant polymer is high in the range of 0.945–0.965 g/cm³. However, HDPE is also prepared by coordination polymerization using Ziegler-Natta catalyst (Triethyl aluminium and Titanium tetrachloride).

High density polyethylene: density is 0.965 g/cc.

It is prepared by using coordination chain polymerization mechanism.

Production of HDPE by coordination polymerization requires:

- temperature 50-75°C
- slight pressure
- a coordination catalyst is prepared as a colloidal suspension by reacting an aluminium alkyl and titanium chloride (TiCl₄) in a solvent such as heptane (C₇H₁₆).
- The polymer (polythene) forms as a powder or granules which are insoluble in the reaction mixture. When the polymerization is completed, the catalyst is destroyed by adding water or alcohol to the reaction mixture. The polymer (polythene) is then filtered or centrifuged off, washed and dried.

Properties & uses: -

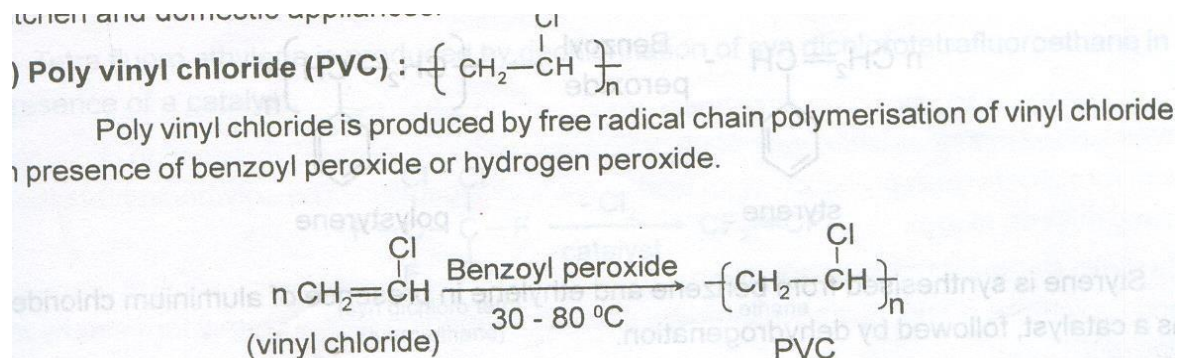
- The HDPE molecules are linear and their packing is easy. Hence HDPE has high density (0.95-0.97) and more percentage of crystallinity (80-90%). Softening temperature of HDPE is also high.
- It has excellent chemical resistance and electrical insulation property. It is stiffer, harder and possesses greater tensile strength. Polyethylene is a rigid, waxy white, translucent, non – polar material with high symmetrical structure.
- Polyethylene is a good electrical insulator.
- Resistant to strong acids, alkalis and salt solution at room temp.
- Its soft flexible polymer
- Resistant to atmospheric conditions like O₂, CO₂, moisture.
- HDPE has MP 144 - 150°C it has higher tensile strength and hardness with less gas permeability
- LDPE possess branched chain structure and its M.P is 81°C

Engineering Applications:-

Polyethylene used for making high frequency insulator parts, bottle caps, packing materials, tubes, coated wires, in chemical plants for kitchen and domestic appliances.

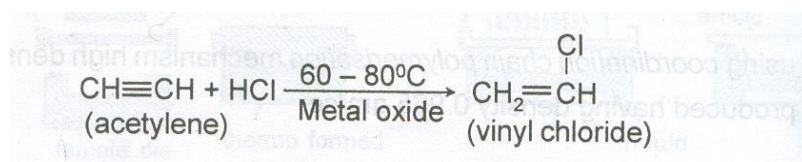
Q6. Mention the properties and uses of PVC.

Poly vinyl chloride:-



Vinyl chloride is prepared by treating acetylene with HCl at 60-80°

In the presence of metal oxide catalyst,



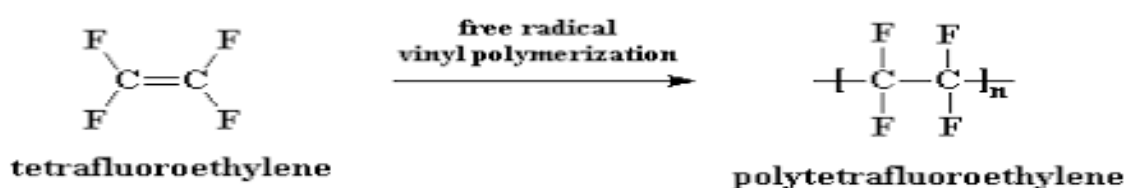
Properties: PVC is colourless, odourless, non-inflammable and chemically inert powder. Pure resin possesses greater stiffness and rigidity compared to poly ethylene. It is brittle in nature.

Engineering applications:-

1. Used for electrical insulations.
2. Injection moulding articles like tool handles ,radio and telephone components.
 - Used for making safety helmets, refrigerator components,tyres
 - And motor cycle mudguards.

Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene is commercially known as Teflon. It is a homo-polymer and its monomer unit is tetrafluoroethylene. It is a thermoplastic polymer. It is usually prepared emulsion polymerization of tetrafluoroethylene using peroxide or ammonium persulphate as initiators. The reaction for preparation of Teflon can be shown:

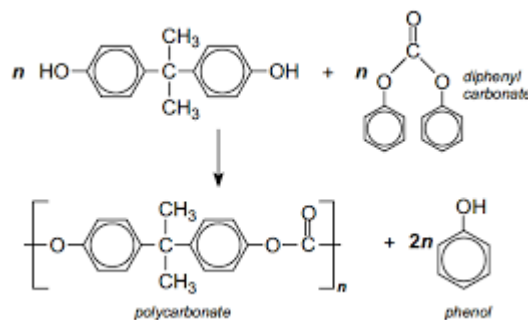


Properties:

- It is a highly crystalline polymer (93-98% crystallinity).
- It has high chemical resistance.
- It is practically insoluble in all solvents and is not wetted by either water or oil.
- It has low coefficient of friction and remains slippery over a wide range of temperature (-40-300°C).
- It is resistant to temperature with high temperature stability.
- It has excellent electrical insulating properties.

