

Chapter 3: Polymers

- The word polymer is derived from a Greek word polymeros.
Poly- many,
Meros - parts.
- This term was introduced by Berzelius in 1833.

Definitions:

- **Polymer**- A complex giant molecule of high molecular mass, built by linking together a large number of monomers.
- **Monomer**- Small repeating unit in polymer are called monomers.

Examples of polymer: - polyethylene, polystyrene, rubber, starch, protein etc.

- **Polymerization**- A process of formation of high molecular weight compound by reacting monomer molecules together in a chemical reaction.
- **Degree of polymerization**- It is the total number of monomers present in a given polymer.
- **Functionality**- It is the number of bonding sites present on a monomer.

Classification of polymers:-

There are different ways in which polymers can be classified. They are as follows.

1. Based on the origin-

- Natural polymers- polymers which are available from the natural sources are known as natural polymers.
Example- Starch, Cellulose, Proteins, Natural rubber, cotton, jute, silk etc.
- Synthetic polymers- polymers which are synthesized in lab or industries are known as synthetic polymers or man-made polymers.
Example- Nylon, Synthetic rubber, polyethylene, polypropylene, PVC etc.
- Semi-Synthetic polymers- polymers which are obtained by modifying natural polymers are called semi-synthetic polymers.
Example- Cellulose acetate, Halogenated rubber, tericot etc..

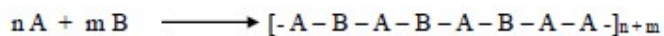
2. Based on the monomer present:

They are classified as homopolymer and copolymer.

- **Homopolymer**: In this polymer the repeating units (monomers) are the same. E.g. rubber



- **Copolymer**: In this polymer, the repeating units are not same, but are derived from two or more molecules.



3. Based on chemical composition:-

- Organic polymer: - A polymer whose backbone chain is essentially made of carbon atom is termed as organic polymer. The atoms attached to the side valencies of the backbone carbon atom are usually hydrogen, oxygen, nitrogen. The majority of synthetic polymers are organic. E.g :- polyethylene , polypropylene ,PVC.
The body of the living organism contains organic polymer in the form of proteins, DNA, RNA etc.
- Inorganic polymer: - If the backbone of the polymer chain contains atoms other than carbon, then it is called inorganic polymer.
For E.g :- polysilane, polyphosphate

4. Based on response to heat :-

- Thermo softening plastic: These are polymers which become soft on heating. They can be moulded into different shapes and shape is retained on cooling. They can be remoulded number of times by heat treatment. Hardness of such plastic is temporary.
E.g:- Polyethylene, Polypropylene, Polystyrene, PVC
- Thermosetting plastic: - These are polymers which cannot be reformed once they are set. They are also called as thermosetting resins. They have somewhat 3-D structure and high molecular weight.
E.g:- Urea formaldehyde, Phenol formaldehyde.

Distinguish between **Thermoplastics** and **Thermosetting polymers**

Thermoplastics polymers		Thermosetting polymers	
1	Softens on heating and stiffen on cooling, reversibly by the action of heat.	1	On heating they are converted into an infusible mass and once set they cannot be reshaped.
2	They can be remoulded.	2	They cannot be remoulded.
3	Formed by addition polymerization.	3	Formed by condensation polymerization.
4	Soluble in organic solvents	4	Insoluble in organic solvents
5	They are soft, weak and less brittle.	5	They are hard, strong and more brittle.
6	They have low molecular weight as compared to thermosetting.	6	They have high molecular weight as compared to thermoplastics.

7	Chemical change does not occur on heating only physical changes are involved.	7	Chemical changes occur on heating.
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Polymerization

Polymerization- A process of formation of high molecular weight compound by reacting monomer molecules together in a chemical reaction.

