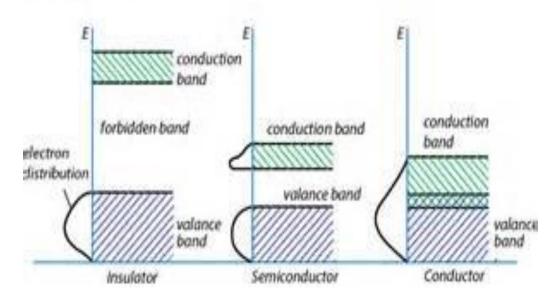
#### **UNIT IV- ENGINEERING MATERIALS-II**

#### Q1. What is a semiconductor? What are intrinsic and extrinsic semiconductors?

A semiconductor is a substance, usually a solid chemical element or compound that can conduct electricity under some conditions but not others, making it a good medium for the control of electrical current.

It has almost filled valence band, empty conduction band and very narrow energy gap i.e., of the order of 1 eV. Energy gap of Silicon (Si) and Germanium (Ge) are 1.0 and 0.7 eV respectively. Consequently Si and Ge are semiconductors.

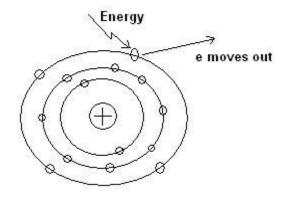


Semiconductors :

Effect of temperature on conductivity of semiconductors: At 0 K, all semiconductors are insulators. At finite temperature, the electrical conductivity of a semiconductor material

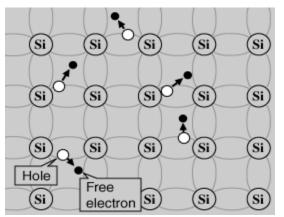
increases with increasing temperature. With increase in temperature, outermost electrons acquire energy and hence by acquiring energy, the outermost electrons leave the shell of the atom.

Hence with increase in temperature, number of carriers in the semiconductor material increases and which leads to increase in conductivity of the material.



Types of semiconductors:

*Intrinsic Semiconductor:* An intrinsic semiconductor material is chemically very pure and possesses poor conductivity. It has equal numbers of negative carriers (electrons) and positive carriers (holes). A silicon crystal is different from an insulator because at any temperature above absolute zero temperature, there is a finite probability that an electron in the lattice will be knocked loose from its position, leaving behind an electron deficiency called a "hole".



This hole can travel from one atom to the adjacent atom by accepting an electron from later one.

This process involves formation of new covalent bond and breaking an existing bond by filling up the hole and creating a new hole.in this way, the holes travel fromone atom to the adjacent atoms in crystal lattice.

If a voltage is applied, then both the electron and the hole can contribute to a small current flow.

*Extrinsic Semiconductor:* Extrinsic semiconductor is an improved intrinsic semiconductor with a small amount of impurities added by a process, known as doping, which alters the electrical properties of the semiconductor and improves its conductivity. Introducing impurities into the semiconductor materials (**doping process**) can control their conductivity.

Doping process produces two groups of semiconductors: the negative charge conductor (**n-type**) and the positive charge conductor (**p-type**). Semiconductors are available as either elements or compounds. Silicon and Germanium are the most common elemental semiconductors. Compound Semiconductors include InSb, InAs, GaP, GaSb, GaAs, SiC, GaN.

Si and Ge both have a crystalline structure called the diamond lattice. That is, each atom has its four nearest neighbours at the corners of a regular tetrahedron with the atom itself being at the centre. In addition to the pure element semiconductors, many alloys and compounds are semiconductors. The advantage of compound semiconductor is that they provide the device engineer with a wide range of energy gaps and mobilities, so that materials are available with properties that meet specific requirements. Some of these semiconductors are therefore called wide band gap semiconductors.

#### Q2. How doping of semiconductors is done?

The Doping of Semiconductors

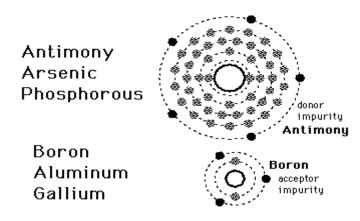
The addition of a small percentage of foreign atoms in the regular crystal lattice of silicon or germanium produces dramatic changes in their electrical properties, producing **n-type** and **p-type semiconductors**.

