POLYMERS

Module : 05

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PREREQUISITE: Students should know the term Molecular weight and its related calculation.

COURSE OUTCOME 5: Apply the knowledge of various polymers, fabrication methods, conducting polymers in various industrial fields.

INTRODUCTION: The term "polymer" derives from the Greek word *polus*, meaning "many, much" and *meros*, meaning "part", and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties.

The course provides an introduction to polymers, properties of polymers and numericals based on it, Effect of heat on polymers, Conducting polymers. Classification of Plastics, Compounding of plastic, Fabrication techniques, Preparation, properties and uses of PMMA and Kevlar.

Q1. Define Polymer and Polymerisation.

A. i. Polymers are long chain molecules produced by linking small repeat units together. These small repeat units/molecules are known as monomers.

ii. The process by which the monomer molecule are linked to form big polymer molecule is called Polymerisation.

iii. During polymerisation the polymer molecules formed are of different sizes depending upon number of monomers involved.

$$\mathbf{nCH_2{=}CH_2} \Longrightarrow \mathbf{-(-CH_2-CH_2-)-n}$$

Ethylene (Monomer) → Polyethylene (Polymer)

Q2. Explain degree of polymerisation.

A. i. Degree of polymerisation [DP] is defined as the average number of monomer units in a macromolecule or a polymer.
ii. The polymers with high degree are called **high polymers** while the polymers with low degree are called **oligopolymers**.
iii. If DP has molecular weight below 20,000 then the polymer is either fragile powder or liquid. It provides indirect method of expressing molecular weight and the relation is as follows:

$$M = DP \times m$$

where ‘M’ is the molecular weight of polymer and’ m’ is the molecular weight of monomer.

Q3. Explain Molecular Weight of polymer.

A. i. Molecular weight of a polymer is defined as sum of the atomic weight of each atoms of a molecule, which is present in the polymer.

ii. Molecular weight have very strong influence on physical and mechanical properties of a polymer. Increasing the molecular weight and the chain length of a polymer increases the impact strength and thermal properties of a polymer.

iii. The 3 main types of molecular weight of polymers are :

a. Number-average molecular weight. b. Weight -average molecular weight. c. Viscocity-average molecular weight.

iv. It is calculated by following equation :

$$\text{Molecular Weight} = \frac{\text{Sample weight}}{\text{No of moles in sample}}$$

i.e. **M = W/N**

Q4. Define Number-average molecular weight [$\overline{Mn}$]? State its mathematical expression. Also state its significance.

A.i. It is defined as the total weight of all polymer molecules in a sample, divided by the total number of polymer molecules present in a sample. It is denoted by ‘ $\overline{M_n}$.

ii. If N_1, N_2, N_3, ... are the number of molecules having molecular weights M_1, M_2, M_3,.... in a polymer sample, then the number average molecular weight is given as follows:

$$\overline{Mn} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N1+N2+N3+......}$$

$$\overline{Mn} = \frac{\sum N_i M_i}{\sum N_i}$$

Where N_i is the number of moles of i^{th} polymer having molecular weight of M_i

$$\overline{Mn} = \sum X_i M_i$$

Where X_i is the mole fraction of i^{th} polymer having molecular weight of M_i.

iii. <u>Significance</u> $\overline{M_n}$: It represents the physical properties of polymer such as impact and tensile strength.

Q5. What is Weight-Average molecular weight [$\overline{M_w}$]? State its mathematical expression. Also state its significance.

A. i. It is defined as the total weight [W] of all the molecules in a polymer sample divided by the weight- fraction of molecular polymer.

ii. If N_1, N_2, N_3, ... are the number of molecules having molecular weights M_1, M_2, M_3,.... in a polymer sample, then the number average molecular weight is given as follows:

$$\overline{Mn} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N1+N2+N3+......}$$

$\overline{Mn} = \dfrac{\sum N_i M_i^2}{\sum N_i M_i} = \dfrac{\sum X_i M_i^2}{\sum X_i M_i} = \dfrac{\sum W_i M_i}{\sum W_i}$

Where N_i is the number of moles of i^{th} polymer having molecular weight of Mi;

