

UNIT 3 POLYMERS

3.1 Introduction

Polymer – Definition:

Polymers are the substances consisting of giant or macromolecules made by linking a large number of smaller molecules (monomers).

Polymer is a molecule formed by joining of thousands of smaller molecular units together by chemical bonds.

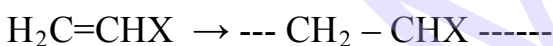
A chemical process that leads to the formation of polymer is known as polymerization.

Degree of polymerization: The number of repeat units (or) monomeric units available in the polymer is known as degree of polymerization.

Functionality:

Definition: The number of bonding sites (or) reactive sites or functional groups present in the molecule.

Ex: The double bond in vinyl monomers ($\text{CH}_2 = \text{CHX}$) can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.



1. When the functionality of monomer is two bifunctional linear (or) straight chain polymer is formed.

Ex: (a)vinyl monomers (b)adipic acid (c)hexamethylene diamine (d)terephthalic acid(e)ethylene glycol (f)amino acid

Example for polymer: HDPE (high density polythene)

2. When the functionality of monomer is three (tri-functional), three-dimensional net work polymer is formed.

Ex: phenol, glycerol

Examples for polymers : Urea formaldehyde, phenol formaldehyde.

Examples for bifunctional monomers:

i)Vinyl monomers ($\text{HC}_2 = \text{P-CH}$) [where P = pendant group]

a)ethylene b)propylene c)vinyl chloride d)vinyl cyanide e)vinyl acetate

f)styrene g)acrylic acid h)methyl methacrylate

ii)Dicarboxylic acids having general formula ($\text{HOOC} - \text{R} - \text{COOH}$)

a)succinic acid b)adipic acid c)terephthalic acid

iii)Amino acids with the general formula $\text{H}_2\text{N} - \text{R} - \text{CH} - \text{COOH}$

a)glycine b)alanine c)valine d) ϵ - amino caproic acid

iv)Diols with the general formula $\text{HO} - \text{H}_2\text{C} - \text{R} - \text{CH}_2 - \text{OH}$

a)ethylene glycol

v)Diamines with the general formula $\text{H}_2\text{N} - \text{CH}_2 - \text{R} - \text{CH}_2 - \text{NH}_2$

a)hexamethylene diamine

when a trifunctional monomer is mixed in small amounts with a bifunctional monomer, a branched chain polymer is formed.

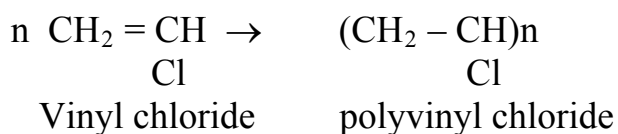
Ex: LDPE (LOW density polyethene)

Polymerisation:

Definition: “ The process in which the simpler molecules combine together to form very large molecule having high molecular weight is known as polymerization”. The molecule is known as polymer.

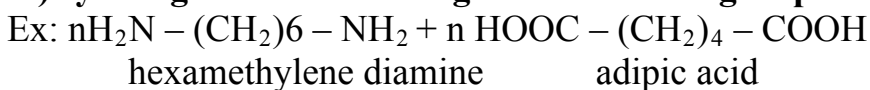
The different ways of doing polymerization are –

i)By opening a double bond



ii)By opening a ring

iii)By using molecules having two functional groups



3.2 Types of polymerization:

Polymers can be synthesized by the following polymerization processes.

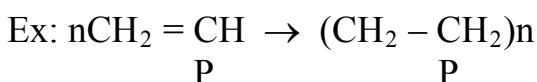
- I. Addition polymerization (or) chain polymerization
- II. Condensation or, step or, step growth polymerization
- III. Copolymerisation

I) Addition polymerization:

The addition polymerization is the process in which the linking together of monomer molecules by a chain reaction is observed.

Polymer synthesized by addition polymerization has the same empirical formula as that of monomer.

No molecule is evolved during polymerisation and the polymer is an exact multiple of the original monomeric molecule.



Where P = pendant group

P	-H	-CH ₃	-Cl	-C ₆ H ₅
Polymer	Polythene	Polypropene	Polyvinyl chloride	Polystyrene

* Addition polymerization is usually induced by light, heat or, a catalyst for opening the double bond of the monomer and creating the reactive sites.

II) Condensation polymerization:

An intermolecular reaction involving two different bifunctional reactants with affinity for each other and taking place through repeated condensation reaction is known as condensation polymerization.

* Monomers having – COOH and – OH or, –COOH and –NH₂ undergo condensation polymerization.