Types of polymerization:-

1. Addition polymerization.
2. Condensation polymerization.
3. Co- polymerization.

Distinguish between addition polymerization and condensation polymerization
Properties of polymers

SR. No	Addition Polymerization	Condensation polymerization
1.	Monomer molecules having multiple bonds undergo addition reactions.	Monomers having simple polar groups condensed together by elimination of small molecule such as H ₂ O, CH ₃ OH etc.
2.	The monomer should contain one or more double bond (i.e. they should be bifunctional)	Monomers should have functionality more than two. They should have groups like - OH, -COOH, -COOR, NH ₂ .
3.	Also called as chain reaction.	Also known as step polymerization
4.	The reaction is very fast.	It is a slow reaction.
5.	No byproducts are formed.	Byproducts like H ₂ O, CH ₃ OH, NH ₃ , and HCl are formed.
6.	Addition polymers have comparatively low molecular weight.	High molecular weight products are formed.
7.	This polymerization takes place in three steps: - Initiation, propagation, termination.	Only one type of reaction i.e. condensation between two functional groups is involved.
8.	Polymers are thermosoftening (thermoplastic)	Polymers are thermosetting

9.	Eg: - polyethylene, polypropylene, polystyrene.	Eg: - urea and phenol formaldehyde.
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Molecular Weight-

1. The important properties of polymers are influenced by the molecular weight of polymers as the intermolecular force of attraction between different polymeric chains increase with the length of the polymeric chains.
2. Higher molecular weight polymers are tougher and more heat resistant.
3. Their softening temperature are also higher compared to the low molecular weight polymers.

There are two methods for determining molecular weight of polymers

1. Number Average Molecular Weight
2. Weight Average Molecular Weight

1. Number Average Molecular Weight (M_n)

M_n is defined as the total weight (w) of all molecules in a polymer sample divided by the total number of molecules present.

$$M_n = \frac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3} = \frac{\sum N_i M_i}{\sum N_i}$$

$$M_n = \frac{\sum W_i}{\sum N_i}$$

$$M_n = \frac{\sum W_i}{\sum W_i / M_i}$$

Where, N_i is the number of molecules of molecular mass M_i

M_n is determined by measurement of colligative properties such as freezing point depression, Boiling point elevation, Osmotic pressure.

M_n is a good measure of physical properties such as tensile strength.

2. Weight Average Molecular Weight M_w

M_w is defined as the total weight (w) of all molecules multiply by molecular mass M_i in a polymer sample divided by the total weight of molecule (w)

$$M_w = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$M_w = \frac{W_1 M_1 + W_2 M_2 + W_3 M_3}{W_1 + W_2 + W_3} \dots\dots\dots (NM = W)$$

$$M_w = \frac{\sum W_i M_i}{\sum W_i}$$

M_w is obtained from light-scattering and ultra-centrifugation techniques M_w is a good measure of molecular size.

Numericals

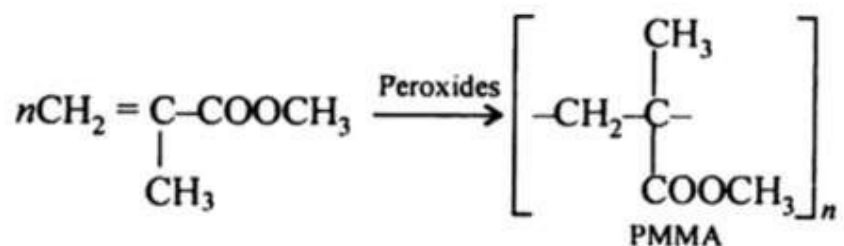
1. A polymer sample consists of 10% by weight of macromolecules of molecular weight 10,000 and 90% by weight of macromolecules with molecular weight 100,000. Calculate M_n and M_w .
2. A polymeric mixture is prepared by mixing three polymers A, B, C having M_n , M_w and weight in mixture as given below

Polymer	M_n	M_w	Wt. in Mixture (gms.)
A	1.2×10^5	4.5×10^5	200
B	5.6×10^5	8.9×10^5	200
C	10×10^5	10×10^5	100

3. In a polymer, there are 100 molecules of molecular weight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10,000 find M_n and M_w .