Xi is the mole fraction of i^{th} polymer having molecular weight of Mi and

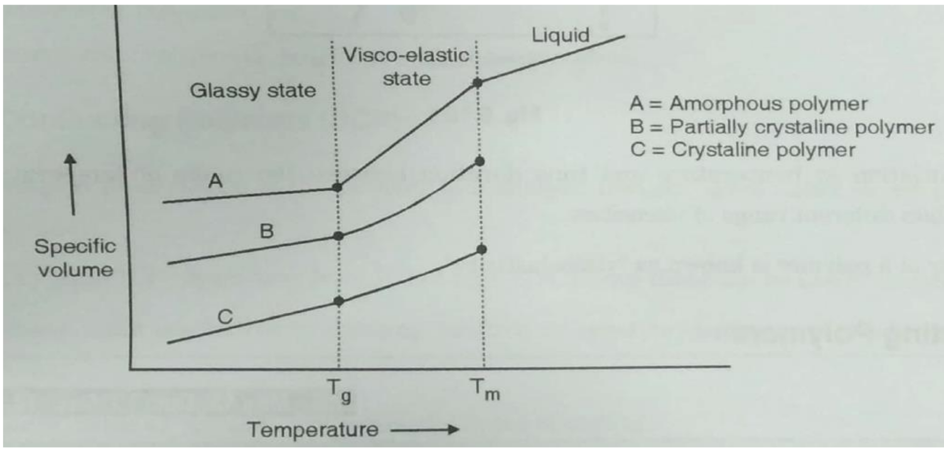
W_i is the weight fraction of molecules of mass M_i

Note : Always $\overline{Mw} > \overline{Mn}$; but in case of monodisperse system where all the molecules have similar molecular mass then $\overline{Mw} = \overline{Mn}$.

iii. Significance: It represents the light scattering property of a polymer molecule.

Q6. Explain Glass Transition Temperature and Melting Temperature. What is its significance?

A. Glass Transition temperature:



Definition: Amorphous polymers when cooled below certain temperature, becomes hard, brittle and glassy but above this temperature, they are soft, flexible and rubbery. This transition temperature of polymer is called as the glass transition temperature [Tg].

Factors affecting Tg value:

i. Molecular Weight : Tg is directly proportional to molecular weight of the polymer.

ii. Cross-links : Tg is directly proportional to degree of cross-links.

iii Flexibility: Flexibility of a polymer decreases with increase in Tg value.

[Tg α 1/flexibility]

iv. Plasticiser: Addition of plasticiser decreases the Tg value. *[Tg α 1/plasticiser]*

v. Intermolecular Forces: Tg value increases in polymers as they possess strong forces of attraction.

vi. Side chain/bulky groups : Presence of side chain or bulky groups increases the Tg value.

Significance :

i. It helps to anticipate flow properties/softening temperature of polymers.

ii. Knowing Tg, different samples can be compared & selection of polymers for desired moulding/ article can be done more efficiently.

Melting Temperature [Tm] :

When a polymer is heated beyond Tg, it changes from glassy state to rubbery/elastic state. On further heating the polymer becomes soft, flexible and melts to flow like a liquid/fluid. The temperature below which the polymer is in rubbery state and above which it is a liquid is called Melting Temperature of the polymer (Tm).

Q7. Write a short note on Viscoelasticity.

A. i. When a polymer is heated above its glass transition temperature(Tg), it becomes soft, flexible and elastic.

ii. When it is heated beyond Tg, it passes from glassy state to rubbery state.

iii. Further heating much beyond Tg causes melting of the polymer and further temperature makes it elastic. This property of the polymer is called 'Visccoelasticity' i.e. the polymer is viscous and elastic at the same time.

iv. The degree of viscoelasticity is strongly dependent upon the temperature of test and the rate at which the polymer is deformed, as well as structural variables such as degree of crystallinity, crosslinking, and molecular mass.

v. Viscoelastic materials are used for isolation vibration, dampening noise and for absorbing shock.

vi. burning of a piece of camphor illustrates the property of viscoelasticity.

Q8.What are conducting polymers? Explain in detail.

A. I. Definition: An organic polymer with highly delocalised π –electron system showing conductance similar to that of a metal and a semiconductor is called as conducting polymer.