#### Pentavalent impurities

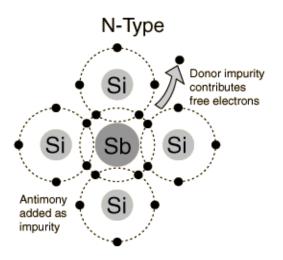
(5 valence electrons) produce n-type semiconductors by contributing extra electrons.

#### Trivalent impurities

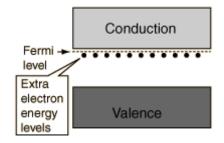
(3 valence electrons) produce p-type semiconductors by producing a "hole" or electron deficiency.



#### **N-Type Semiconductor:**



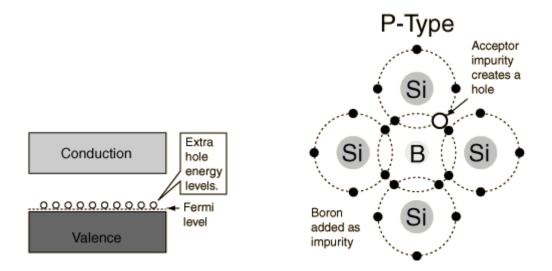
The addition of pentavalent impurities such as antimony, arsenic or phosphorous contributes free electrons, greatly increasing the conductivity of the intrinsic semiconductor. Phosphorous may be added by diffusion of phosphine gas (PH3).



#### **P-Type Semiconductor**

The addition of trivalent impurities such as boron, aluminum or gallium to an intrinsic

semiconductor creates deficiencies of valence electrons, called "holes". It is typical to use  $B_2H_6$  diborane gas to diffuse boron into the silicon material.



Note: positive holes are less mobile than free electrons so the conductivity of a P-type semiconductor is inherently less than that of N-type semiconductor.

## Q3. What are the differences between p-type and n-type semiconductors?

Differences between p-type and n-type semiconductors:

N-type Semiconductor	P-type Semiconductor	
It is an extrinsic semiconductor which is	It is an extrinsic semiconductor which is	
btained by doping the impurity atoms such obtained by doping trivalent impurity		
as antimony, phosphorus, arsenic, etc. to the	ny, phosphorus, arsenic, etc. to the such as boron, gallium, indium etc.to the put	
pure germanium or silicon semiconductor	germanium or silicon semiconductor.	
The impurity atoms added, provide extra	The impurity atoms added, create vacancies of	
electrons in the structure, and are called	electrons (i.e. holes) in the structure and are	
donor atoms.	called acceptor atoms.	
The electrons are majority charge carriers	e majority charge carriers The holes are majority charge carriers and	
and holes are minority charge carriers.	electrons are minority carriers.	

## Q4. How semiconductors are prepared by different techniques? Describe in detail.

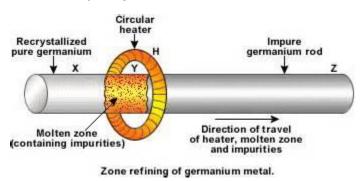
**Preparation of Semiconductors:** For preparing semiconducting devices, the basic materials such as Si and Ge must at least 99.9999% pure. Consequently extreme precautions have to be taken during the preparation of these elemental semiconductor materials. Various steps followed during the preparation of highly pure materials are as follows:

*Preparation of pure Ge/Si:* This is carried by using the following methods:

**1.** *Distillation:* is based on tge separation of materials due to difference in boiling points. The starting raw materials employed are germanium tetrachloride and trichloro silane for the preparation of pure Ge and Si respectively.

For example  $\text{GeCl}_4$  (b.p. 83.1<sup>o</sup>C) is taken in a series of distillation stills and a layer of HCl placed over the charge, which facilitates in the removal of As (usually present as an impurity). Chlorine gas is then passed through the charge, which is heated electrically. The vapours passing through the fractionating column finally distils over in a receiver, kept in an ice bath. Pure GeCl<sub>4</sub> so obtained is then treated with extra pure water to get germanium oxide which is subsequently reduced (in an atmosphere of hydrogen) to get elemental Ge, which is subjected to further purification. Similarly, distilled trichloro silane (SiHCl<sub>3</sub>) is employed to get silicon of high purity.