The reaction always accompanies the elimination of H₂O, HCl, CH₃OH, NH₃ molecules.

Examples:

1)Nylon 6.6 : [polymerization involving adipic acid and hexamethylene diamine]

2) Terelene: (polyethylene terephthalate)

[polymerization involving ethylene glycol and terephthalic acid]

3) Polyurethane: Polymerisation involving a diol

Ex: bisphenol A and a diisocyanate (ex: toluene diisocyanate) to give polyurethane.

Condensation polymerization involving trifunctional reactants give rise to a cross – linked three-dimensional polymer.

Differences between addition and condensation polymerization:

Addition polymerization	Condensation polymerisation
1) It requires the presence of a double bond in the monomer	1) It requires two reactive functional groups to be present at both ends of the monomer. There should be at least two different bi-or, poly- functional monomers having functional groups with affinity for each other.
2. In this reaction, no by product is formed	2) generally a by product is formed in this reaction.
3. Homo-chain polymer is obtained. (generally thermoplastic)	3) Hetero-chain polymer is obtained (either thermoplastic or, thermostat)
4. The growth of chain is at one active centre.	4) The growth of chain occurs at minimum of two active centres.
5.Examples: a) polymerisation of ethylene to form polythene(PE) $n \text{ CH}_2 = \text{CH}_2 \rightarrow (\text{CH}_2 - \text{CH}_2)_n$ <div style="display: flex; justify-content: space-around; width: 100%;"> ethylene polythene </div>	5) Examples: a) condensation polymerisation of hexamethylene diamine and adipic acid to form Nylon 6.6 $n \text{ H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2 + \text{hexamethylene diamine}$ $n \text{ HOOC} - (\text{CH}_2)_4 - \text{COOH} \text{ adipic acid}$
b) polymerisation of vinyl chloride to form poly-vinyl chloride (PVC) $n \text{ CH}_2 = \text{CH} \rightarrow (\text{CH}_2 - \text{CH})_n$ <div style="display: flex; justify-content: space-around; width: 100%;"> Cl vinyl chloride Cl polyvinyl chloride </div>	b) condensation polymerisation of terephthalic acid and ethylene glycol to give polyethylene terephthalate (terelene)

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<p>c) polymerisation of styrene to form polystyrene. $n \text{CH}_2 = \text{CH} \rightarrow (\text{CH}_2 - \text{CH})_n$</p> <p style="text-align: center;">styrene polystyrene</p> <p>d) polymerisation of acrylonitrile (vinyl cyanide) to form polyacrylonitrile (orlon). $n \text{CH}_2 = \text{CH} \rightarrow (\text{CH}_2 - \text{CH})_n$</p> <p style="text-align: center;"> CN CN Vinyl cyanide polyacrylonitrile (acrylonitrile) (orlon) </p> <p>e) polymerisation of methyl methacrylate to form polymethyl methacrylate (plexiglas, Lucite) methyl methacrylate polymethyl methacrylate (Plexiglas, Lucite)</p>	<p>c) condensation polymerisation of toluene diisocyanate and diol to form polyurethane</p> <p>d) Nylon -6: $\text{NH}_2 - (\text{CH}_2)_5 - \text{COOH} \rightarrow \epsilon$ - amino caproic acid $(\text{NH} - (\text{CH}_2)_5 - \text{C})_n$ Nylon - 6</p> <p>e) condensation polymerisation of hexamethylene diamine and sebaic acid to form nylon - 6, 10. $\text{NH}_2 - (\text{CH}_2)_6 - \text{NH}_2 + \text{hexamethylene diamine}$ $\text{HOOC} - (\text{CH}_2)_8 - \text{COOH} \rightarrow$ Sebaic acid $(\text{N} - (\text{CH}_2)_6 - \text{N} - \text{C} - (\text{CH}_2)_8 - \text{C})_n$ Nylon - 6, 10</p> <p>f) Nylon - 11: $\text{NH}_2 - (\text{CH}_2)_{10} - \text{COOH} \rightarrow$ amino decanoic acid $(\text{N} - (\text{CH}_2)_{10} - \text{C})_n$ Nylon - 11</p>
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III) Copolymerisation:

Addition polymerisation involving a mixture of two (or) more suitable or compatible monomers gives a copolymer and the process is known as copolymerization.

(OR)

A reaction in which a mixture of two (or) more monomers is allowed to undergo polymerisation is known as copolymerization. The polymer is known as copolymer.