II. There are four types of conducting polymer namely:

i. Intrinsically conducting polymer [ICP] ii. Doped conducting polymer [DCP]

iii.Extrinsically conducting polymer [ECP] iv. Co-ordination conducting polymer [CCP].

i. Intrinsically conducting polymer[ICP] :

- This is a polymer which possess conjugated pi electron [delocalised electron] backbone.
- Electrons get excited when such polymer faces electric field & spreads in the entire polymeric material.
- Over lapping of orbitals over the entire backbone results in the formation of valence band & conduction bands that makes the polymer to conduct electricity.
- Eg : Polyacetylene, Polyquinolene, Polyaniline etc.

ii. Doped conducting polymer [DCP] :

- They are prepared by exposing polymer to a charge transfer agent either in the gas phase or liquid phase.
- Doping is of 2 types : P-doping and N-doping.
- P-doping is a technique in which an ICP is oxidised with lewis acid [p-dopant] for eg $FeCl_3$ or I_2 or Br_2.

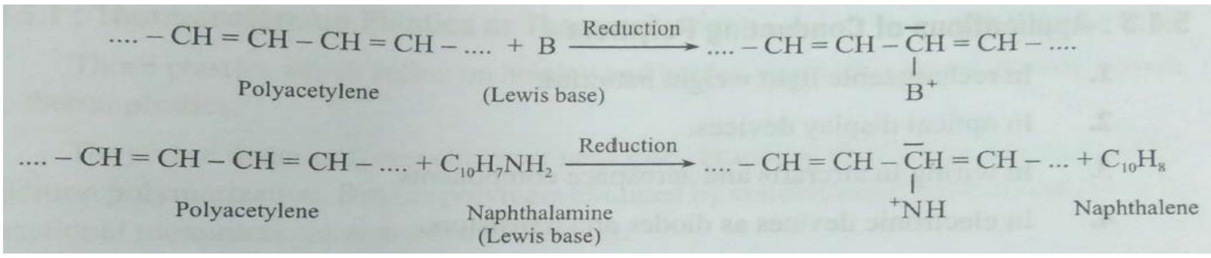
- Oxidation reaction takes place thereby creating a positive charge on the backbone of polymer.

Poly Acetylene   Lewis Acid   + vely charged backbone

$$2\,(C_2H_2)_n + 3I_2 \rightarrow 2\left[(C_2H_2^{+})_n\, I_3^{-}\right]$$

- N-doping involves reduction of ICP with lewis base to form negative charge on the backbone of polymer.

- N-dopants are Li, Na, Ca, tetrabutyl ammonium etc.



iii. Extrinsically conducting polymer [ECP] :

- It possessess conductivity when an external ingredient is added to the polymer..

- 2 types of ECP:

- a. Conductive element- filled polymer : It is a resin or polymer filled with conducting element like carbon black, metal oxides, metallic fibres etc. The polymer act as a binder to hold the conducting elements together in the solid structure.

  b. Blended conducting polymer : It is a blend of normal polymer with conducting polymer. It possess good physical, chemical and mechanical properties.

iv. Co-ordination conducting polymer [CCP]:

- Inorganic in nature. Polymer is combined with a complex carrying charge or a metal atom is combined with polydentate ligands.

- They have low degree of polymerisation.

- They are corrosion resistant.

III. Applications of Conducting Polymer:

- Used in rechargeable light weight batteries. They are about 10 times lighter than conventional lead storage batteries.

- In making analytical sensors for pH, O_2, SO_2, NH_3, glucose, etc.

- In the preparation of ion exchangers, wiring, aircrafts & aerospace components.

- In controlled release of drugs and bio-medical applications.

- In telecommunication systems.

- In optical filters and in electromagnetic screening material.

- Solar cells, photovoltaic devices, transistors, diodes, switches.

Q9. What are plastics? Give its classification.

A. I. Definition: These are high molecular weight polymers which may occur in nature or can be manufactured synthetically using raw materials mostly from gas & petroleum or from coal mines, forests, paper & textile mills.

II. Classification: This depends on the basis of setting manner in final stage of manufacture on application of heat & pressure. Thus there are two classes: Thermoplastics and Thermosetting plastics.

Q10. Distinguish between Thermoplastics and Thermosetting plastics.