2. Zone refining:



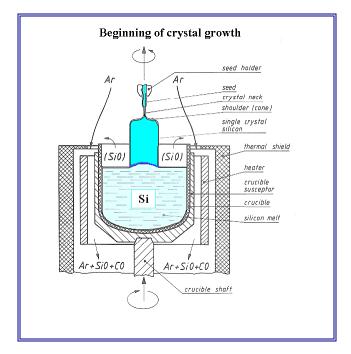
The zone refining technique involves melting a narrow zone of long ingot of the material to be processed. This molten zone is then slowly moved by moving the heater gradually along the length of the ingot in one direction. This process is repeated multiple times till the required purity level is reached. In this process difference between solubility of impurities in the molten and solid phases is used to concentrate impurities at the end section of the ingots.

This method is particularly used when metals are required in high degree of purity. It is based on the principle that when an impure metal in a molten state is allowed to cool, only the metal crystallizes while the impurities remain present in the molten state (mass) or melt.

The impure metal converted into a rod which is heated at one end with a circular heater. A narrow zone of metal is melted. The heater is slowly moved along the rod. The pure metal recrystallizes out of melt while the impurities remain in the melt which moves along with the melted zone of the rod with the movement of heater. The process is repeated several times. The end of rod where impurities have collected is cut off. This method is employed for the purification of germanium, silicon, gallium etc, which are used in semi – conductors.

#### 3. Czochralski Crystal pulling Technique:

Ge or Si obtained by zone refining method is polycrystalline, i.e., there is no regularity in their crystal structure and contain crystals of different sizes. But fabrication of most of the semiconductor devices requires single crystal of semi conducting materials. Consequently, they are grown in the form of single crystals. This method involves growing the crystal on a single crystal seed; thereby the atoms reproduce identical atomic arrangement as that of the seed crystal. In this process, solid polycrystalline semiconducting material is taken in a quartz chamber and heated by using RF power source, till it melts. Then the temperature is lowered to just above the melting point of Ge. At this stage, properly oriented single crystal of Ge, attached to a puller rod is carefully lowered into the melt, till it is in contact with the surface of the charge. Then the crystal is rotated slowly and then gradually pulled out so that the melt in contact with the seed crystal starts solidifying producing the orientation identical as that of the seed crystal. After this, the pull rate is kept at about 1.5 to 5 cm/minute and the rotation speed is maintained at about 100rpm.Finally, an intrinsic crystal of Ge of 5cm diameter and 25 cm length is obtained. This crystal is tested for its conductivity and cut into wafers with the help of a diamond-tipped saw.



**Doping techniques:** For getting a doped material, calculated quantity of dopant (Boron or Phosphorus) is added to the melt before crystal pulling stage. Usually dopant atoms added are of the order of one atom of B or P per  $10^{\frac{8}{2}}$  atoms of Ge or Si. Other methods of doping are:

*Epitaxy:* Involves in unified crystal growth or deposition of a thin crystal on another substrate, often with added dopants. The material in the epitaxial layer must have a little spacing and structure closed to that of the substrate. ex. Si on Ge or Ge on Si. The Si or Ge wafer (kept in graphite boat) is placed in a long cylindrical quartz tube reactor, which is then heated (by RF induction coil). Then gases containing compounds of Ge or Si mixed with calculated/appropriate quantities of dopant over the wafer results. The doped wafer so obtained is ready for the fabrication of semiconductor devices. It may be pointed out that for

getting Si epitaxial film, SiCl<sub>4</sub>  $H_2$  and  $N_2$  mixture is used. For carrying out n-type doping, this mixture is mixed with a calculated amount of phosphine (PH<sub>3</sub>) and for p-type doping; Diborane (B<sub>2</sub>H<sub>6</sub>) is employed.

*Diffusion technique:* Involves in conversion of a region of semiconductor material by solid or gaseous diffusion of impurity atom into the crystal lattice of the semiconductor material without any melting and it consists of heating a P-type dopant (Phosphorus or Stilbium). This causes some of the impurity atoms to condense on the surface of water and diffuse thereby resulting in a P-type semiconductor material.

By this technique, the extent of impurity atoms penetration can be controlled even less than a few millions of a centimetre by controlling the concentration of dopant atoms and temperature. This technique is especially employed for preparing n or p type semiconductors, used in very high frequency devices. This doping technique can also be used to prepare n-p-n type transistor with a base width of even 5 microns.

*Ion implantation technique:* Involves in bombarding the semiconductor material with an electrically controlled beam of high energy ions of B or P of 10000ev. This causes the implantation of some dopant atoms into the crystal lattice of semiconductor.

Main advantages of this technique are: 1. Implantation at low temperature 2. Extremely precise control of the dopant amount on desired specific semiconducting material 3. Obtaining deep or shallow regions of very precise and required penetration depths having high or low concentration of dopant. This technique is especially employed for the fabrication of high frequency devices.