Applications: Teflon is used as a non-sticky coating on frying pans, iron. It is used on weapons as an anticorrosive coat. It is used as a coating on pipes and tanks for carrying and storing corrosive chemicals, respectively. It is also used as dry lubricant on burette stoppers.

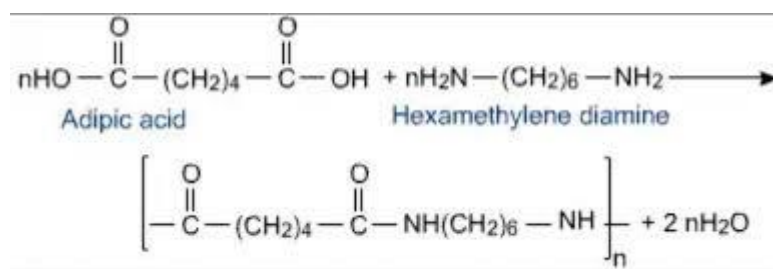
Poly carbonate (PC) : Merlon are prepared by interaction of diphenyl carbonate with bisphenol [2,2 bis-(4-hydroxyphenyl) propane]



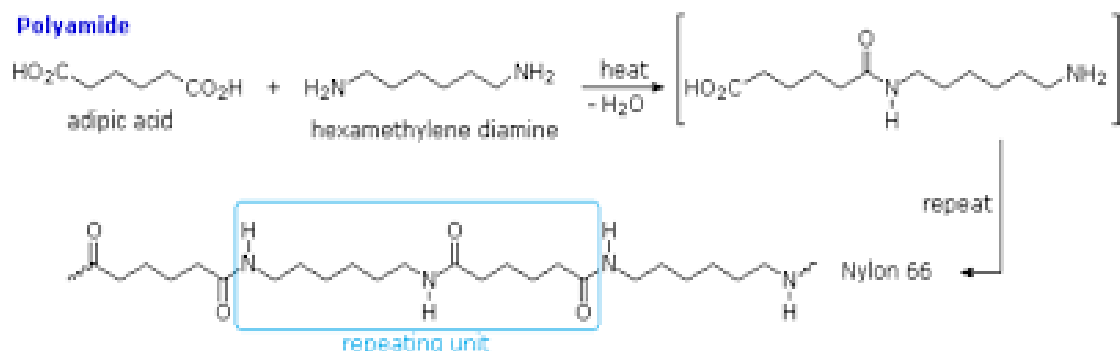
- Properties: High impact and tensile strength of wide range of temp.
- Soluble in organic solvents and alkalis

Uses; For preparing moulded domestic ware, housing for apparatus, electrical insulator in electronic and electrical industries

Nylon -6:6: Is obtained by the polymerization of adipic acid with hexamethylene diamine



Polyamide



Typical Physical Characteristics of Nylon 66			
Property ^a	Unit	Value	Method/Standard ^b
Specific gravity		1.14	ASTM D792
Density	kg/m ³ (lb/ft ³)	1140 (71.17)	ISO R1183
Melt density	kg/m ³ (lb/ft ³)	965 (60.24)	
Bulk density	kg/m ³ (lb/ft ³)	ca. 670 (41.83)	
Water absorption (24 h)	%	1.3	ISO 62
	%	1.2	ASTM D570
Melting point	°C (°F)	260 (500)	ISO 1218 or ASTM D789
Glass transition temperature	°C (°F)	100 (212)	ISO 75
	°C (°F)	90 (194)	or ASTM D648
Self-ignition temperature	°C (°F)	>420 (788)	ASTM D1929
Flash ignition temperature	°C (°F)	>400 (752)	ASTM D1929
Specific heat	J/g·K (ft·lb/ft·lb·°F)	1.7 (3.16 × 10 ⁻¹)	In-house method
Thermal conductivity	W/m·K (Btu/ft·h·°F)	0.3 (0.17)	Conco-Fisher apparatus
Flammability (UL)		V2	UL94 at 1.6 mm
Dielectric constant		3.9 at 50 Hz	IEC 250 or ASTM D150
		3.7 at 1 kHz	
Volume resistivity		10 ¹³ Ω	IEC 93 or ASTM D257

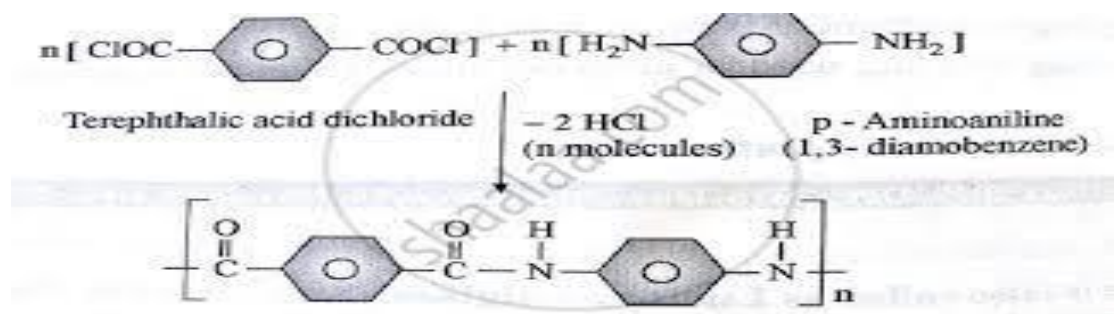
^aActual properties will depend on the type of polymer being used.
^bTest methods and standards may vary depending on the manufacturing region in our worldwide supply network.