The preparation, properties and uses of the following

1. *Polymethyl methacrylate (PMMA) or Lucite or plexiglass.*



Properties:

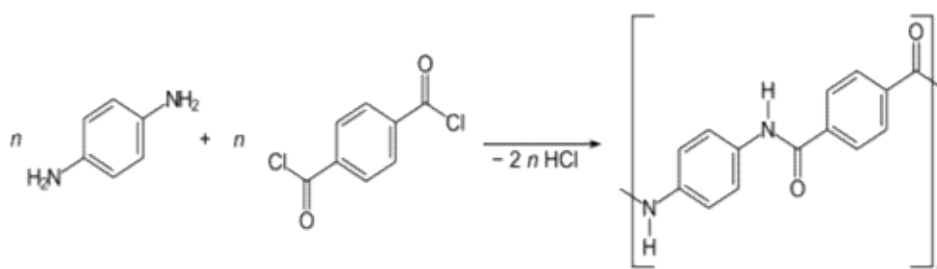
1. It is clear, colorless transparent plastic with high softening point.
2. Good impact strength, high tensile strength.
3. Good optical property i.e. it transmits 98% of the sunlight including ultra violet light.
4. Compared to glass, it weighs only one-third, hence can be easily moulded to any desired shape. Scratches on it can be easily removed by rubbing it with a cloth moistened with acetone. After cracking fragments formed are less sharp, and less harmful.

Uses:

1. It used for tail and signal light lenses.
2. It is an excellent substitute of glass (TV screens, wind screens)
3. It used to make artificial eyes, contact lenses, dentures.
4. It is used for making dome-shaped covers of solar collectors (i.e solar heaters).

2.Kevlar (Aromatic Amide):

Preparation:



Properties:

1. Highly strong, i.e. 5 times strong than steel, 10 times strong than Aluminium.
2. High heat stability and flexibility.
3. Rigid than nylon.

Uses:

1. Aerospace and aircraft industry
2. For making car parts such as tyres, brakes.

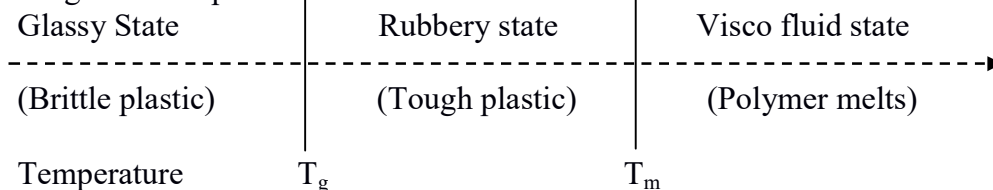
3. Protective clothing- bullet proof jackets, helmets etc.
4. For making ropes and cables.

Glass Transition Temperature:

- This temperature below which a polymer is hard, brittle and glassy and above which it is soft, flexible and rubbery is called glass transition temperature. The hard brittle state is known as the **glassy state**
- The soft flexible state as **rubbery or viscoelastic state**.
- On further heating, the polymer becomes a highly viscous liquid and this state is known as **viscofluid state**.

The glass transition is a property of only the amorphous portion of a semicrystalline solid. The crystalline portion remains crystalline during the glass transition.

Diagrammatic representation:-



Factors Influencing Glass Transition Temperature:-

Mobility of the polymer chain is the main factor that affects glass transition temperature..

A polymer chain that can move easily will change from a glass to a rubber at a low

If the polymer chains don't move as easily, then it will require a relatively high temperature to change the compound into a rubbery form.

Thus lesser the mobility higher the T_g .

Value of T_g depends upon molecular characteristics that affect chain stiffness.

Chain flexibility is diminished and T_g is increased due to following

1. Presence of Polar side atoms or groups of atoms increases glass transition temperature.

For example: PVC T_g is **87°C**

PP T_g is **- 18°C**

PVC (poly vinyl chloride) has stronger intermolecular forces than polypropylene (PP) because of the dipole-dipole forces from the C-Cl bond.

2. Pendant Groups: The influence of pendant groups on the glass transition temperature is somewhat more complicated.

A) Bulky pendant groups, such as a benzene ring, can catch on neighboring chains like a "fish hook" and restrict rotational freedom. This increases T_g .

For example:-

PP is polypropylene **T_g - 18°C**

PS is polystyrene **T_g 100 °C**

Due to Presence of bulky side groups, T_g of polystyrene greater than polypropylene.