Cutting into chips: the wafers obtained by above methods are then cut into chips by using methods such as chemical etching, ultrasonic vibrations, laser beams etc.

#### **POLYMERS**

#### 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 & CO<sub>2</sub>
- 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.

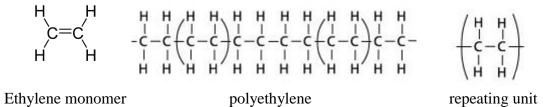
Polymers possess the desirable properties like high strength light wt., good flexibility, special electrical properties resistance chemicals and fabrication into complex shapes in a wide variety of colors.

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



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.

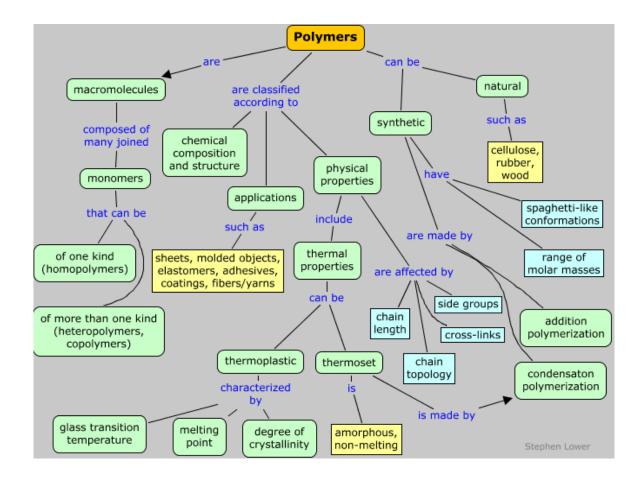
These do not possess engg. properties.

• 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



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

#### Addition (or) chain Polymerization: -

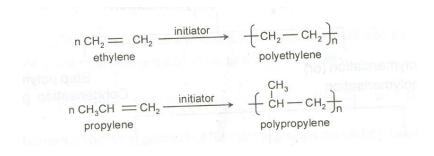
It is a reaction that yields a product which is an exact multiple of the original monomeric molecule.

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

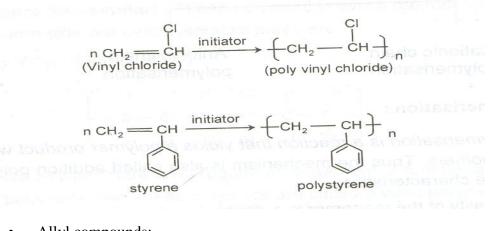
It must be initiated by light, Heat, Pressure (or) a catalyst for breaking down double covalent bonds of a monomer.

Ex: Olefins, Vinyl compounds, Allyl and dienes.

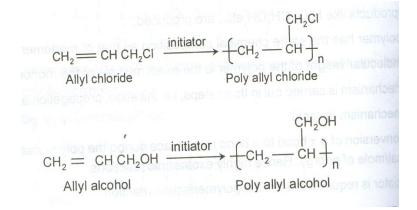
Olefins:-



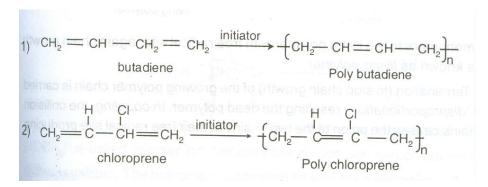
Vinylcompounds:-



Allyl compounds:-



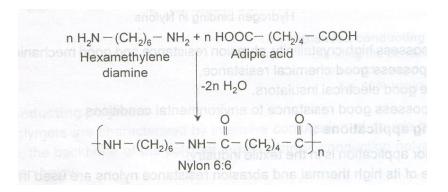
• Diene compounds:-



#### II. Condensation (or) step polymerisation: -

It involves the reaction occuring 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 from nylon 6:6



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

--OH] + --COOH[ -- OOC -- with elimination of H<sub>2</sub>O

Ex: polyethylene terephthalate(terylene)

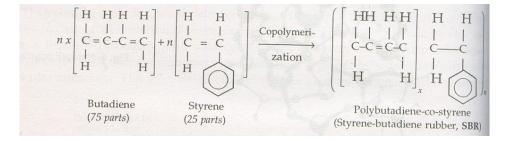
 $--\mathrm{NH}_2 + --\mathrm{C} \mathrm{O} \mathrm{O} \mathrm{H} \longrightarrow --\mathrm{NH} --\mathrm{CO} -- +\mathrm{H}_2 \mathrm{O}$ 

Polyamide

Ex: spandex fibre

*III <u>copolymerization</u>* : - (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 Polymerisation (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  $(C_2H_5)_3Al$  (or)  $(CH_3)_3Al$  polymerization can be carried out. It explains the stereo specific type of polymerization.