- They are light, horny and high melting
- They are insoluble in common solvents
 - Good abrasion resistance
- They are very flexible and retain original shape after use
 - Excellent high-speed processing
 - High stretch and recovery
 - High durability and strength
 - Good hand

USES OF NYLON:

- Textiles: Apparel, tooth brushes, Tyre cord
- Automotive: Bearings, slides, door handles, door & window stops.
- Furniture: Locks, hangers, chairs etc.,
- Packaging: Film sheet
- Mech. Engg.: Drive gears, bearings, fish plates for railways lines tubing.
 - Weaving and Warp Knitting
 - Coated Fabrics
 - Carpeting
 - Furnishings/Floor Coverings

Kevlar: Is an aromatic polyamide similar to nylon. Polycondensation between aromatic dichloride and aromatic diamine



Kevlar preparation

PROPERTIES:

- Kevlar is exceptionally strong (5 times stronger than steel and 10 times stronger than Al on weight for weight basis.
- High stability and flexibility

- For more rigid
- The high electron –density in the chains of Kevlar

USES;

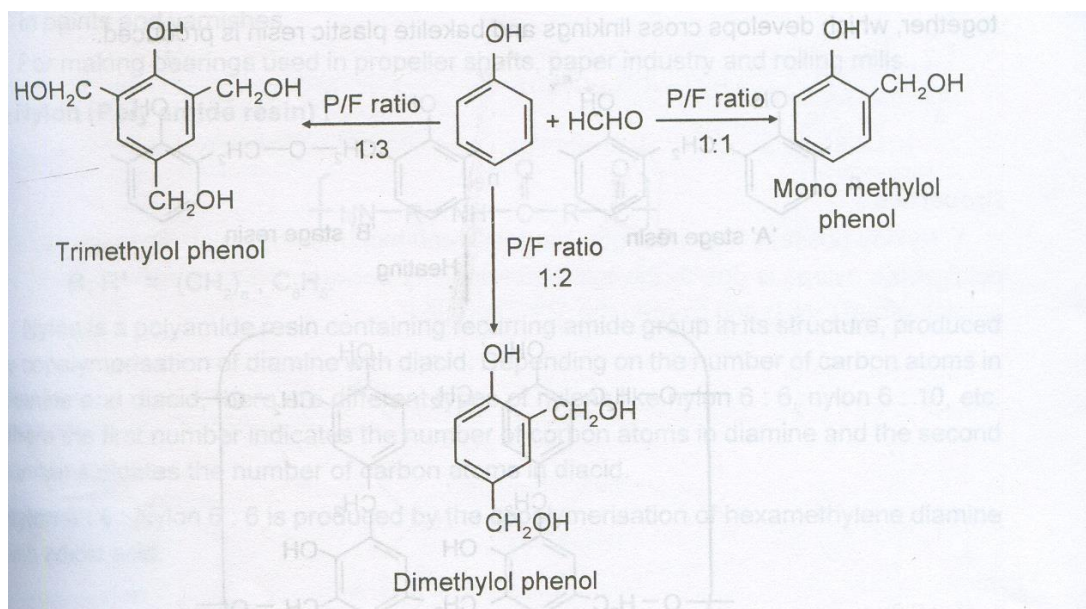
- Aerospace & aircraft industries
- Car parts (Such as tyres, breakes, clutch linings)
- Ropes cables and protective clothing
- Bullet-proof vests
- Motorcycle helmets and high performance materials

Q7. Explain the preparation properties and uses of Bakelite.

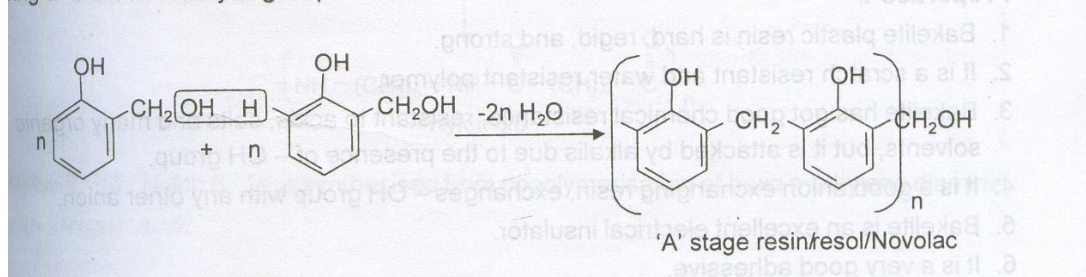
Bakelite:-

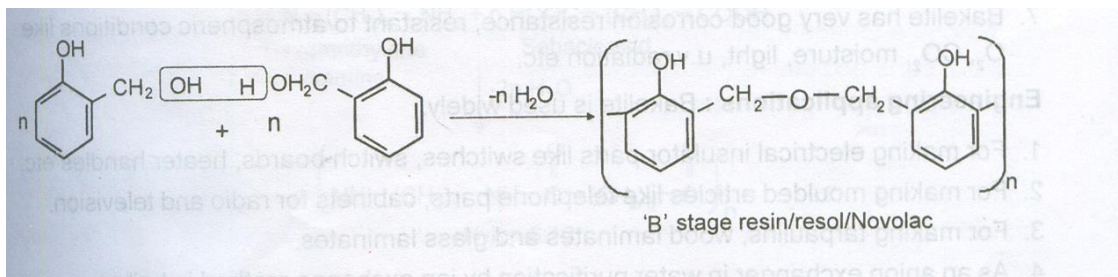
(Phenol-formaldehyde resin). This belongs to thermoset resin.

Phenol reacts with formaldehyde in presence of acid or alkali produces mono di and triMethylol phenols depending on phenol formaldehyde ratio.