B)Flexible pendant groups, such as aliphatic chains, tend to limit how close chains can pack. This increases rotational motion and lowers T_g .

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3. Cross-Linking:

The presence of cross-links between chains restricts mobility and raises the Tg.

4. Molecular weight: Increase in the molecular weight tends to raise Tg

5. Presence of Double chain bonds and aromatic chain groups stiffen molecular backbone and raises the Tg.

6. Plasticizers:

Plasticizer molecules cause separation of polymer chains which results in increase in the mobility of the molecule. Hence Tg decreases.

Random copolymerization reduces molecular packing and inter-chain forces of attraction 7.

Co-polymerization:

which result in increase in chain mobility. Hence Tg decreases.

Significance of glass transition temperature:

1. It is used as a measure for evaluating the flexibility of a polymer molecule and type of response the polymeric material would exhibit to mechanical stress
2. Tg value along with Tm values gives an indication of temperature region at which a polymeric material transform from a rigid solid to a soft viscous state.
3. It helps in choosing the right processing temperature in which material can be converted into finished product.

Viscoelasticity

- Majority of the engineering polymers are **neither 100% crystalline nor 100% amorphous**
- They are combinations of amorphous and crystalline.
- Below Tg the polymer becomes hard brittle and glassy solid.
- Above Tg, the polymer becomes soft flexible and rubbery.
- On further heating at melting temperature Tm and beyond Tm the polymer become viscous liquids and start flowing.
In case of polymers above Tg, There exists an intermediate stage where movement of the polymer chain is activated this corresponds to liquid state, but the movement of the polymer molecule as a whole is prevented or forbidden. This is solid state.
- This state is a combination of liquid and solid, and is called the rubbery state or viscoelastic state.

- Under the influence of applied stress it exhibits properties of a viscous fluid as well as an elastic solid. This property is known as viscoelasticity and the deformation is known as viscoelastic deformation.

Plastic:

1. The word plastic originated from Greek, meaning a material that can be moulded or formed into any shape of one's own choice.
2. The plastic is defined as, "An organic material of high molecular weight, which can be moulded into any desired form, when subjected to heat and under pressure". properties like,
3. They have gained lot of importance in every walk of life, due to their unique
 - Lightness in weight.
 - Good thermal and electrical insulation.
 - Good corrosion resistivity.
 - Low fabrication cost and decorative surface effect.
 - Chemically inert to action of light, oils, acids and dampness.
 - Low maintenance cost and high refractive index.

Compounding of Plastic:

(Additives of plastic or constituents of plastics)

- In order to impart certain definite properties to the finished product, plastic is compounded with other ingredients.
- These ingredients are known as additives.
- **The selection of additives and the operation of mixing them with the polymer constituent are known as compounding.**

The various additives/ingredients added are as follows,

1. Resin(Binder)

FUNCTIONS:

- It forms the major part of plastics and holds the different constituents of plastic together.

EXAMPLES:

- Binders are of two types: thermoplastic and thermosetting.
- Thermoplastic- PE, PP, PVC, Thermosetting- urea and phenol formaldehyde.

2. Fillers FUNCTIONS:

Fillers are added to plastics in order to,

- Reduce the cost of plastic.
- Reduce shrinkage on setting and brittleness.
- Improve hardness.
- Improve solvent resistance etc.

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EXAMPLES:

The most common fillers are carbon black, calcium carbonate, calcium sulphate, talc, silica, alumina, clay, iron oxide, wood flour and metallic powders.

3. Reinforcements

FUNCTIONS:

- In some respects reinforcements may be regarded as fillers, but they are added mainly to improve the tensile strength properties of the plastic material.

EXAMPLES:

- Typical reinforcing materials available as fibers are glass, asbestos, boron, carbon, ceramic, cotton flock, jute, synthetic fibers of nylon, polyethylene terephthalate etc.

4. Plasticizers FUNCTIONS:

- To improve plasticity and flexibility.
- To improve processing and reduce brittleness of the end product.
- They lower the glass transition temperature below room temperature, so that the properties of a material change from hard, brittle, and glass-like to soft, flexible and tough.

EXAMPLES:

Phosphates, vegetable oil, camphor, esters of oleic acid.