Sr.No	Thermoplastics [Thermosoftening plastics]	Thermosetting plastics [Thermohardening plastics]
1.	Formed by addition polymerisation	Formed by condensation polymerisation.
2.	Linear structure -R-R-R-R-R-	Cross linked structure.3D network
3.	Bifunctional monomers are used	Higher functionality monomers are used.
4.	Have low molecular weight.	Have high molecular weight.
5.	Soft, weak & brittle.	Harder, stronger & more brittle.
6.	Soluble in some organic solvents	Insoluble in almost all organic solvents.
7.	Softens on heating & becomes hard on cooling	Softens on first heating & becomes hard on further heating.
8.	Can be reclaimed, recycled & reused.	Cannot be reclaimed.
9.	Their intermolecular forces of attraction are weaker.	Their intermolecular forces of attraction are stronger.
10.	e.g. Polyethylene, Polyvinyl chloride, Teflon, etc	e.g.Urea formaldehyde, Phenol, Polyurethane, Nylon etc.

Q11. What is compounding of plastic? Explain the different ingredients added to a plastic?

A To impart certain properties to the finished products, plastic is compounded with other ingredients. These ingredients are as follows:-

1. Binders :

i. The purpose of binders is to hold the other constituents together in a plastic.

ii. It is also decides the type of treatment needed to mould the articles from the plastic.

iii. Almost 30-90% of binder is added to the plastic.

iv. It can be natural or synthetic resins or cellulose derivatives.

v. If low molecular weight resin/binder is used, the plastic gets moulded easily.

2. Fillers: The proportion of fillers is 50%. They serve following purposes:

i. reduce the cost of plastic.

ii. reduce shrinkage on setting.

iii. impart better tensile strength, opacity, hardness, finish and workability.

Examples: Wood flour, cotton pulp, saw dust, mica, quartz, talc, asbestos, carbon black, graphite, metallic oxides like ZnO, PbO, metal powders like Fe,Cu, Pb,Al.

3. Plasticizers: The proportion of plasticizer is 60%. They serve the following purposes:

i. improves the plasticity & flexibility to reduce the temperature & pressure required for moulding.

ii. reduces brittleness.

iii. increases flame proofness.

Examples: vegetable oils, esters of fatty acids, tributyl phosphate etc.

4. Dyes & Pigments : They serve the following purposes:

i. impart decorative colours to the plastic.

ii. are organic dyestuffs & opaque inorganic pigments.

Examples: Ferric acid(red), Antimony sulphide(crimson red), zinc oxide(white), calcium carbonate(white), carbon black(black), ultramarine(blue).

5.Catalysts/Accelerators: They are added in the case of thermosetting plastics. They serve the following purposes:

i. accelerate the polymerisation of fusible resin during moulding process.

ii. added in small quantities.

Examples: Hydrogen peroxide, Benzoyl peroxide, metallic oxides etc

6. Lubricants: These additives are widely used to help plastics flow in moulds. They serve the following purposes:

i. impart good & flawless finish.

ii. reduces friction & prevents sticking of plastic to the mould.

Examples: waxes, oils, soaps, stearates.

7. Stabilisers: They are added only in thermosoftening plastic. They serve the following purposes:

i. improve thermal stability of the plastic.

ii. prevents degradation of the plastic during moulding process.

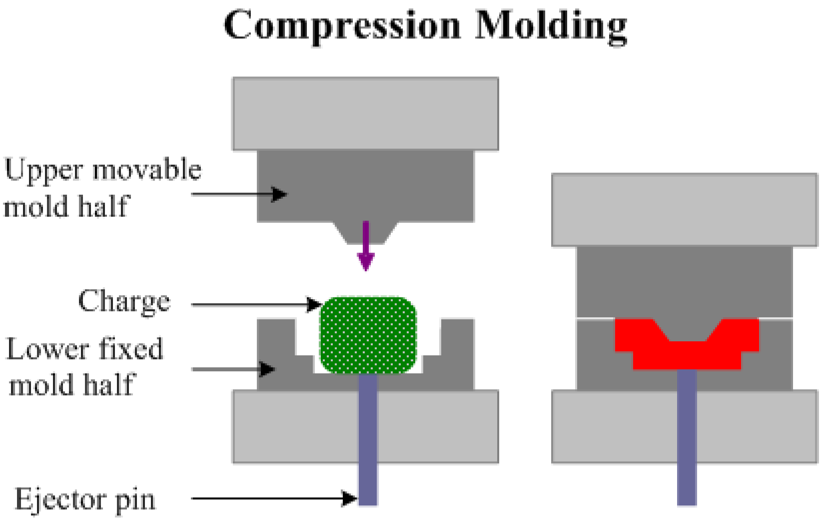
Examples: white lead, lead chromate, red lead etc.