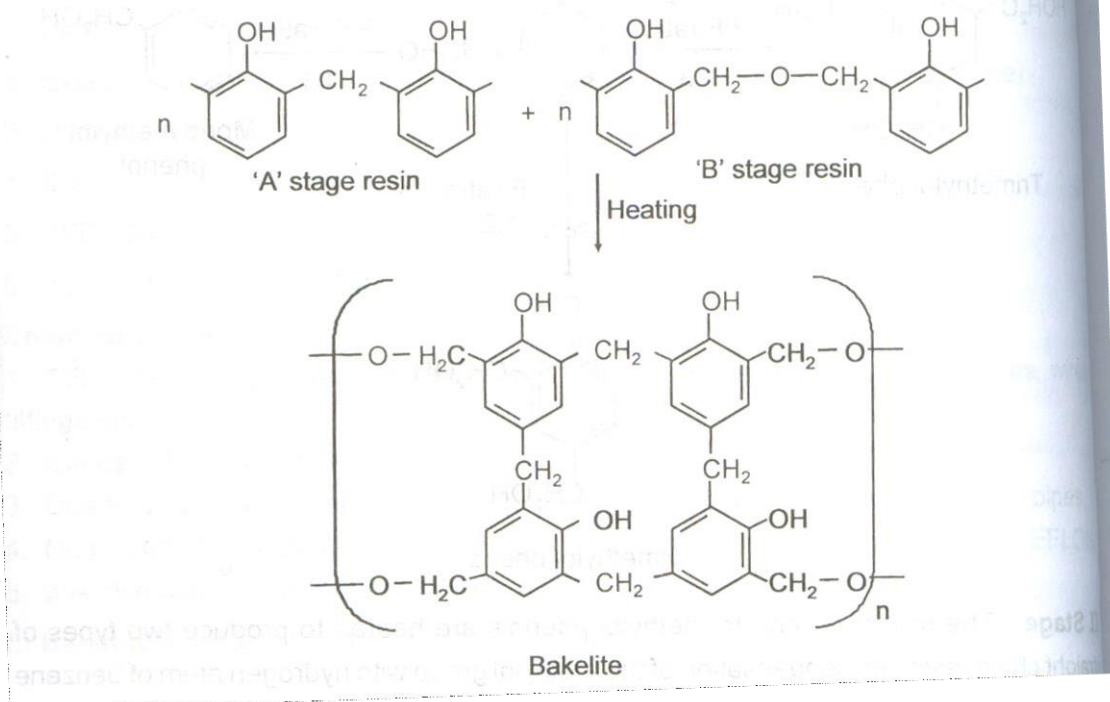


II Stage : The mono, di, and tri methylol phenols are heated to produce two types of straight chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.





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



Properties: phenolic resins set to rigid, hard, scratch resistant, water resistant, insoluble solids, which are resistant to non-oxidizing acids and many organic solvents.

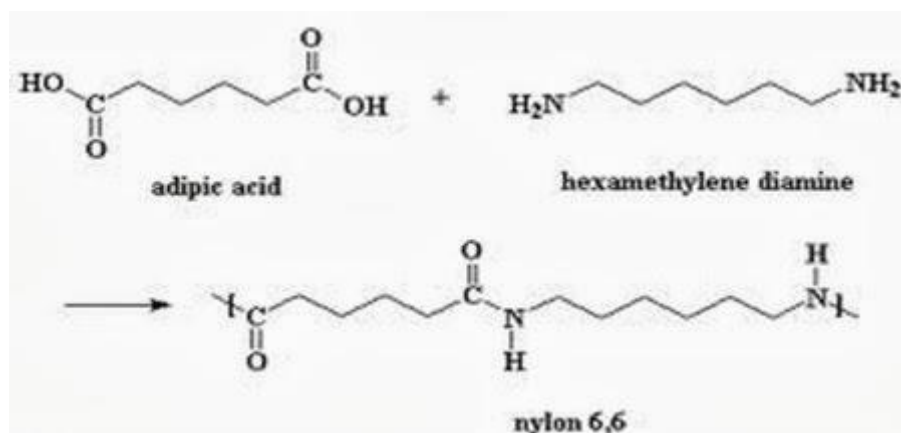
Engineering applications:-

- a. for making electric insulator parts like switches, plugs, switch boards etc...
- b. for moulding articles like telephone parts, cabinets for radio and television.
- c. as adhesives for grinding wheels.
- d. for making bearings, used in propeller shafts for paper industry and rolling mills.

Q8. Explain the preparation properties and uses of Nylon-6,6.

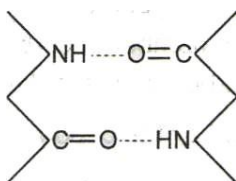
Nylon-6,6 (polyhexamethylene diamine adipamide) is a polyamide made from adipic acid and hexamethylenediamine by polycondensation. The nylon developed by Carothers at Du

Pont was nylon 66. Because of the importance of starting out with equal amounts of the two reactants, salts of the diamine and of the di-acid are made and then used in the commercial synthesis of nylon 66.



Properties:

- Nylons possess high strength, hardness and high melting point. The high melting point of the nylons is due to the hydrogen bonding between the hydrogen atom of the amide group (-NH) and oxygen the C = O group.



Hydrogen binding in Nylons

- Nylons possess high crystallinity, abrasion resistance and good mechanical properties
- Nylons possess good chemical resistance,
- They are good electrical insulators.
- Nylons possess good resistance to environmental conditions.

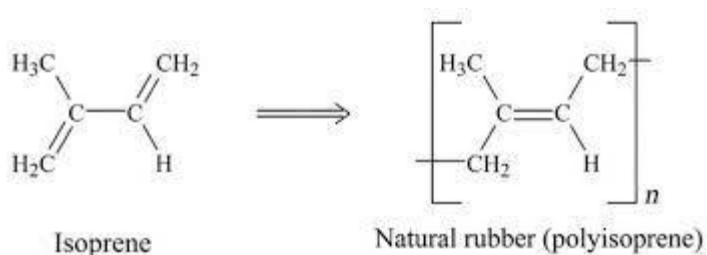
Engineering applications:

- The major application is in the textile industry.
- Because of its high thermal and abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there
- Flexible tubings for conveying petrol etc are made from nylons.
- Nylons are used as electrical insulators.
- Nylon 6 is used for making tire cords.

- Nylons are used in auto mobile industry and telecommunication industry for making radiator parts and coil formers respectively.