5. Lubricants FUNCTIONS:

- They eliminate external friction between the polymer and the metal surface of the processing equipment.
- To impart flawless glossy finish to the product.

EXAMPLES:

Waxes, oils, stearates, oleates

6. Stabilizers

- Stabilizers provide protection against degradation caused by heat, oxidation, and solar radiation. Hence, they can be classified as heat (or thermal) stabilizers, antioxidants and UV light stabilizers.

EXAMPLES:

Heat stabilizers: lead compounds like lead chromate, white lead, stearate of Pb, Cd, and Ba.

- **Antioxidants:** substituted phenols, aromatic amines and sulphur compounds.
- **UV Light stabilizers:** substituted benzophenones; benzotriazoles and acrylonitriles, titanium dioxide and zinc oxide

**7. Fire Retardants
FUNCTIONS:**

Plastic compounds may also contain components that improve the fire resistance of the end product.

EXAMPLES:

The most commonly used fire retardants are compounds containing halogen, derivatives of antimony, phosphorous, boron, and nitrogen.

8. Colorants FUNCTIONS:

- Colorants are added to give colour to the plastic material and also to improve the appearance.

EXAMPLES:

Ultramarine- blue colour, CaCO_3 and zinc oxide- white, chromium trioxide- green, ferric oxide – red colour.

Fabrication of plastics:

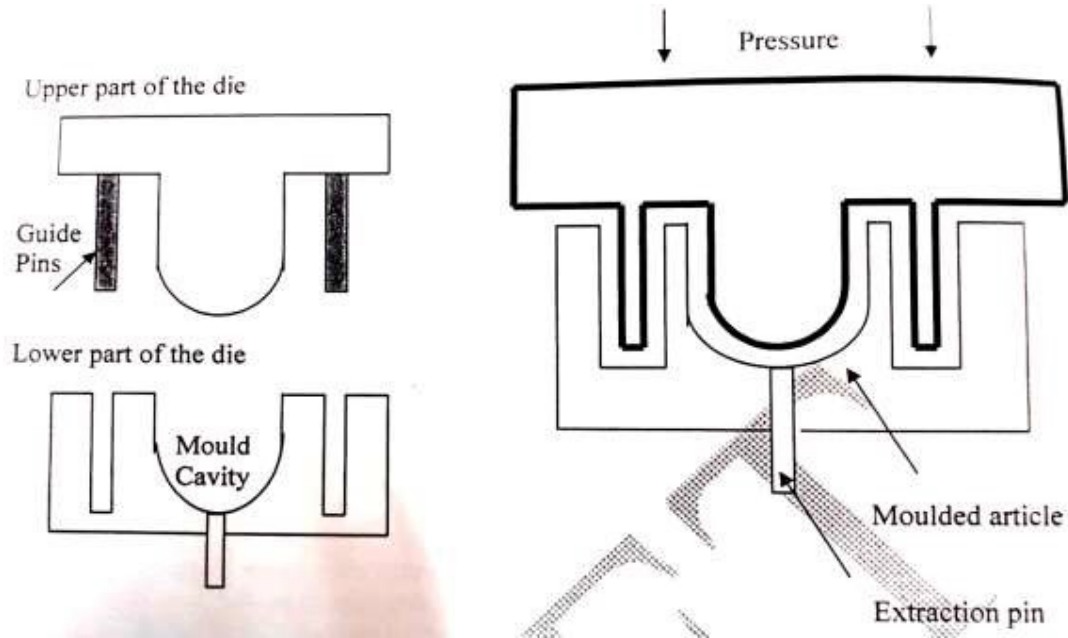
Giving desired shape to plastic is known as fabrication of plastic.

The methods usually depend upon: - types of plastic or resins used i.e. whether thermosetting or thermo softening plastic. Commonly used fabrication methods are,

1. Compression moulding.
2. Injection moulding
3. Extrusion moulding
4. Transfer moulding

1.Compression Moulding

- Compression moulding is used for **thermoplastics as well as thermosetting polymers.**
- Compression moulding is the process that moulds molten plastic, through **compression**, into the desired shape of the moulding.
- The die used for moulding purpose consists of two parts:
Upper cover part & Lower part
In closed condition the gap between two halves gives the desired shape to the product. Generally lower part of the mould is fixed & upper part moves up & down. The movement being properly aligned because of guide pins present. The lower part of the die also has arrangement for heating & cooling by circulating fluid through pipe work.



