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POLYMERS

Definition of polymers: *A polymer is a large molecule of high molecular weight obtained by the chemical interaction of many small molecules of low molecular weight of one or more type. The process of manufacture of a polymer is called the polymerization.*

Monomers: *Small molecules of low molecular weight, which combine to give a polymer, are called monomers.*

Degree of polymerization: *The number of monomers used in the process is called degree of polymerization.*

Functionality: *The total number of functional groups or bonding sites present in a monomer molecule is called the functionality of the monomer.*

Classification of polymers:

I. Based on their sources they are classified into

- 1. Natural polymers:** *The polymers, which are obtained from natural sources such as plants and animals, are called natural polymers.
Egs. Wood, cellulose, Jute, Cotton, Wool, Silk, Proteins, Natural rubber etc.*

2. **Synthetic polymers:** *The polymers, which are synthesized from simple molecules, are called synthetic polymers.*
Egs: Nylon66, PVC, Polystyrene, Teflon, Plexiglass, Polyesters, Polyethylene etc.

II. Based on their thermal behaviour they are classified into

1. **Thermoplastic polymers:** *A thermoplastic, also known as thermosoftening plastic, is a [polymer](#) that turns to a liquid when heated and freezes to a very glassy state when cooled sufficiently. Most thermoplastics are high-[molecular-weight polymers](#) whose [chains](#) associate through weak [Van der Waals forces](#) ([polyethylene](#)); stronger [dipole-dipole](#) interactions and [hydrogen bonding](#) ([nylon](#))^[3]; or even stacking of [aromatic](#) rings ([polystyrene](#)). Thermoplastic polymers differ from [thermosetting](#) polymers ([Bakelite](#)) in that they can be remelted and remoulded. Many thermoplastic materials are [addition polymers](#); e.g., [vinyl](#) chain-growth polymers such as [polyethylene](#) and [polypropylene](#).*

2. **Thermosetting polymers:** *A thermosetting plastic, also known as a **thermoset**, is [polymer](#) material that irreversibly [cures](#). The cure may be done through heat (generally above 200 °C (392 °F)), through a chemical reaction (two-part [epoxy](#), for example), or [irradiation](#) such as [electron beam processing](#).*

Thermoset materials are usually liquid or [malleable](#) prior to curing and designed to be [molded](#) into their final form, or used as [adhesives](#). Others are solids like that of the molding compound used in [semiconductors](#) and [integrated circuits](#) (IC's).

According to [IUPAC](#) recommendation: A thermosetting polymer is a prepolymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing. Curing can be induced by the action of heat or suitable [radiation](#), or both. A cured thermosetting polymer is called a thermoset.^[1]

III. Based on their mechanism of polymerization they are classified into

1. Addition polymers: Addition (chain) polymerization: A polymerization reaction in which monomers containing one or more double bonds are linked to each other without the elimination of any by products, usually in the presence of initiators is called addition polymerization.

Egs: 1. Formation of polythene.

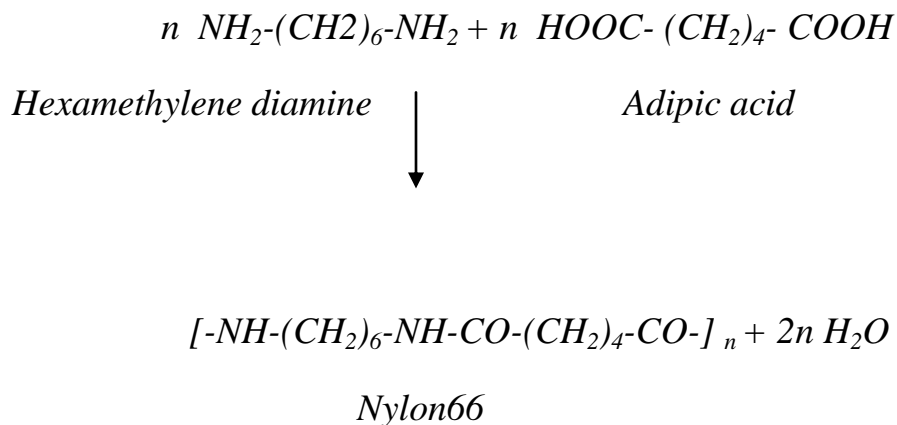


The main features of addition (chain) polymerization are:

1. Only olefinic compounds can undergo addition polymerization.
2. No elimination of by products.
3. Double bond provides required bonding sites.
4. The addition of monomers takes place rapidly.
5. Linear polymers are produced.
6. The addition polymerization is brought about by free radical, ionic or co-ordination mechanism.
7. The molecular weight of the polymer is an integral multiple of the monomer.
8. The elemental composition of the polymer is same as that of monomer.

2. **Condensation polymers:** A polymerization reaction in which bi or poly functional monomers undergo intermolecular condensation with continuous elimination of by products such as H_2O , HCl , NH_3 etc. is called condensation or step polymerization.