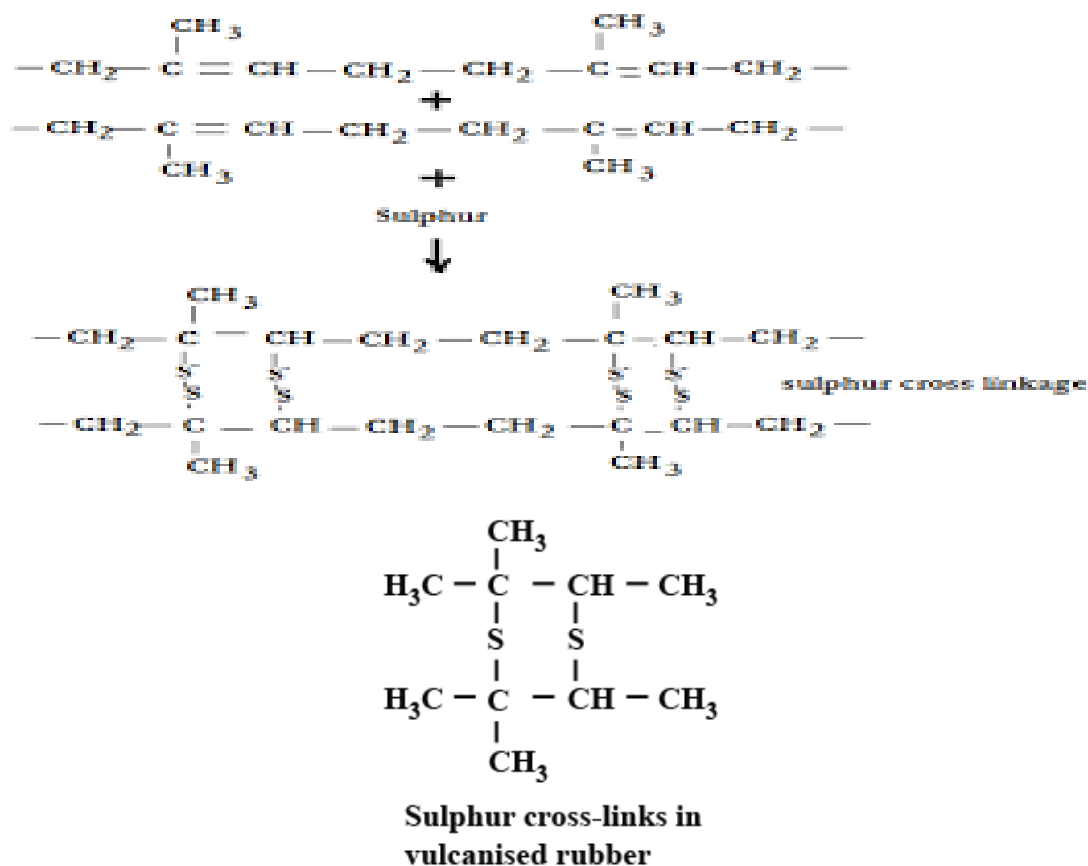
Rubbers: (Elastomers) :

- Rubbers also known as elastomers, they are high polymers, which have elastic properties in excess of 300%.
- *Natural Rubber:-*
- Natural Rubber is a high molecular weight hydrocarbon polymer represented by the formula $(C_5H_8)_x$. It is obtained from a milk emulsion called latex by tapping the bark of the tree. "Hevea brasiliensis". It is a polymer of isoprene units.



- The polymer chain of natural rubber is made of 2000 to 3000 monomer units
- Processing of Natural Rubber:-
- By cutting the bark of rubber tree the milky colloidal rubber milk is obtained. The main constituent of rubber latex is 25-45% of rubber and the remaining are water, protein & resinous materials. The rubber latex is coagulated by using 5% acetic acid and made in to sheets. The rubber sheets are cured under mild heat and then subjected to further processing.
- Crepe rubber:-
- To the rubber latex a small amount of sodium bisulphate is added to bleach the colour and feed in to roller which produce 1mm or more thickness sheets which are dried in air at about 40-50°C. the dried thin sheet of rubber are known as "smoked crepe rubber".
- Mastication:-
- Rubber becomes soft and gummy mass when subjected to severe mechanical agitation. This process is known as mastication. Mastication followed by the addition of certain chemical (compounding) which is carried out on roll mills or internal mixers. After mastication is complete, the rubber mix is prepared for vulcanization.

- **Vulcanization:-**

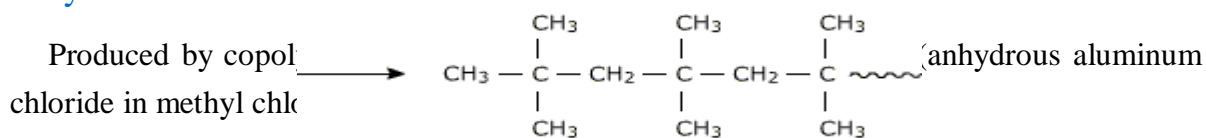


- Vulcanization process discovered by Charles good year in 1839.It consists of heating the raw rubber at 100-1400C with sulphur. The combine chemically at the double bonds of different rubber spring and provides cross-linking between the chains. This cross linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs.
- The amount of sulphur added determines the extent of stiffness of vulcanized rubber.
- For eg, ordinary rubber (say for battery case) may contain as much as 30% sulphur

Property	Raw rubber	Vulcanized rubber
Tensile strength	200 kg/ cm ²	2000 kg/ cm ²
Elongation at break	1200	88
Rapidity of retraction	Good	Very good
Water absorption	Large	Small
Swelling in organic solvents	Infinite	Large
Tackiness	Marked	Slight
Useful temperature range	10-600 ⁰ C	-40 -100 ⁰ C
Chemical resistance	Very poor	Much better
Elasticity	Very high	Low

Q9. Explain properties and applications of butyl rubber.

Butyl rubber: also known as GR-I rubber.



butyl rubber

Properties:

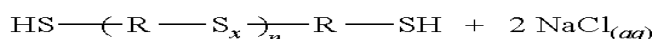
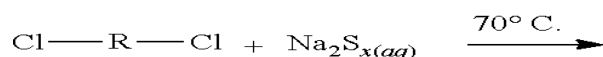
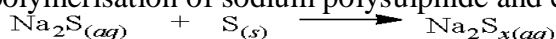
- Strong, tough, low permeability to air and other gases.
- Excellent resistance to heat, abrasion, ageing, and chemicals such as inorganic solvents, polar solvents
- Soluble in hydrocarbons solvents like benzene
- Abrasion resistant
- High resistant to atmospheric gases (ozone)
- Good electrical insulator.