- The predetermined quantity of plastic ingredients in proper proportion is filled into the cavity. A slight excess of material is taken to ensure that the cavity gets completely filled with material.
- The charge in cavity is heated to make the moulding easier. Moulding temperature ranges from 130°C to 180°C with pressure varying from 100 to 500 kg/cm^2 depending upon kind of raw material.
- Due to heat and pressure, the cavity is filled with fluidized plastic. Then two halves are closed very slowly, to ensure the uniform distribution of plastic mass in the mould. It will take the shape of mould.
- Finally curing is done either by heating (in case of thermosetting plastic) or cooling (in case of thermo softening plastic).
- After curing, the moulded article is taken out by opening the mould parts.

Advantages:

- Relatively low capital and tooling cost.
- Low mould maintenance.
- The product has low residual stress.
- Retention of mechanical and electrical properties.

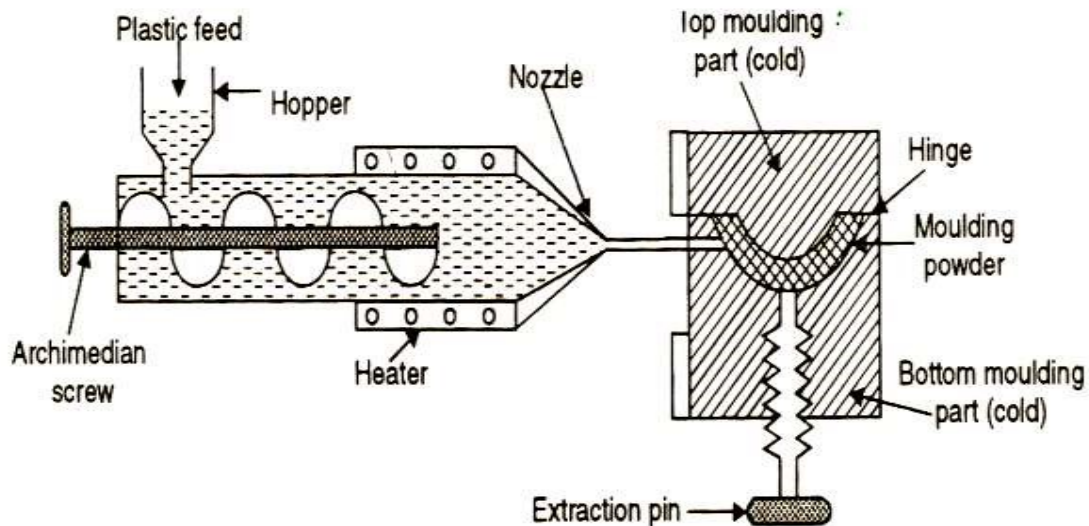
Applications:

Familiar products manufactured by compression moulding include: 3-pin mains plugs, electrical switches, sockets and ashtrays, handles of electric irons etc.

- Thermoplastic products like gramophone records.
- Rubber products like springs, anti- vibration mounting pads

2. Injection moulding:

- **It is used for moulding thermoplastic polymers.**
- Injection moulding is a process where the hot, soft plastic is forced into a cavity in a steel die.
- The size and shape of the cavity is the same as the finished product.
- The shapes may be simple or complex.
- A pigment is added to the plastic powder or granules to produce the desired colour.
- The plastic is placed in a hopper so that it falls into the machine as the screw turned by the gear driven by an electric motor. that converts the plastic into a hot, almost liquid substance.
- As the screw turns it pushes the plastic along the machine and through the heater
- A split die is connected to the end of the machine.
- The screw is pushed into the machine and this forces the soft plastic through a small hole into the cavity of the die.
- **The die and plastic are cooled to harden the plastic (curing).**
- The die is separated and the plastic item is released. The process is then repeated to make another item.