Egs: 1. Formation of Nylon66



The main features of condensation polymerization are:

1. The monomers having two or more reactive functional groups can undergo condensation polymerization.
2. There is elimination of by products.
3. Polymerization proceeds through intermolecular condensation.
4. The polymer chain build up is slow and stepwise.
5. Polymerization is catalysed by acids or alkali.
6. Linear or cross-linked polymers are produced.
7. The elemental composition of the polymer is different from that of the monomers.

IV. Based on their properties they are classified into

1. **Elastomers** egs; Natural rubber
2. **Fibres** egs: Jute, Wood, Silk etc
3. **Resins** egs: Urea- Formaldehyde, Epoxy resins, Phenol- Formaldehyde etc.
4. **Plastics** egs: Plexiglass, PVC, Teflon etc.

Mechanism of addition polymerization: Free radical mechanism:

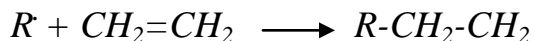
The polymerization of ethylene monomer by free radical mechanism proceeds in three distinct stages:

1. Initiation
2. Propagation
3. Termination.

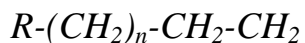
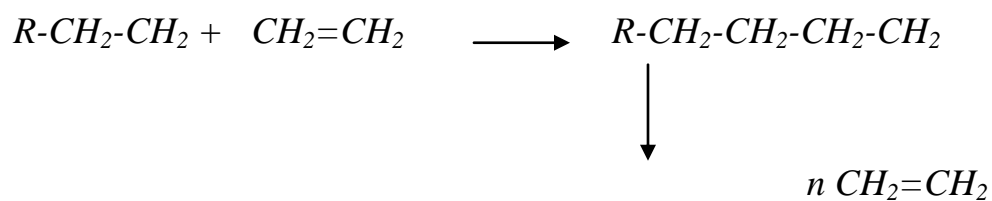
Initiation: It involves two reactions. The first is the production of free radicals usually by the homolytic dissociation of an initiator such as dibenzoyl peroxide to yield a pair of radicals. A free radical is an atomic or molecular species having an odd or unpaired electron. They are highly active species.



The second part of initiation involves the addition of this radical to the first monomer molecule to produce the chain initiating species.

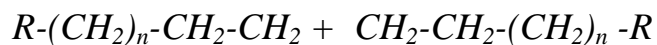


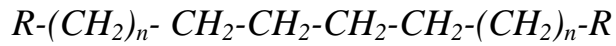
Propagation: *In the propagation, the radical attacks another monomer to produce yet another free radical and the process continues until termination occurs.*



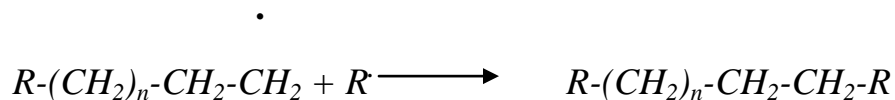
In general

Termination: *At some point, the propagating polymer chain stops growing and terminates. Termination is by 1. **Coupling or combination** i.e. a. the two growing chain may react with each other.*

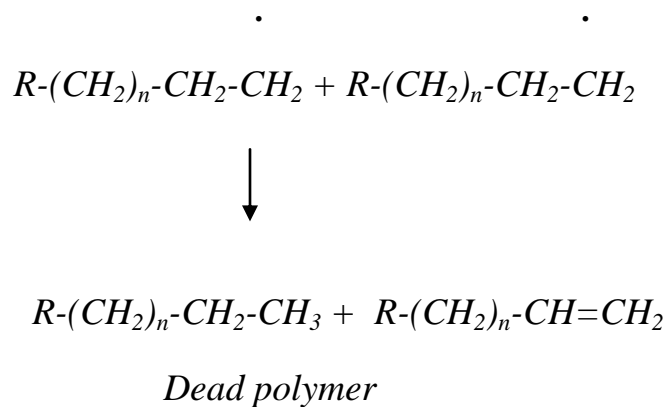




2. Coupling of growing chain with initiator free radical.



3. Or by **disproportionation** in which a hydrogen atom of one radical center is transferred to another radical center. This results in the formation of two polymer molecules one saturated and another unsaturated.



Glass transition temperature (T_g): is the temperature, below which a polymer is hard and above which it is soft and flexible is called the glass transition temperature. The hard, brittle state is known as the glassy state and soft flexible state as the rubbery state.