## 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.

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

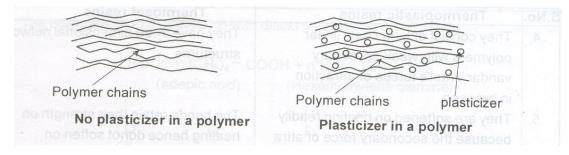
	Thermoplastic Resin	Thermoset Resins	
1	They soften on heating readily	They do not soften on heating on prolong heating, they burn	
2	Consists of long chain linear molecules	They have 3 –d network joined by strong covalent bonds	
3	Formed by Addition polymerization	Condensation – polymerization	
4	They are soft, weak & less brittle	They are hard, strong and more brittle	
5	They can be reclaimed from wastes	Can't be reclaimed from wastes	
6	Usually soluble in some org. solvents	Due to strong bonds & cross liking they are insoluble in all org. solvents	

## Q3. How compounding of plastics is done?

*Compounding of plastics:* - Polymer Resin is mixed with 4 to 10ingredients 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.



## 3. 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.

- 4. 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.
- 5. Calalysts 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.

## 6. 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.

## 7. 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 fives flawless gloss finish to plastics.
   Ex: waxes, oils, stearates and oleates.
- Catalysts | accelerators accelerates the cross linking of thermosetting resin.
   Ex: H<sub>2</sub>O<sub>2</sub>, 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.

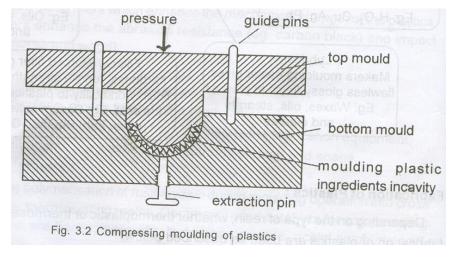
The method chosen depend upon type of plastics (i.e. thermo or thermosetting plastics) and shape of finished product commonly used methods are given below.

#### 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 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 or by cooling in



case of thermoplastic resins

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

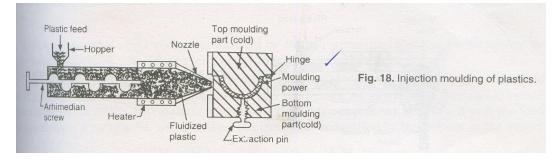
*Uses:* the process is used for manufacturing of cylinders and gear handles.

## 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.

<u>Advantages</u> : - 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.

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

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
- $\circ$  a coordination catalyst is prepared as a colloidal suspension by reacting an aluminium alkyl and titanium chloride (TiCl<sub>4</sub>) in a solvent such as heptane (C<sub>7</sub>H<sub>16</sub>).
- 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 O<sub>2</sub>, CO<sub>2</sub>, 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.

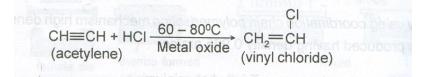
#### Q6. Mention the properties and uses of PVC.

#### Poly vinyl chloride:-

) Poly vinyl chloride (PVC) :  $(CH_2 - CH_2)_n$ Poly vinyl chloride is produced by free radical chain polymerisation of vinyl chloride presence of benzoyl peroxide or hydrogen peroxide.  $n CH_2 = CH_1 \xrightarrow{Benzoyl peroxide}_{30 - 80 \ ^{\circ}C} - (CH_2 - CH_2)_n$ (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:-

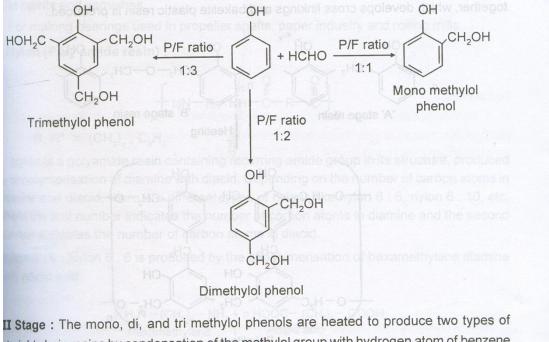
- 1. Used for electrical insulations.
- 2. Injection moulding articles like tool handles ,radio and telephone components.
  - Used for making safety helmets, refrigerator components, tyres
  - And motor cycle mudguards.