Applications:

- Cycle tyres, automobile parts and its tubes
- Conveyor belt in food processing
- Insulator for high voltage wires and cables
- Tank lining

Q10. Explain properties and applications of Thiokol rubber. (Thiokol rubber or polysulphide rubber or grp rubber):

Preparation: by copolymerisation of sodium polysulphide and ethylene dichloride.



Properties:

- Strength, impermeable to gases
- Cannot form hard rubber
- Good resistance to mineral oils, fuels, oxygen, solvents, ozone and sunlight
- Low abrasion resistance

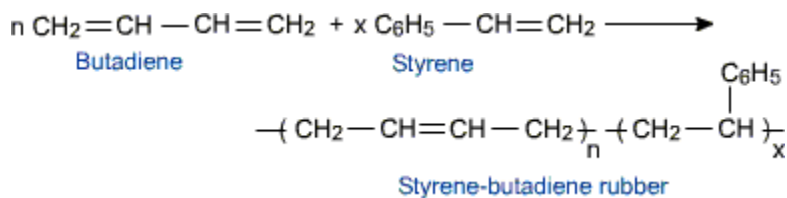
Applications:

- Fabric coated with thiokol used for barrage balloons, lift rafts and jackets which are inflated by carbon dioxide.
- Lining hoses for conveying gasoline and oil
- Making gaskets and seals for printing rolls

Q11. Explain the preparation, properties and uses of SBR rubber.

(Styrene butadiene rubber or SBR or Ameripol):

This is copolymer of 75% butadiene and 25% styrene. These are mixed in reaction mixture containing an aqueous solution of an emulsifying agent. Initiator like cumene hydroperoxide and p-methane hydroperoxide in presence of anti-freeze components to produce cold sbr or cold rubber.

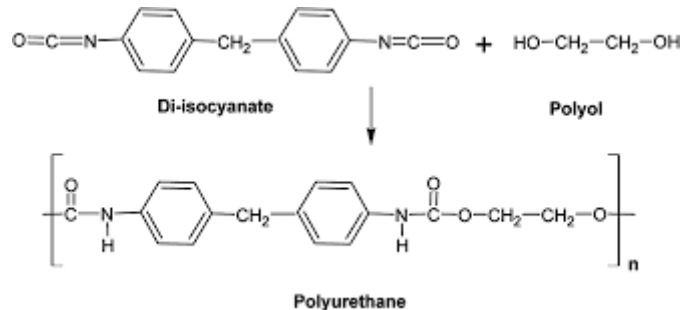


Properties: vulcanisation is similar to natural rubber but less sulphur is required, c-black is added as a filler to improve physical properties.

Uses: light duty tyres, belts, gum, floorings, rubber shoe soles, and for electrical insulation.

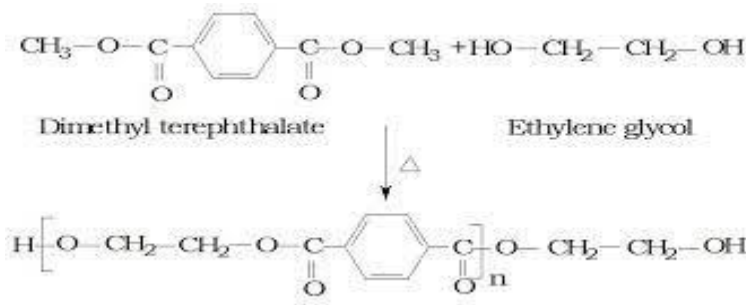
Polyurethane (Perlon-U) preparation properties applications:

Are obtained, commercially, by treating diisocyanate and diol. Perlon-U is obtained by the reaction of 1,4-butane diol with 1,6-hexane diisocyanate



- **Properties:** Polyurethane are less stable than polyamides at elevated temperature
- They are characterized by excellent resistance to abrasion and solvents.
- **USES:** Coatings, films, foams, adhesives and elastomers.
- Polyurethane fibers are used for spandex for foundation garments and swim-suits.
- They also find use as a leather substitute (carfoam).
- Gaskets & seals

Polyester resin: Condensation product of dicarboxylic acid with dihydroxy alcohols



Polyester resin

- Properties: Good fiber forming material and is converted into commercial fibers.
- High stretch-resistance, high-crease and wrinkle-resistance.
- Highly resistance to mineral and organic acids.

USES: Synthetic fibres like terylene, dacron

For bending with woo to provide better crease and wrinkle resistance

As a glass reinforcing material in safety helmets, aircraft battery boxes.

Fiber Reinforced Plastics (FRP):-

Combination of plastic material & solid fillers give hard plastic with mechanical strength & impact resistant is known as reinforced plastic.

The fiber polymers with solid/fillers to impart mechanical strength & hardness without losing plasticity are known as fiber reinforced plastics (FRP).

Fillers like carborandum, quartz & mica – impart hardness & strength.

Barium salt impervious to x-rays.

Asbestos provide heat & corrosion resistant for FRP.

Nature of polymers used for FRP:-

Composition of FRP – 50% of the mould able mixture contain fillers.

- Addition of carbon black to natural rubber increase the 40% strength of rubber & used in the manufacture of tyres.
- China clay improves the insulation property of PVC, Teflon.
- When CaCO₃ is added to PVC, then they are used for insulation of tubing, sear covers, wires & cables. Asbestos filled FRP → for electrical appliances’.
- FRP has good shock & thermal resistances, mould ability, dimensional stability & reparability.

Applications:-

Fiber reinforced plastics find extensive use in space crafts, aero planes, boat nulls, acid storage tanks,

motor cars and building materials.

Melamine FRP is used for insulation & making baskets.