Parameters affecting T_g :

1. **Crystallinity:** Higher the crystallinity, higher is the T_g value of a polymer. In crystalline polymer, the linear or stereo regular chains are lined up parallel to each other and are held by strong cohesive forces. This leads to a high T_g value of the polymer.
Egs: polyethylene has low T_g compared to that of nylon6,6.
2. **Molecular weight:** The T_g of all polymers, in general, increases with molecular weight up to 20,000 and beyond which the effect is negligible.
3. **Effect of side group:** Poly [α -methyl styrene] has higher T_g value while polystyrene has lower T_g value, is due to the presence of effective methyl side group which hinders the free rotation about carbon-carbon bond of chain back bone, and restricts the chain mobility, thereby increase T_g value.
4. **Intermolecular forces:** Presence of large number of polar groups in the molecular chain lead to strong intermolecular cohesive forces which restrict the molecular mobility. This leads to an increase in T_g . Egs: polypropylene has lower T_g compared to nylon6,6 .
5. **Presence of plasticizers:** Addition of plasticizers reduces the T_g value. Egs: Diisooctyl phthalate, which is added to PVC reduces its T_g .
6. **Stereoregularity of polymers** increases T_g . Thus T_g of a isotactic polymer is greater than that of the syndiotactic polymer whose T_g is greater than atactic polymer.

Importance of T_g :

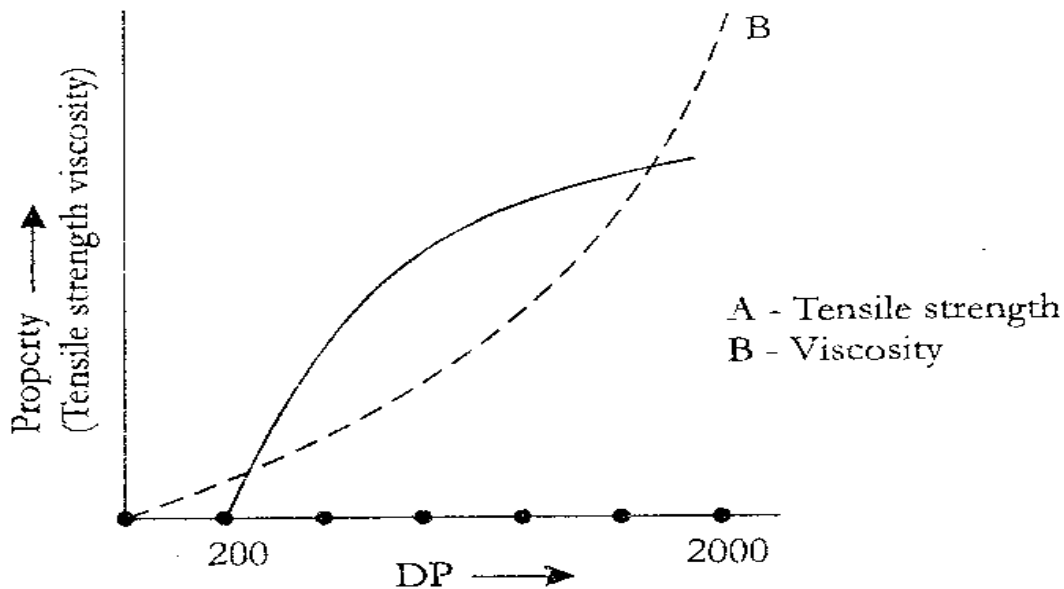
1. T_g value is a measure of flexibility of a polymer.
2. T_g gives us idea of the thermal expansion, heat capacity, electrical and mechanical properties of the polymer.
3. The use of any polymer at any temperature is decided by its T_g value.
4. Knowledge of T_g is useful in choosing appropriate temperature range for such processing operations.

Structure property relationship of polymers:

The fundamental properties, which influence the structure property relationship are molecular mass, polarity, crystallinity, molecular cohesion, the nature of the polymeric chains and stereochemistry of the molecule.

Impact and tensile strength of polymers and molecular mass: Density, melt viscosity, impact and tensile strength are a few mechanical properties of a

polymer. Tensile strength and impact strength increases with molecular mass up to a certain point and then become constant. The melt viscosity of the polymer initially shows a gradual increase with the molecular mass and steep increase at higher molecular masses. For polymer to be commercially useful it should have low melt viscosity, high tensile and impact strength.



Crystallinity: Any polymer will contain a definite percentage of crystalline part and amorphous part. The degree of crystallinity depends on how best the polymer chain can be closely packed. Crystalline regions of a polymer are formed when their individual chains are linear (without branching), contain no bulky substituents and are closely arranged parallel to each other. The chains of polymer may be held together by vander wall's force, hydrogen bonding or polar interaction. A polymer with high degree of crystallinity has high tensile strength, impact and wear resistance, high density and high fusion temperature, it has high T_g , and melt viscosity.

Crystallinity of a polymer also depends on the stereo regular arrangement. Polymers like HDPE, isotactic and syndiotactic polypropylene etc are highly crystalline. On the other hand atactic polypropylene, polystyrene, PVC which have their substituents in a random arrangement are less crystalline.