## Q7. Explain the preparation properties and uses of Bakelite.

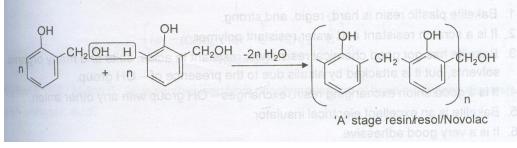
## Bakelite:-

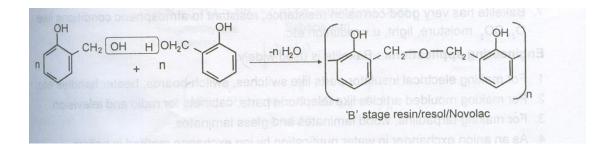
(Phenol-formaldehyde resin). This belongs to thermoset resin.

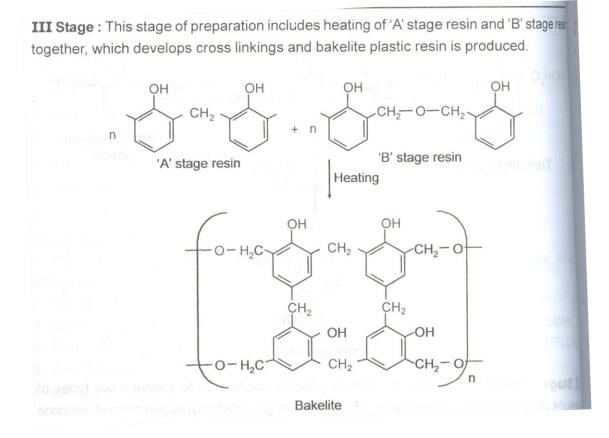
Phenol reacts with formaldehyde in presence of acid or alkali produces mono di and triMethylol phenols depending on phenol formaldehyde ratio.



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







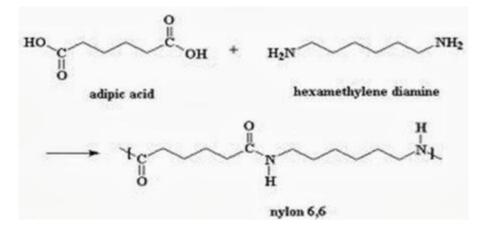
*Properties:* phenolic resins set to rigid, hard, scratch resistant, water resistant, insoluble solids, which are resistant to non-oxidizing acids and many organic solvents.

#### 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.

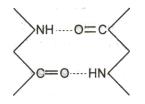
#### Q8. Explain the preparation properties and uses of Nylon-6,6.

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:**

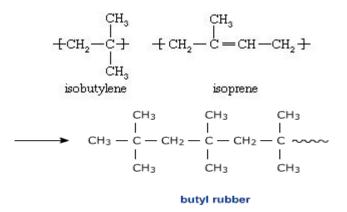
- The major application is in the textile industry.
- Because of its high thermal and abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there
- Flexible tubings for conveying petrol etc are made from nylons.
- Nylons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

## Q9. Explain properties and applications of butyl rubber.

Butyl rubber: also known as GR-I rubber.

Produced by copolymerisation of isobutene + 1-5% of butadiene (anhydrous aluminium chloride in methyl chloride)



#### **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.

$$Na_2S_{(aq)} + S_{(s)} \longrightarrow Na_2S_{x(aq)}$$

 $Cl - R - Cl + Na_2 S_{x(aq)}$  70° C.

 $HS \longrightarrow R \longrightarrow S_x \xrightarrow{}_n R \longrightarrow SH + 2 NaCl_{(aq)}$ 

## **Properties:**

- o Strength, impermeable to gases
- Cannot form hard rubber
- o 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.
- o Lining hoses for conveying gasoline and oil
- o 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.

n CH<sub>2</sub>=CH - CH = CH<sub>2</sub> + x C<sub>6</sub>H<sub>5</sub> - CH = CH<sub>2</sub> 
$$\longrightarrow$$
  
Butadiene Styrene C<sub>6</sub>H<sub>5</sub>  
-(CH<sub>2</sub>-CH=CH-CH<sub>2</sub>), -(CH<sub>2</sub>-CH),  
x Styrene-butadiene rubber

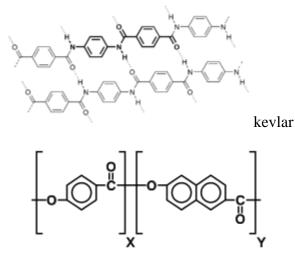
*Properties:* vulcanisation is similar to natural rubber but less sulphur is required, c-black is added as a filler to improve physical properties.