Q12. Define fabrication. Give different methods for fabrication of plastics.

A. Fabrication or moulding of plastics is the process to convert raw plastic material into desired shape in a mould by applying heat and pressure. The different methods of fabrication are:

a . Compression Moulding. b. Injection Moulding. c. Transfer Moulding. d. Extrusion moulding.

Q13. Explain Compression moulding in detail with diagram.



A

.i. It is used for moulding both thermoplastics and thermosetting plastics.

ii. This process consists of compressing the molten resinous material into the desired shape by the use of moulds, heat and pressure.

iii. A known quantity of resin [plastic] powder or pellets is preheated to about 120c before it is introduced in the mould.

iv. The molten plastic is then charged in between the top and bottom parts of the mould and closed carefully at low pressure.

v. The pressure applied is 2000 to 10000 p.s.i and the temperature is 100 to 200c.

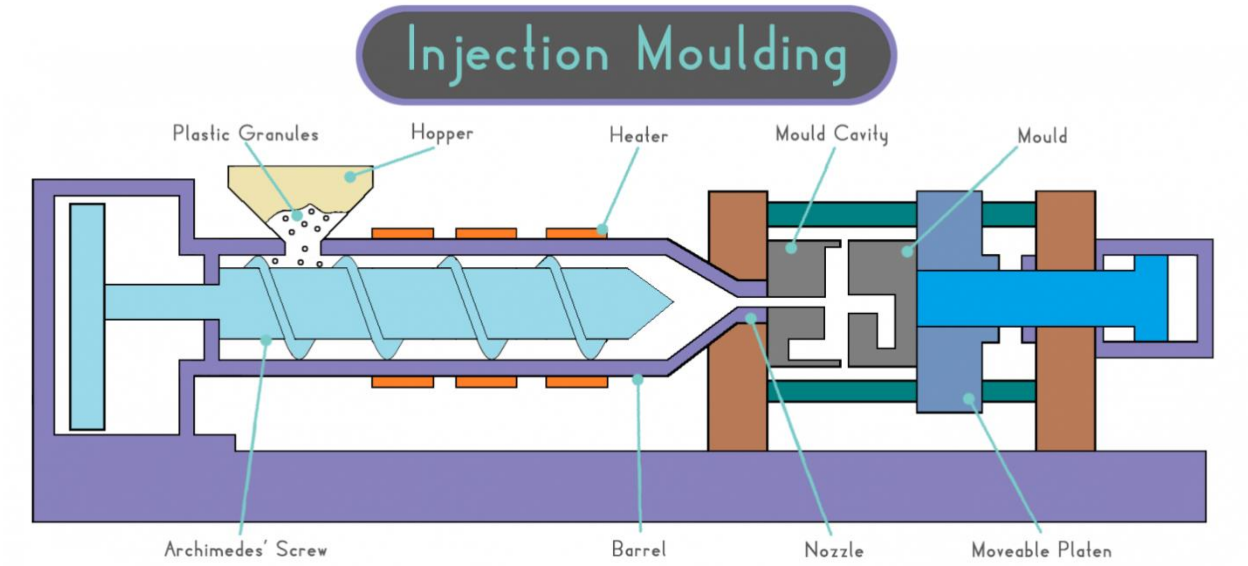
vi. Due to high temperature and pressure the plastic melts and fills the cavity.

vii. The curing is done by heating the plastic further in case of thermosetting plastic whereas it is cooled further in case of thermoplastic.

viii. After curing the moulded articles are taken out by opening the mould apart.

eg : trays , electric switch boxes.

Q14. Explain Injection moulding in detail with labelled diagram.



A.

i. It is used for high speed moulding thermoplastics.

ii. A known quantity of resin [plastic] powder or pellets is preheated to about 120c before it is introduced in the mould.

iii. The hot molten plastic is then injected through a nozzle at a controlled rate into the tightly locked mould by means of a screw arrangement or a piston plunger.

iv. The temperature applied is 90 to 260c and the pressure is 1758Kg/cm^2.

v. The curing is done by cooling the hot plastic inside the mould to become rigid.