Elasticity: *Elasticity of a polymer material is mainly because of the uncoiling and recoiling of the molecular chains on the application of force. For a polymer to show elasticity the individual chains should not break on prolonged stretching. Breaking takes place when the chains slip past each other and get separated. In rubber this is avoided by molecular engineering such as 1. Introducing cross- link at suitable molecular position 2.*

Avoiding bulky side group such as aromatic and cyclic structure in the repeat unit 3. Introducing more non- polar groups in the chains so that the chains do not separate on stretching. The structure should be amorphous, this can be brought about by introducing plasticizer molecule in the polymer chain by co-polymerization or by compounding the rubber with a suitable plasticizer liquid.

Elastic deformation(rheology) of polymer: *This can be studied by applying stress on the polymer material and finding the deformation caused. Polymers, since they contain both crystalline and amorphous regions, exhibit a complex behavior. The deformation depends upon on the degree of crystallinity, degree of cross- linking and the glass transition temperature.*

Chemical resistivity: *If a polymer is attacked by a reagent it undergoes softening, swelling and loses strength. Chemical resistivity of polymers depends on number of factors like presence of polar and non- polar groups, the molar mass, degree of crystallinity, extent of cross linking.*

Polymers with non- polar groups undergo a welling and dissolution in non-polar solvents like benzene, toluene and carbon tetra chloride etc. Polar polymers containing –OH group or –COOH group are soluble in polar solvents like water,

alcohol etc. Polymer containing ester group (polyester) undergo hydrolysis with strong alkalis at high temperature. Polyamide like nylon containing –NHCO-group, NHCOO group can be hydrolysed by using strong acids or alkali.

Polyalkenes, PVC, Flourocarbon are some polymers, which have high degree of chemical resistance. For a given polymer resistivity increase with increase in molar mass. Linear polymers have lower resistivity than branched chain and cross- linked polymers.

Deficiencies of natural rubber and advantages of synthetic rubber.

<i>Natural rubber</i>	<i>Synthetic rubber</i>
<i>Attacked by sunlight and air</i>	<i>Not attacked by air and sunlight (nitrile Rubber, neoprene rubber)</i>
<i>Less resistance to heat and cold.</i>	<i>Greater resistance to heat and cold (nitrile Rubber)</i>
<i>Holds less air and water at high pressure.</i>	<i>Hold more air and water even at high pressure (egs: Butyl rubber used in inner tubes of cars)</i>
<i>Softens and swells on storing organic solvents.</i>	<i>Don't swell and can hold solvents better. (egs: polysulphide rubber)</i>

<i>Rubber property is lost at extreme Range of temperature.</i>	<i>Rubber property is retained over wide temperatures. Egs: silicone rubber -90°c to 360°c</i>
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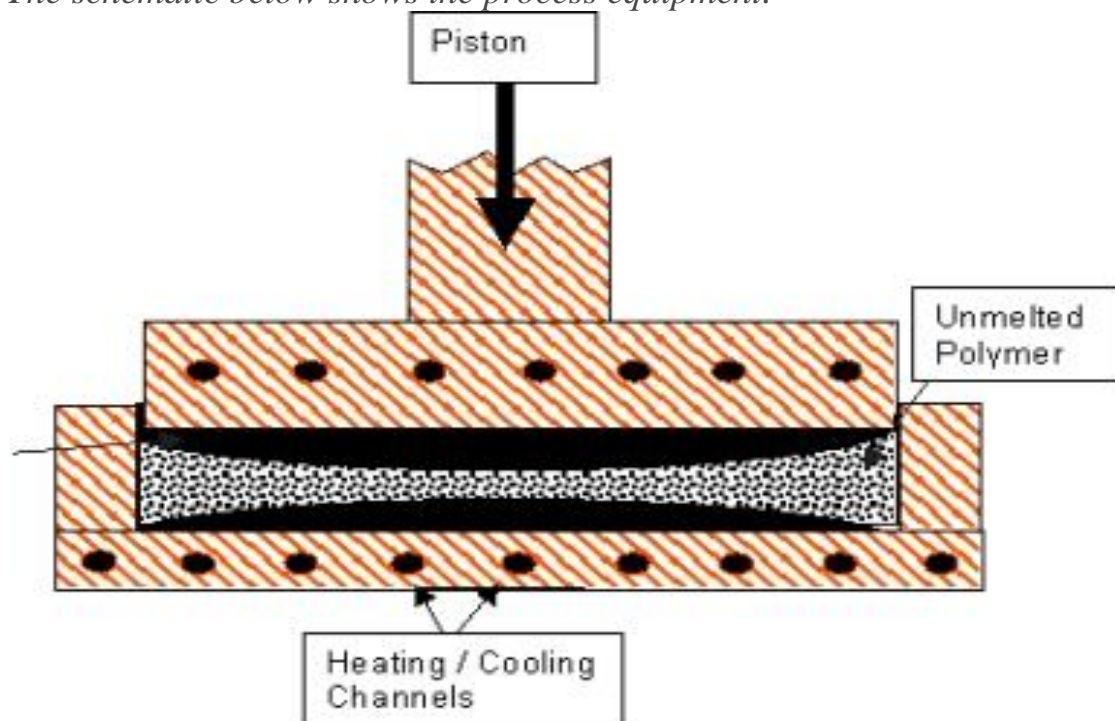
MANUFACTURE OF PLASTICS BY COMPRESSION & INJECTION MOULDING, PROTRUSION METHOD.