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

#### Q12. Write a short note on liquid crystal polymers.

Liquid crystals are materials that behave in some ways like solids and in some ways like liquids. The first known polymer liquid crystal solution was invented by Kwolek from a polyamide known as Kevlar .Its repeat unit had this following structure which forms very strong fibres.

Liquid crystallinity in polymers may occur either by dissolving a polymer in a solvent (lyotropic liquid-crystal polymers) or by heating a polymer above its glass or melting transition point (thermotropic liquid-crystal polymers). Liquid-crystal polymers are present in melted/liquid or solid form. In solid form the main example of lyotropic. LCPs is the commercial aramid known as Kevlar.





#### Properties of liquid crystal polymers:

- These polymers are capable of forming regions of highly ordered structure while in liquid phase. The degree of order is somewhat less than that of a regular solid crystal.
- The liquid crystal polymers have high mechanical strength at high temperatures.
- These liquid crystal polymers possess extreme chemical resistance.
- They possess inherent flame retardancy and good weatherability.
- They can be easily fabricated into a variety of forms.
- LCP can be welded. The lines created by welding are the weak points in the resulting product.
- LCP has high z- axis coefficient of thermal expansion.
- LCP resist stress cracking the presence of most chemicals at elevated temperatures.

## Applications of LCP:

LCP are sometimes called 'super polymers'. Their wide range of exceptional properties and case of processing make them design for many demanding applications.

- LCP thermoplastic fibres possess exceptional strength and rigidity, suitable for industrial, electronic and also space applications as well as high performance ropes and tennis rackets.
- LCP finds extensive applications as coatings, composites and additives.
- The electrical motor components are made from LCP.
- LCP finds its applications in electronic industry as LED's and SMT components.
- LCP has an interesting application like information storage media.

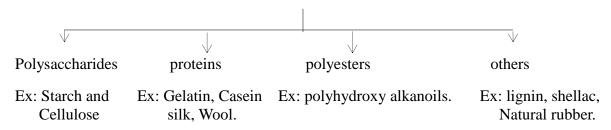
#### Q13. Write a short note on biodegradable polymers.

*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.

*Synthesised 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.

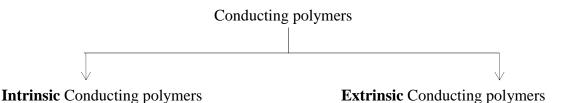
*Applications:* **1.** biodegradable polymers are synthesized from the processing of crops or from petrochemical feed stock with normal or conventional processing methods.

- The compostable bags help in the disposal of vegetable matter being converted to CO<sub>2</sub> and CH<sub>4</sub>.
- The problem of landfills by solid waste can be reduced.

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

#### Q14. What are conducting polymers. Write their applications and uses.

**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.



(Conjugation due to presence of Double bond)

(Due to externally added reagents)

Intrinsic polymer	Doped	Conductivity	Blended
with conjugation	Conducting	element filled	Conducting
	polymers	polymer	polymers

Intrinsic Conducting polymers: Due to presence of intrinsic conjugation of double bonds in their structure. It is classified into two types.

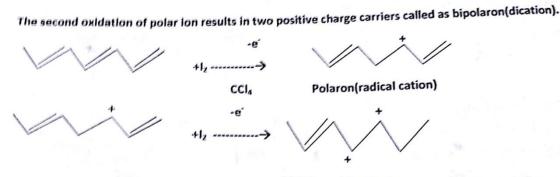
1. Conducting polymers having conjugation: polymers having conjugative double bonds in backbone possess due to pi electrons.

**2.** Doped Conducting polymers: Conducting polymers having II electrons can easily oxidize or reduce because of low ionization potential and high electron affinities. This can be done by 2 ways.

1. p-doping (creating positive site on polymer backbone):-

It can be done by oxidation of conducting polymer like poly acetylene with Lewis acid or iodine vapour. Also called as oxidative doping.