Injection

moulding

Advantages:

- High speed production,
- low moulding cost,
- Loss of material is less and low finishing cost,
- ability to make complex shapes in single operation,

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Limitations:

High capital cost of injection moulding machine.

Moulds are also costly.

Applications:

Products such as the case of a mobile phone, computer parts, TV cabinets, mugs, buckets, milk crates, safety helmets, ice-block trays and food containers are prepared by injection moulding.

3. Extrusion moulding:.

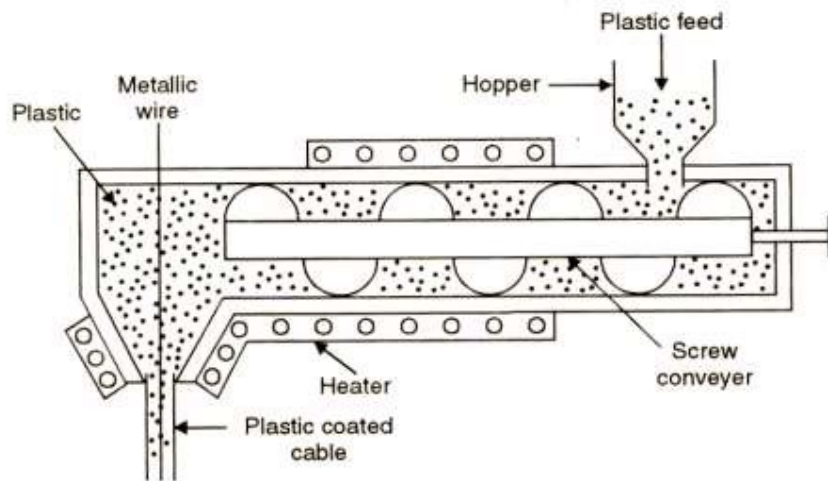
- It is used for moulding **thermoplastic polymers**.
- In extrusion moulding the plastic powder (or granules) is placed in a hopper and then falls into the machine
- The screw turns and pushes the raw plastic along the machine where it is heated to soften the plastic.
- The softened plastic is then forced through a hole in the extrusion die.
- The extruding process is also very much like that of an old, hand operated meatmincer.
- **The extruded plastic is cooled (curing)** and then cut into the desired lengths.
- The shape and size of the extrusion is the same as the shape and size of the hole in the die.
- Changing the shape of the hole in the extrusion die will produce different shapes.

Advantages and applications:

It is most efficient and most rapid method for producing long continuous article such as tubing, tooth paste tubes, rods and filaments, pipes etc.

Limitation:

However this method can be used for obtaining linear shapes only.



Moulding of insulated electric cable of vertical extrusion moulding

4. Transfer moulding

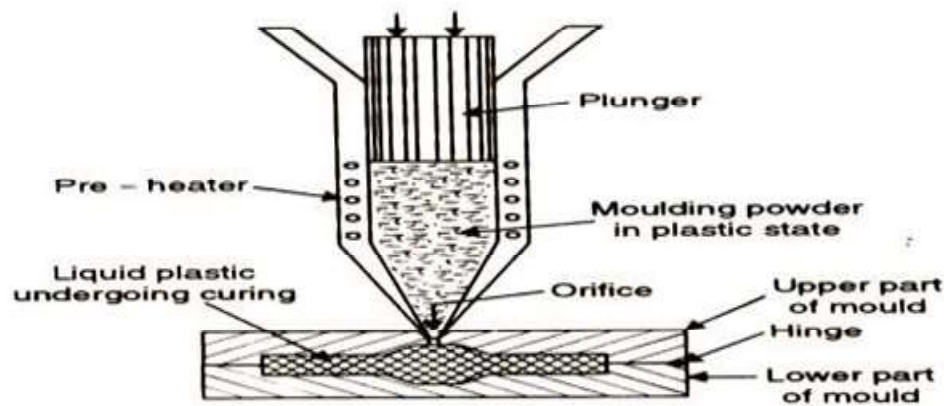
- The method is applicable for **thermosetting plastic** but the technique used is that of injection moulding.
- In this method the mould powder is kept in a heated chamber which is maintained at a temperature at which the moulding powder just starts to become plastic.
- This plastic is then injected through an orifice into mould by a plunger, working at a high temperature.
- The temperature of the material at the time of injection from the orifice becomes so high that moulding powder becomes liquid and flows quickly into the mould.
- **Mould is then heated up to the curing temperature required for setting.**
- The moulded article is then ejected mechanically.