Compression Molding

Originally developed to manufacture composite parts for metal replacement applications, compression molding is mostly used to make larger flat or moderately curved parts such as hoods, fenders, scoops, spoilers, lift gates and the like for automotive end-uses. Although this technology is the main processing method used with thermoset resins, it can also be employed to process thermoplastic resins such as Ticona's Compel® and Celstran® long fiber reinforced thermoplastics (LFRT), and GUR® ultrahigh molecular weight polyethylene (UHMWPE).

Compression Molding

The schematic below shows the process equipment.



The material to be molded is placed in the mold cavity and the heated platens are closed by a hydraulic ram. Thermoset resins, either bulk molding compound (BMC) or sheet molding compound (SMC), are conformed to the mold shape by the applied pressure and heated until the curing reaction occurs. SMC feed material usually is cut to conform to the surface area of the mold. The mold is then cooled and the part removed.

Thermoplastic resins may be loaded into the mold either in the form of pellets or sheet, or the mold may be loaded from a plasticating extruder. Thermoplastic materials are heated above their melting points, formed and cooled. For both thermosets and thermoplastics, the better the feed material is distributed over the mold surface, the less flow orientation occurs during the compression step.

Injection molding (British English: **moulding**) is a [manufacturing](#) process for producing parts from both [thermoplastic](#) and [thermosetting plastic](#) materials. Material is fed into a heated barrel, mixed, and forced into a mold cavity where it cools and hardens to the configuration of the mold cavity. After a product is designed, usually by an [industrial designer](#) or an [engineer](#), molds are made by a [moldmaker](#) (or toolmaker) from metal, usually either [steel](#) or [aluminum](#), and precision-machined to form the features of the desired part. Injection molding is

widely used for manufacturing a variety of parts, from the smallest component to entire [body panels](#) of [cars](#).

Injection Molding

Injection Molding is a process, in which a polymer is heated to a highly plastic state and forced to flow under pressure into a mold cavity, where it solidifies. The part, called a *molding*, is then removed from the cavity:

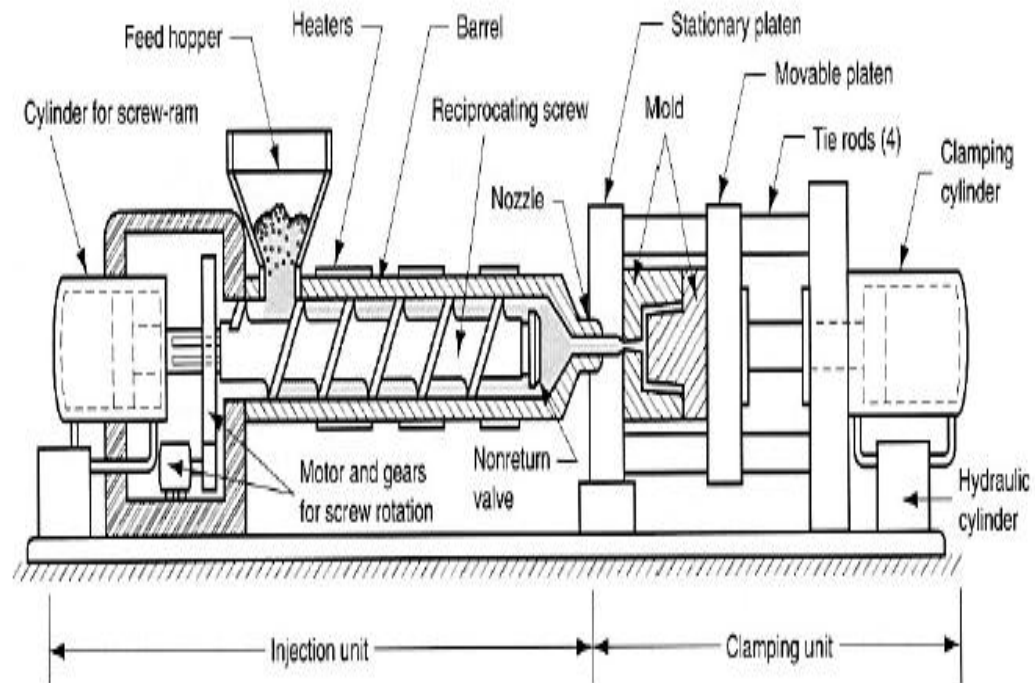
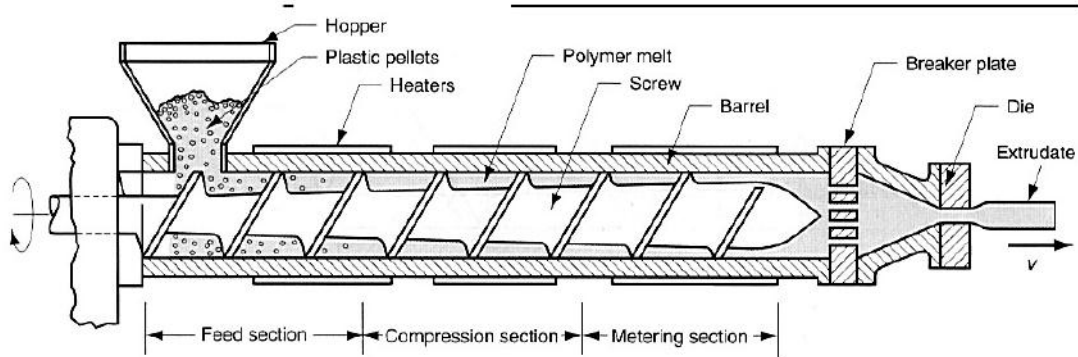