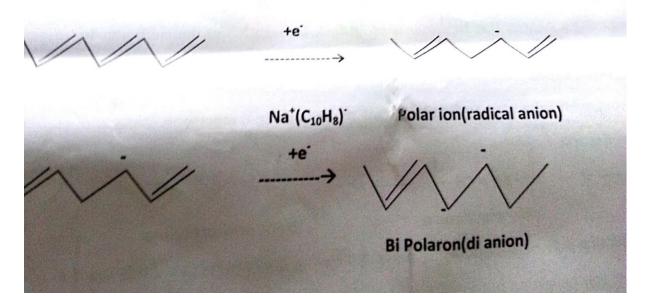
During oxidative doping removal of II electron from polymer backbone lead to formation of delocalized radical ion called as polar ion.



Bi Polaron(dication)

n-doping:- It is carried out by reduction process by addition of electron to polymer backbon reducing agents like sodium naphthalide.

The electron added to polyacetylene by reductive doping causes bipolaron(dianion). The electrons (holes) caused on the polymer backbone results the generation of conduction presult conductivity increases.



**Extrinsic:** 

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

xtrinsic conducting polymers: The conductivities of theses polymers is due to the esence of externally added ingredients in them, they are two types

- 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.
- 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, O<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub> and glucose.
- Used for electron beam lithography.
- They are applicable in photo voltaic cells.

#### Advantages:-

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

#### Q15. Write a short notes on OLED's.

Organic light emitting diodes generate light from electrical charges by exploiting the process of electro-luminescence or electro-phosphorescence. An organic light emitting diode (OLED) is basically a light emitting diode (LED). A suitable organic compound (organic semiconductor) which emits the light in response to an electric current is situated between two electrodes; Typically, at least one of these electrodes is transparent for transmitting the emitted light. By applying potential difference between anode and cathode, holes and electrons are injected respectively in to the organic layer, which emits the light on recombination.

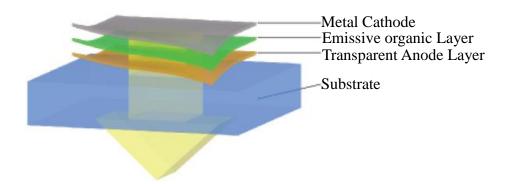
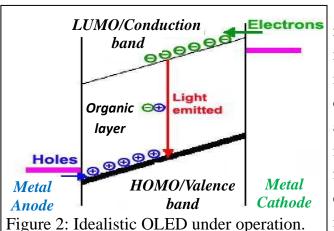


Figure 1: Schematic representation of an OLED

The energy diagram (Figure 2) explains the working principle of the idealistic OLED. Negatively charged Electrons and positively charged holes are injected into the Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) of the organic layers respectively, and move towards each other in the applied external field. As they approach each other close enough, the recombination occurs due to attraction and releases the energy as radiation (light).



This simple device geometry however relies on the fact that exactly the same number of electrons and holes are injected into the organic layer to make sure that no carrier passes the sample without meeting a partner to recombine. Hence, the injection barriers for electrons and holes from the cathode and anode have to be equal. Furthermore, the charge carrier mobility for electrons and holes needs to

be equal for the recombination to take place in the centre of the organic layer.

**OLED's Production:** Based on the type of organic component used, OLED's are of two types; made up of a) small molecules and b) macro molecules (polymers).

OLED's based on small molecules usually manufactured via organic vapour phase deposition or vacuum deposition; the organic molecules are evaporated and carried with an inert gas followed by deposition on a substrate through very small nozzles held near the substrate surface. This technique involves vacuum and temperatures higher than room temperature which reflects in the higher production cost. However, highly uniform films can be made and it is easy to fabricate complex multi-layer structures for higher efficiency.

In the case of PLED's, relatively small amount of power required for the amount of light produced as PLED's are quite efficient. Vacuum deposition is not a suitable method for forming thin films of polymers. However, polymers can be processed in solution, and spin coating is a common method of depositing thin polymer films. This method is more suited to forming large area films than thermal evaporation. No vacuum is required, and the emissive materials can also be applied on the substrate by a technique derived from commercial inkjet printing. However, as the application of subsequent layers tends to dissolve those already present, formation of multilayer structures is difficult with these methods.

## Advantages of OLED Technology:

- Lightweight and flexible
- Ability to create a full spectrum color display
- Very bright with low energy requirements
- Wider viewing directions/angles
- Ability to create non-planar displays with light emitting polymer films
- Faster response times and high refresh rates