Examples:

1) Copolymerisation of styrene and methyl methacrylate

2) Copolymerisation of acrylonitrile and vinyl chloride

3) Copolymerisation of styrene and 1,3-butadiene.

$m\text{CH}_2 = \text{CH} + n\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ copolymerisation

Depending on the linkage, the following four types of monomers are possible.

S.No.	Copolymer	Structure	Description
1)	Alternate	$-\text{M}_1-\text{M}_2-\text{M}_1-\text{M}_2-\text{M}_1-\text{M}_2-$	Monomers are arranged in regular alternate fashion
2	Block	$-\text{M}_1-\text{M}_1-\text{M}_1-\text{M}_2-\text{M}_2-\text{M}_2-$	A block of repeating unit of one kind of monomer is followed by block of another kind of monomer
3	Random	$-\text{M}_1-\text{M}_2-\text{M}_2-\text{M}_1-\text{M}_2-\text{M}_1-$	Monomers randomly distributed along the polymer chain
4	Graft	$-\text{M}_1-\text{M}_1-\text{M}_1-\text{M}_1-\text{M}_1-$	Have branched structures in which the monomer segments on the back bone and branches differ

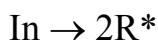
3.3 Chain growth mechanism : [Free radical mechanism]

The mechanism involves three steps.

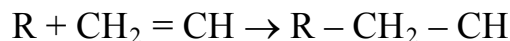
I. Chain initiation II. Chain propagation III Chain termination

I. Chain Initiation: This involves two steps.

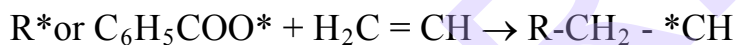
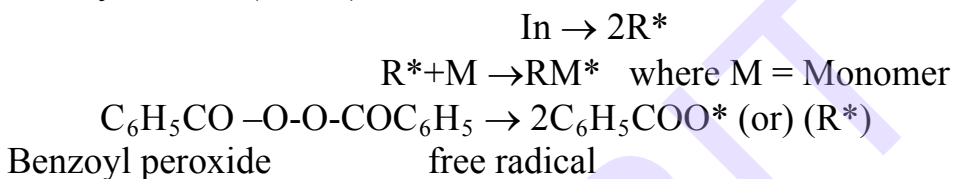
i) Decomposition of the initiator to form free radicals



ii) Addition of the first vinyl monomer molecule to the free radical to form intermediate (I)



I) chain initiation : Initiator added to the monomer undergoes dissociation to form free radicals. Initiators commonly used are acetyl peroxide ($\text{CH}_3\text{CO} - \text{O} - \text{O} - \text{COCH}_3$), benzoyl peroxide ($\text{C}_6\text{H}_5\text{COO} - \text{O} - \text{COC}_6\text{H}_5$) and azobis – isobutyronitrile (AIBN).



II) Chain propagation: The intermediate (free radical) immediately reacts with a monomer molecule to form the reactive species which is responsible for the growth of the polymer chain.

III) Chain termination: Termination reaction may occur due to a coupling reaction or a disproportionation reaction.

- In coupling or combination reaction two reactive or, free radical polymer chains combine together to form a dead polymer.
- The disproportion reaction involves the transfer of a hydrogen atom from one of the free radical polymer chain to another free radical giving rise to one saturated and one unsaturated polymer molecules. Disproportionation also terminates the propagation or growth of the polymer chain resulting in a dead polymer
- The chain can be terminated by reaction with the solvent molecules like carbon tetrachloride.
- Chain can be terminated by the reaction of growing polymer chain with inhibitors like hydroquinone and trinitrobenzene.

3.4 Step – Growth polymerisation:

It proceeds by step – wise fashion

Monomer \rightarrow Dimer \rightarrow Trimer $\rightarrow \rightarrow$ oligomer \rightarrow n times polymer.

Monomer in step – growth polymerisation is capable of combining with itself or with any other species present with equal reactivity, hence it disappears early in the reaction.

The degree of polymerisation and hence the molecular weight of the polymer rises steadily throughout the reaction. The reactivity is governed by the functional groups.

It can be either addition or, condensation polymerisation.

Ex -1: As a diamide, urea is capable of forming polymers. It reacts with formaldehyde to form urea-formaldehyde resins. A space-network polymer is formed.