Diagram of an injection molding machine, reciprocating screw type

Manufacturing processes for polymers

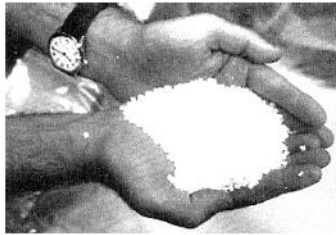
Extrusion

In polymer extrusion, the feedstock is fed into an extrusion barrel where it is heated, melted, and forced to flow through a die opening by means of rotating screw:

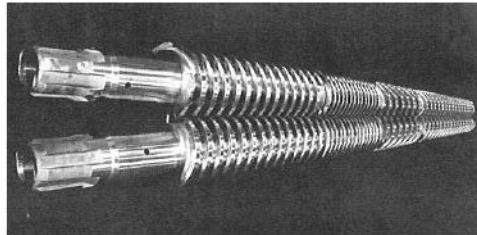


Components and features of a single-screw extruder for thermoplastics and elastomers

The raw materials not only in extrusion but also in most polymer processes are plastic pellets:



Plastic pellets are the raw material in many shaping processes for polymers



Twin extruder screws

In *twin-screw extruders* both screws are parallel and side-by-side inside the barrel. These extruders are suitable for extrusion of difficult-to-extrude polymers, and for materials that require greater mixing.

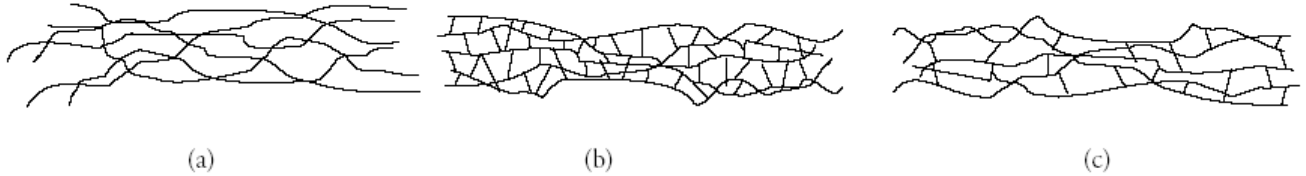
Elastomers (rubbers)

Exhibit extreme elastic extensibility under low mechanical stresses.

The most important rubbers are:

- | | | |
|---|----------------------------------|--|
| ❖ | Natural rubber (<i>Latex</i>): | tires, shoes, seals |
| ❖ | Silicones: | seals, thermal insulation, electronics |
| ❖ | Polyurethane: | seals, gaskets |

The difference in properties of the polymers are attributable to so-called cross-linking, which occurs in thermosets and partially in elastomers:



Models of long polymer molecules with (a) no cross-linking in thermoplastics, (b) intensive cross-linking in thermosets, and (c) low degree of cross-linking in elastomers

Elastomers: Rubber are high polymers which undergo elastic changes when subjected to an external force but readily regain their original position when external force is removed. Rubbers are therefore referred to as elastomers. A rubber band can be stretched to 4 to 10 times to its original length. Elastomers can be obtained from two processes, which may be natural or synthetic.

ADHESIVES: They are mainly used to join a variety of substances such as metals, glasses, plastics, paper etc.

An adhesive is defined as a polymeric substance used to bind together two or more similar or dissimilar materials by surface attachment.

Adhesives join the surfaces in three distinct ways, they may keep the surfaces together by valence or intermolecular forces of attraction. They may fill the voids of porous or rough surfaces and hold the surfaces by interlocking action. The surfaces may partially dissolve in the adhesive.

The effectiveness and strength of an adhesive depends on various factors 1. The materials bonded.2. The solvent used and the effect of external conditions such as heat, light and environment. 3. It should not soften when used for binding plastics.