Advantages of FRP:-

- (a) Low efficient of thermal expansion
- (b) High dimensional stability
- (c) Low cost of production
- (d) Good tensile strength
- (e) Low dielectric constant
- (f) Non inflammable & non-corrode and chemical resistance

Polymers in medicine & Surgery:

Biomaterials are materials that can be implanted in the body to provide special prosthetic functions or used in diagnostic, surgical and therapeutic applications without causing adverse effect on blood and other tissues. Biomaterials have been developed from among metals, ceramics,& polymers.

Characteristic of biomedical polymers:

Applications:

Polymer	Applications
Polyurethane	Heart valves, blood filters, artificial heart & vascular tubing etc.,
Polydimethylsiloxane	Drain tubes & Heart valves
Polyalkylsulphone	Membrane oxygenator
PMMA	Contact lenses, dental restoratives etc.,
Acrylic hydrogels	Grafting
PVC	Disposable syringes etc.,
PP	Blood filters, heart valves
PE	Disposable syringes etc.,

- o Purity & reproducibility
- o Optimum physical and chemical properties
- o Should be fabricated into the desired shape or form, without being degraded and adversely affected in its properties.
- o Easy sterilization, with no alteration in its properties.

Biopolymers that are to come with blood & tissues of the body must not destroy cellular elements of blood, enzymes, proteins, produce toxic and allergic reactions, and deplete electrolytes present in the body

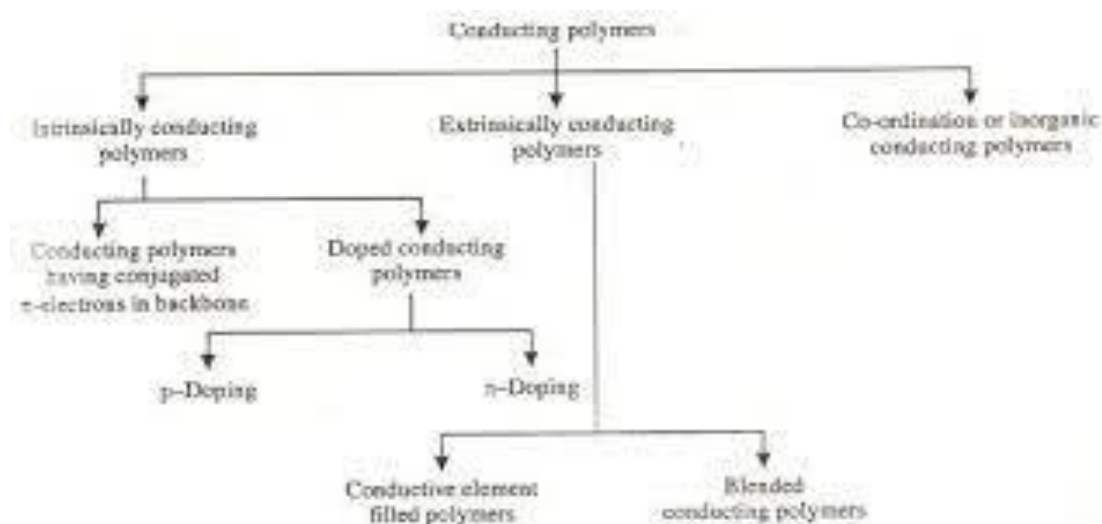
CONDUCTING POLYMERS:

What are conducting polymers. Write their applications and uses.

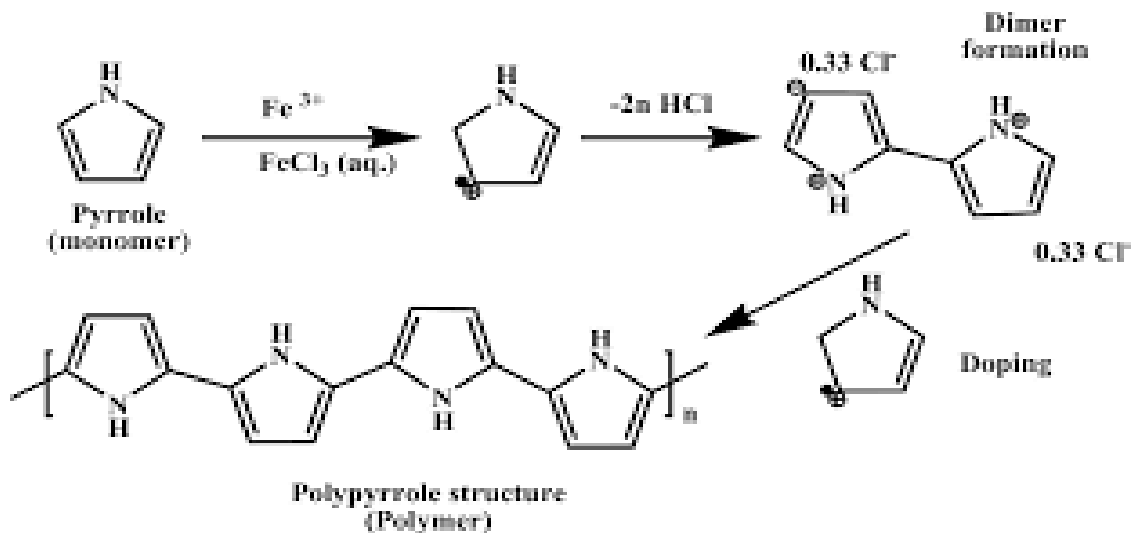
Most polymers are poor conductor of electricity, because of the non-availability or large number of free electrons in the conduction process. Within the past several years, polymeric materials has been synthesized which possess electrical conductivity on par with metallic conductors, such polymers are called conducting polymers. Conductivities as high as $1.5 \times 10^7 \text{ ohm}^{-1} \text{m}^{-1}$ have been attained in this polymeric materials.