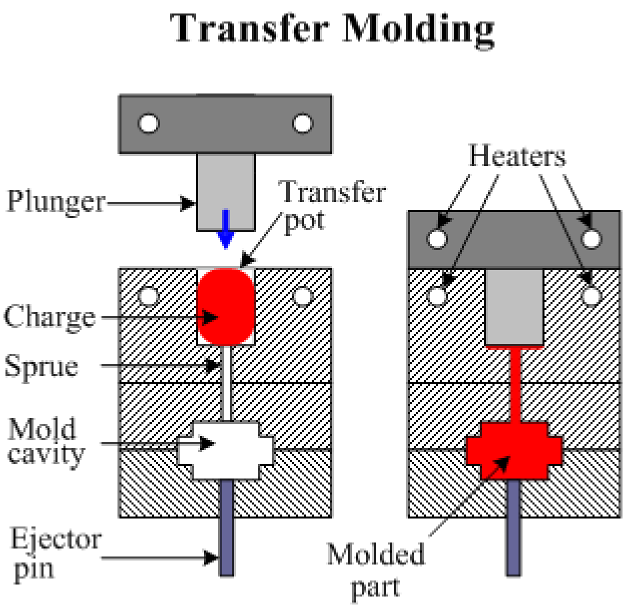
vi. After cooling the finished article is ejected without any deformation.

Advantages of injection moulding : The cost is low, low loss of material, high finishing production.

Disadvantage : A large number of cavities cannot be filled simultaneously, due to which there is limitation of design of article to be moulded.

Examples: wire spools, bottle caps, automotive parts and components, Gameboys, pocket combs, some musical instruments (and parts of them), one-piece chairs and small tables, storage containers, mechanical parts (including gears).

Q15. Explain Transfer moulding with neat labelled diagram.



i. This method is used for moulding thermosetting plastic similar to injection type of moulding.

ii. A known quantity of powdered resin is heated in the chamber at the minimum temperature in which the resin just starts to become plastic.

iii. This plastic material is then injected through an orifice into the mould by plunger, working at a high pressure.

iv. Due to a very high friction developed at the orifice, the temperature rises to such an extent that the moulding powder almost becomes liquid and flows into the mould.

v. The curing is done by heating the plastic further for thermosetting plastic.

vi. The moulded article is ejected mechanically.

Advanatges:

i. Mould cost is low.

ii. Finishing of the article is not required.

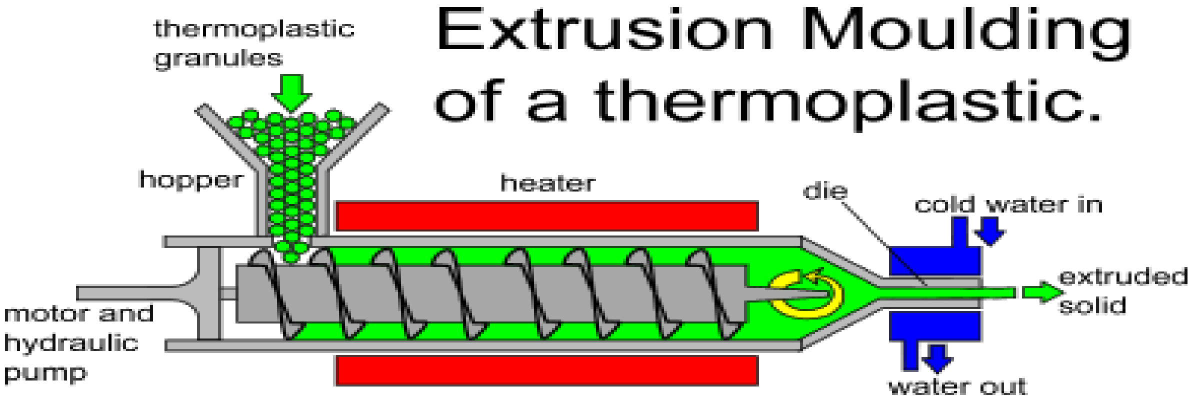
iii. Suitable for intricate shapes.

iv. Blistering is eliminated.

Examples: Electrical & Electronic components; Rubber & Silicone parts

Q16. Explain Extrusion moulding with neat labelled diagram.