Adhesives are applied to surfaces by brushing, rolling, dusting or by trowel. Care must be taken to maintain a uniform thickness of the film. Adhesion is achieved by pressing together the materials to be bonded. To ensure good cohesion of adhesives the surfaces of materials to be joined must be cleaned before the adhesive is applied with paper and wood. Layers of grease, oil and lubricants are removed by means of suitable solvents. Loose dirt and oxide layers can be removed by brushing. The time required for an adhesive bonded joint to develop full strength varies from few second to few hours.

Types of adhesives: *There are two types of adhesives*

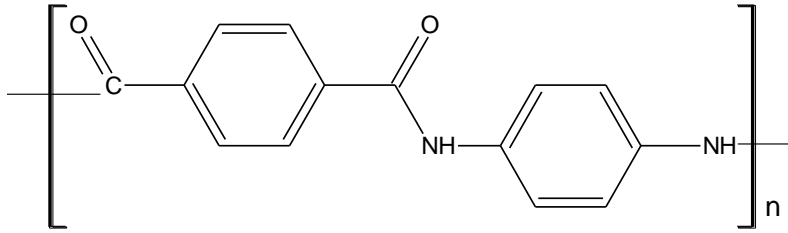
1. Natural adhesives :

Egs, gum, glue, starch etc.

2. Synthetic adhesives: *are low molecular weight polymers called resins.*

egs, epoxy resins, phenol-formaldehyde, urea-formaldehyde etc. These resins have high strength, resistance to water and corrosion and are unaffected by weather.

- 1. They are much stronger and durable than conventional metals like steel and aluminum.*
- 2. They have high fatigue strength.*
- 3. They have good corrosion resistance.*
- 4. They are most suitable for aerospace applications due to their lightweight.*



It has higher tensile strength and modulus than fiberglass. Kevlar fibers are used for structures requiring good stiffness, high abrasion resistance and lightweight.

Polymer composites:

Two or more distinct components, which combine to form a new class of material suitable for structural applications are referred to as composite materials. A composite containing polymer matrix is known as polymer composite.

The properties of the composite system are not attainable by the individual components acting alone.

Properties of polymer composites:

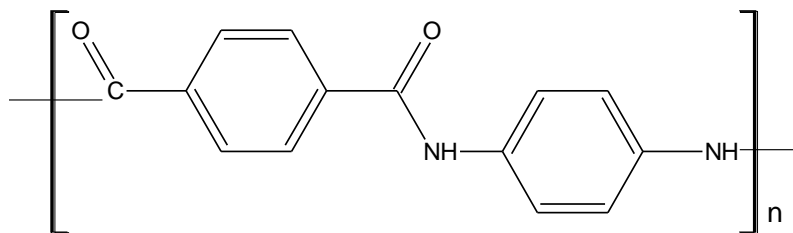
- 5. They are light in weight.*
- 6. They have high strength to weight ratio.*
- 7. They are much stronger and durable than conventional metals like steel and aluminium.*
- 8. They have high fatigue strength.*
- 9. They have good corrosion resistance.*
- 10. They are most suitable for aerospace applications due to their lightweight.*

Applications of polymer composites:

1. *In aerospace: wings, fuselage, antennae, helicopter blades, landing gears, seats, floors rocket motor cases.*
2. *In automobiles: body panels, bumpers, shafts, gears, bearings, automobile brakes, clutches.*
3. *In boats: hulls, decks, masts, engine shrouds.*
4. *Interior and exterior panels, chairs, tables etc.*
5. *Protective helmets, archery bows, surfboards, fishing rods, diving boards.*
6. *Pipes, tanks, pressure vessels, hoppers, valves, pumps etc.*

Kevlar: *Kevlar belongs to a family of aramids. It is a aromatic polyamide with the name poly [para-phenylene terephthamide]*

The linkage through Para positions of the phenyl rings gives Kevlar a strong ability to stretch and hence its extra strength.