Advantages:-

- Intricate shapes can readily be produced by transfer moulding.
- Article produced is free from flow marks.
- Even thick pieces cure almost completely and uniformly.
- Shrinkage and distortion are minimum due to uniform and through curing. Hence the mechanical strength and density of fabricated plastic pieces is higher.
- Moulding and finished cost are very less.
- Blistering is almost eliminated, since air and waste gases are expelled in the plasticizing chamber itself.

Limitations:

- Tooling is costly and complex
- It increases wear and maintenance cost.



Transfer moulding

Applications:

Utensil handles, electric appliance parts, electronic components, coils, integrated circuits, plugs, etc.

Conducting polymers

- i) Most polymeric materials are poor conductor of electricity, because of the non availability of large no. of free electrons in the conduction process.
- ii) Within past several years, polymeric materials have been synthesized which posses electrical conductance on par with metallic conductors.
- iii) Polymers that conduct electricity are called conducting polymers.
- iv) Conducting polymers are long, carbon-based chain, composed of simple repeating units called monomers & are capable of conducting electricity.
- v) These polymers are widely used over conventional conducting materials because of their ease of processing, relative conductivity, & stability.
- vi) Conducting polymers are much more electrically conductive than standard polymers, but much less than metals such as copper.

E.g. polyaniline, polythiophene

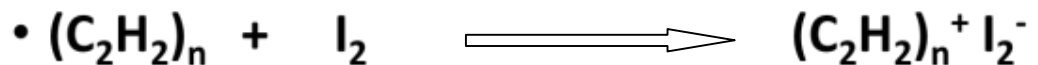
Classification:-

Intrinsic polymers (polymers containing conjugated pi electrons)

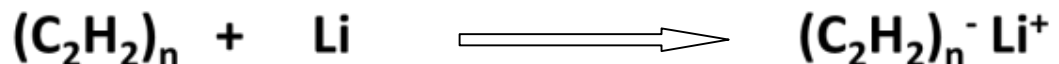
- This type of polymers contain conjugated-electron system in the backbone.
- Presence of delocalized electron pair increases the conductivity of polymer.
- E.g:- polyacetylene polymer, Polyaniline, Polythiophene.

A) Doped conducting polymer

- These polymers are obtained by exposing intrinsically conducting polymers like: polyacetylene, Polyaniline, Polythiophene with a charge transfer agent.
- These polymers are usually doped with appropriate impurities so that their conductivity increases.
- P-doping impurities are lewis acids like I_2 , Br_2 , AsF_5 and BF_3 etc which act as oxidizing agent.



- N- Doping impurities are Li, Na, Ca, etc. here the polymer is treated with the impurity so that reduction takes place & negative charges are created on the backbone of the polymer.



C)Extrinsic conducting polymers:

- **Conductive element filled polymer:** Here conductive element such as carbon black, metallic fibres and metal oxides are added to the polymer. Here the polymer acts as a binder to hold the conductive element together.
- **Blended conducting polymer:** Here a conventional polymer is blended with conducting polymer like polyacetylene, Polyaniline, Polythiophene either by physical or chemical change.
- **Co-ordination conducting polymer (inorganic polymer):**
This is a charge transfer complex containing polymer obtained by combining a metal atom with a polydentate ligand

Applications:-

- 1) In rechargeable light weight batteries, these batteries are 10 times lighter than Pb-storage batteries.
- 2) In optically display devices.
- 3) Wiring in aircrafts & aerospace components.
- 4) In antistatic materials: To avoid static electricity in plastic, carpets in office, theaters, doped aniline is used as antistatic material.

- 5) They are used in construction of photovoltaic cells like, Al / conducting polymer / Pt
- 6) In telecommunication system.
- 7) Electronic devices like transistors and diodes.
- 8) In solar cells and drug delivery system for human body.