A.



i. This method is used for moulding thermoplastic resins. They undergo continuous moulding to form articles of uniform cross-section.

ii. A known quantity of resin powder or granules is first fed through the hopper into the rear of the heated chamber which has a revolving screw.

iii. The plastic melts and then is forced through a die having the required shape.

iv. The finished product is cooled by atmosphere or by blowing air or by spraying water.

v. A long conveyor carries away the cooled product continuously.

vi. There are two types of moulding :

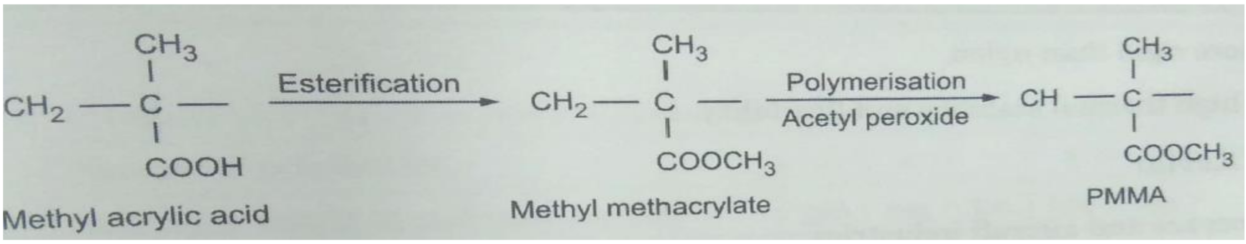
a. Vertical Extruder moulding. b. Horizontal extruder moulding.

Examples: Insulated electric wires, cables, tubes rods, strips.

Q17. Describe the preparation, properties and applications of PMMA.

A. i. Method of preparation of Polymethyl Methacrylate or Lucite or Plexiglass [PMMA]:

It is prepared by polymerisation of methyl methacrylate which is an ester of methyl acrylic acid CH_2=C.(CH_3)-COOH in the presence of acetyl peroxide. It is an acrylic polymer.



ii. Properties of PMMA:

a. Colourless, hard, thermoplastic and fairly rigid material.

b. High softening temperature 130-140·c, becomes rubbery above 65c.

c. High optical transparency having refractive index 1.59.

d. Low resistance to hot acids, alkalies and to scratches.

e. High resistance to sunlight and ability of transmitting light accurately.

iii. Uses/Applications:

a. For protective coating on spectacles and also for manufacturing safety glasses.

b. Acrylic resin emulsions are used for textiles and leather finish.

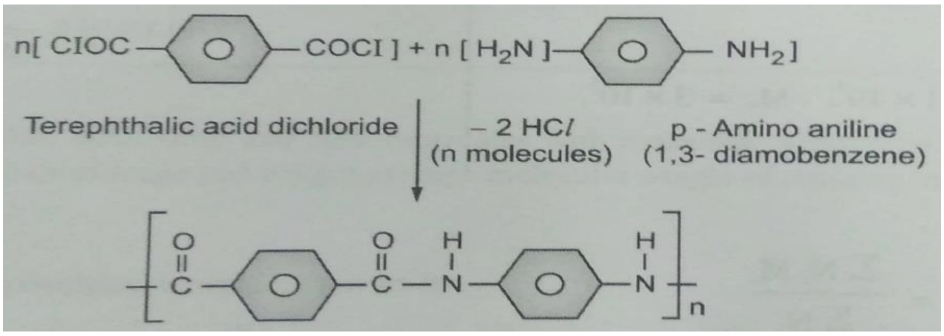
c. Making lenses, artificial eyes, wind screens, TV screens, jewellery, bone splints, decorative articles, light fixtures, window glasses etc.

d. As a cloud and pour point depressant additives in lubricants.

Q18. Describe preparation, properties and applications of Kevlar.

A. i. Method of preparation of Kevlar/ Poly Paraphenylene Terephthalamide:

It is an aromatic polyamide prepared by polycondensation between aromatic dichloride and aromatic diamines.



ii. Properties of Kevlar:

a. It is very strong, almost 5times stronger than steel and 10times stronger than aluminium.

b. It is more rigid than nylon.

c. It has high thermal stability and flexibility.

d. It remains stronger even at -196c.

e. It has resistance against almost all the solvents except some powerful acids.

iii. Applications of Kevlar:

a. In aerospace and aircraft industries.

b. In car parts: tyres, brakes, clutch linings etc.

c. In ropes, cables, bulletproof vests/jackets, motorcycle, helmets etc.

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