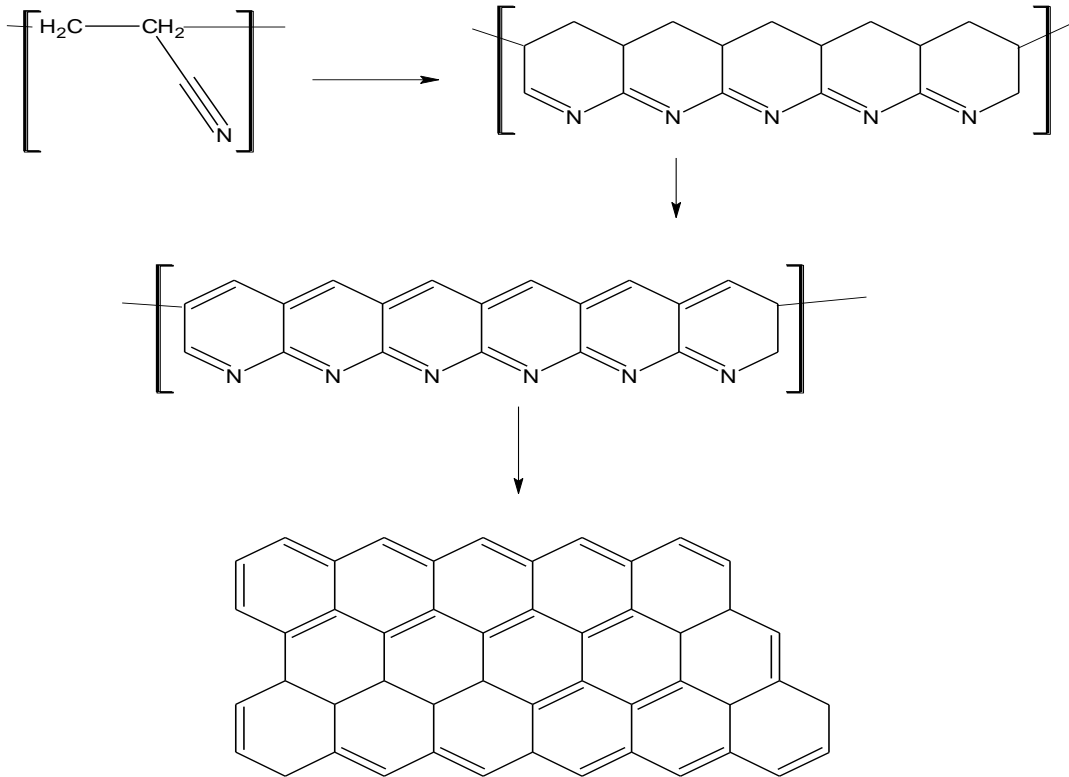


It has higher tensile strength and modulus than fiberglass. Kevlar fibers are used for structures requiring good stiffness, high abrasion resistance and lightweight.

Used in lightweight boat hulls, aircraft fuselage panels, pressure vessels, high performance racecars, bulletproof vests and puncture resistant bicycle tyres.

Carbon fiber: Carbon fiber is a polymer, which is a form of graphite with carbon ring structure.

Preparation of carbon fibre: is made by heating polyacrylonitrile. The polymer cyclises through the cyanogroups to form a polycyclic chain. The resulting solid is heated gradually. Then it is slowly roasted at 400-600°C when the adjacent chains join together losing more hydrogen gas. Then the temperature is gradually raised to 2000°C to get wider ribbon like mass.



Carbon fiber reinforced composites are very strong and are often stronger than steel but lighter. They are used for making parts of aero planes and the space shuttle, tennis rackets and golf clubs, weaving machines, missiles, agricultural etc.

Compounding of resins to plastics

Conversion of resin into plastic is called compounding of resin. The purpose of compounding is to improve the property of resin. This is done by mixing the resin with ingredients which among include filler, plasticizer and dye.

Resin: The basic component of plastic is resin. The resin gives the desired properties like plasticity and electrical insulating properties to the plastic.

Examples of resins are polyethylene, polystyrene and PVC.

Filler: Fillers are cheap substances which are long, thin and thread like polymer chains do not undergo stretching or deformation like elastomers.

Ex. Wood, Silk, Cotton, Jute etc.,

Hardener: Hardeners enable the conversion of resin into solid state by forming a polymer having three dimensional structures.

Accelerator: Accelerators are used in the case of thermosetting plastics with the object of accelerating the polymerization of fusible resin into the cross linked infusible. They increase the necessary rate of solidification at a lower temperature.

Ex. Hydrogen peroxide, Benzoyl peroxide and acetyl sulphuric acid.

Stabilizer: Stabilizers enable the plastic to retain its properties for a long time and improve their thermal stability

Ex. White lead, lead chromate, Lead silicate etc.

Lubricant: Lubricants make moulding easier and impart glassy finish to the product.

Ex. Wax, soap and oils.

Dye and pigment: They are added to impart desired colour to plastics

Vulcanization:

Because of many deficiencies of natural rubber, pure rubber has practically no applications. However, the utility value of natural rubber could be immensely improved if vulcanized.

Rubber vulcanization is a process of heating the raw rubber mixed with sulfur and other agents at 120-150⁰c for 1-4 hours. It is believed that sulfur cross links (bridges) are introduced between polymer molecules of rubber, which involve residual double bonds of polymer chains.

The degree of vulcanization introduced in vulcanized rubber depends on the amount of sulfur used. Tyre industry uses 3-5% sulfur. If the amount of sulfur is increased to 30%, a hard and rigid rubber called 'Ebonite' is produced.

CONDUCTING POLYMERS.

Polymers are generally considered as insulators. Most common applications of polymers in industry are based on this characteristic.

However since 1970's many polymeric materials have been made and found to have high conductivity, sometimes almost equivalent to that of a metal like copper. This has led to the new concept- "Synthetic metals".

Polyacetylene.