Polymers	Electrical conductance ($\text{ohm}^{-1} \text{m}^{-1}$)
Phenol formaldehyde	$10^{-9} - 10^{-10}$
Poly methyl methyl acrylate	$< 10^{-10}$
Nylon6,6	$10^{-12} - 10^{-13}$
Polystyrene	$< 10^{-14}$
Polyethylene	$10^{-15} - 10^{-17}$
PTFE	$< 10^{-17}$

Conducting polymers: Those polymers which conduct electricity are called *conducting polymers*. The conduction of the polymers may be due to unsaturation or due to the presence of externally added ingredients in them. The conducting polymers can be classified in the following way.



Intrinsic Conducting polymers: Is a polymer whose backbone or associated group consists of delocalized electron pair or residual charge. Such a polymer essentially contain conjugated π -electrons backbone: Conducting polymers having π electrons are (i) Polyacetylene polymers, poly-p- phenylene, polyquinoine etc.,

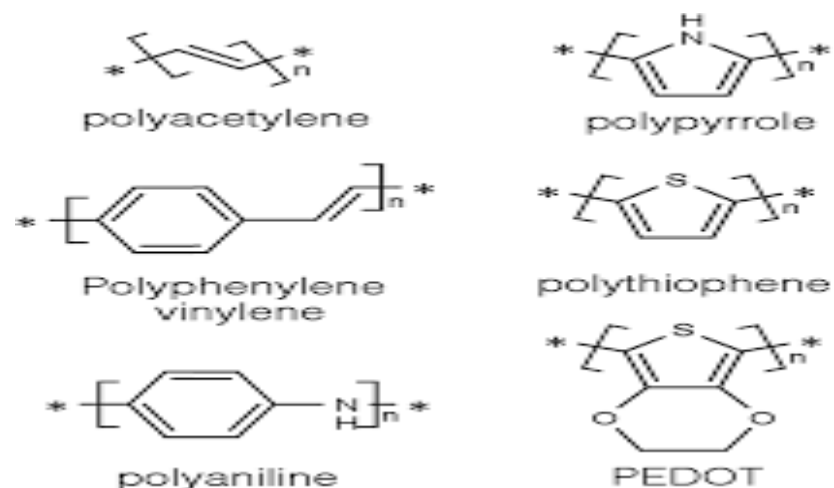
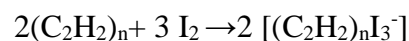
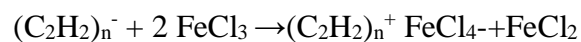


Doped conducting polymers:

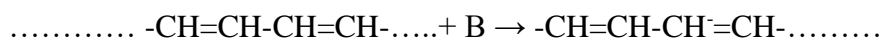
Is obtained by exposing a polymer to a charged transfer agent in either gas phase or in solution. Conductivity of ICP can be increased by creating either positive or negative charges on the polymer backbone by oxidation or reduction is two types.

p-doping: Involves treating an intrinsically conducting polymer with a lewis acid, thereby oxidation process takes pace and positive charge on the backbone are created.

p-dopent used are I_2 , Br_2 , AsF_5 , PF_6 & Naphthylamine



(ii) *n-doping:* Involves treating an intrinsically conducting polymer with a lewis base thereby resolution process takes pace and negative charge on the backbone are created. Ex: Li, Na, Ca & Tributyl ammonium, FeCl_3 etc.,



Extrinsic Conducting polymers:-(Due to externally added reagents).

Extrinsic conducting polymers: The conductivities of these polymers is due to the presence of externally added ingredients in them, they are two types

1. **Conducting element filled polymers:** the polymer acting as a binder to hold the conducting element such as c-black, metallic fibers, metallic oxides etc., the minimum concentration of conducting filler is added so that the polymer starts conducting.
2. **Blended conducting polymers:** The conventional polymer is blended with a conducting polymer to improve physical chemical electrical and mechanical properties along with the processing properties. Ex: 40% poly pyrrole in a conventional polymer give higher impact strength.

Applications:-

- The conducting polymers are used in rechargeable batteries.
- Used for making analytical sensors for pH, O₂, SO₂, NH₃ and glucose.
- Used for electron beam lithography.
- They are applicable in photo voltaic cells.
- In electromagnetic screening materials
- In non-linear optical material
- In wiring aircraft & aerospace components
- In telecommunication system
- In solar cells, drug delivery system for human body, etc.,
- In photo voltaic devices.

Advantages:-

- Polymers possess good conductivity.
- They can store charge.
- They absorb visible light to give coloured complex.

Write a short note on biodegradable polymers.

Biodegradable polymers: polymers are not attacked by environmental conditions including biological attack. Polymers are degraded by oxidation, u.v. radiation etc. but not by bacteria. Biodegradable polymers are defined as degradable polymer in which degradation results from the nature of naturally occurring microorganisms such as bacteria fungi and algae. The biodegradable

polymers may be naturally occurring or they may be synthesized to chemicals.

Naturally occurring biodegradable polymers : they are classified into four groups.

Natural polymers are for environment degradation. The rate of degradation depends upon the structural complexity of material and environmental conditions.

Synthesized Biodegradable polymers: polymers derived from petrochemicals or biological sources are biodegradable. They are used in dissolving suture material in medical field, and bio-polyesters. Because of their high prices new type of polymers were developed of chemicals derived from farming of particular crops, which laid foundation to new synthetic biodegradable polymers.

Exs: 1. Polyalkaline esters, 2. Polylacticacid and its copolymers, 3.Polyamide esters, 4. polyvinyl esters, 5. Polyvinyl alcohol, 6.poly anhydrides .All the above biodegradable polymers possess particular properties and potential applications.

Applications: 1. biodegradable polymers are synthesized from the processing of crops or from petrochemical feed stock with normal or conventional processing methods. Polysaccharides

proteins polyesters others



Ex: Starch and Cellulose

Ex: Gelatin, Casein silk, Wool.

Ex: polyhydroxy alkanols.

Ex: lignin, shellac, Natural rubber.

- The compostable bags help in the disposal of vegetable matter being converted to CO₂ and CH₄
- The problem of landfills by solid waste can be reduced.

Drawbacks: They are more expensive than the products manufactured from commodity resins.