Condensation (Step-growth) Polymerisation:

Ex-1: Phenols and formaldehyde react to form phenol-formaldehyde resins (Bakelite and related polymers)

When phenol is treated with formaldehyde in the presence of acid or alkali, a high-molecular weight substance is obtained in which many phenol rings are held together by $-\text{CH}_2-$ groups

The stages involved in the formation of the polymer are –

a) phenol reacts with formaldehyde to form O – or P – hydroxyl methyl phenol.

b) Hydroxy methyl phenol reacts with another molecule of phenol to form a compound in which two rings are joined by a $-\text{CH}_2-$ link. During this reaction one water molecule is eliminated.

c) This process continues to yield a product of high molecular weight.

The final product contains many cross-links and hence has a rigid three-dimensional structure because three positions in each phenol molecule are susceptible to attack. Thus it is a space-network polymer.

Ex-2: A diol reacts with a dicarboxylic acid to form an ester. But each moiety of the simple ester still contains a group that can be react to generate another ester linkage and hence a large molecule, which itself can react further and so on.

If each monomer molecule contains just two functional groups, growth can occur in only two directions. A linear polymer is obtained.

Ex: Dacron

If the reaction occurs at more than two positions in a monomer, highly cross –linked space network polymer is obtained.

Ex: Glyptal

Carboxylic acids react with amines to yield amides, and with alcohols to form esters.

When an acid containing more than one-COOH group reacts with an amine that contains more than one –NH₂ group to form polyamides.

Ex: Nylon – 6, 6.

When an acid containing more than one-COOH group reacts with an alcohol that contains more than one – OH group to form polyesters.

Ex: Dacron, Glyptal

3.4 Plastics:

Plastics are the high polymers that can be molded by the application of heat and pressure. During molding process, there is no chemical change. The plastics have linear structure.

Examples: Polythene, polyvinyl chloride, polystyrene, nylons, polyesters.

Thermoplastics:

Thermo plastics are the polymers that become soft on heating and hard on cooling and the process can be repeated for a number of times. They undergo reversible changes on heating.

Examples: Polythene (PE), polypropylene (PP), polyvinyl- chloride (PVC), polytetrafluoroethylene (PTFE or Teflon), polystyrene (PS), plexiglass, nylons, polyesters, PMMA, PVA, HIDS.

(Polymethyl methacrylate)

Thermoplastics –

- are formed by addition polymerisation
- consists of linear polymer chains with negligible cross-linking
- are soft and less brittle.
- are soluble in organic solvents.
- soften on heating and hence are amenable for moulding into any shape in the hot condition on cooling, the resin becomes hard and rigid and retains the moulded shape.
- can be reheated and moulded into any other shape reversibly any number of times without any change in the chemical nature.

Thermosetting polymers or, Thermosets:

Thermosets are the polymers that undergo chemical changes and cross-linking on heating and become permanently hard, rigid and infusible. They will not soften on heating, Once they are set.

Examples: Phenol-formaldehyde resin, urea-formaldehyde resin, epoxy resins (araldite), melamine, bakelite

Thermosets (Thermosetting resins):

- are mostly formed by condensation polymerisation.
- are mostly branched polymer chains with potential to form a 3-dimensional structure.
- become hard and rigid on heating during moulding process.
- are not soluble in common organic solvents.
- exhibit their characteristic properties of non-softening and non-swelling nature, hardness and brittleness.
- cannot be softened, reformed, reshaped once they are set.
- cannot be reclaimed from wastes.

Differences between thermoplastics and thermosettings:

Thermoplastics	Thermosettings
1. Formed either by addition or by condensation polymerisation reactions	1. Formed by condensation polymerisation reactions.
2. They have either linear or branched	2. They have 3-dimensional, cross-linked network structure.

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structures.	
3.Adjascent polymer chains are held together by either vanderwaals forces, or by dipole-dipole forces or by hydrogen bonds.	3.Adjascent polymer chains are held together by strong covalent bonds called crossed-links.
4.They soften on heating and stiffen on cooling	4.They do not soften on heating.
5.Low molecular weight thermoplastics are soluble in their suitable solvents.	5.They are insoluble in any solvent.
6.They can be remoulded, re-shaped and re-used.	6.They cannot be remoulded and hence cannot be used.
7.They can be reclaimed from waste i.e., they can be recycled.	7.They cannot be reclaimed from waste. They cannot be recycled.
8.There is no change in chemical composition and structure during moulding process.	8.They undergo chemical changes such as further polymerisation and cross-linking during moulding process.
9.They undergo reversible changes, on the application of heat.	9.They undergo irreversible changes on the application of heat.
10.They are soft and flexible.	10.They are hard, rigid and infusible.
11.They swell or dissolve in organic solvents.	11.They neither dissolve nor swell in organic solvents.
12.They are tough materials	12.They are brittle materials.
13.The moulded articles are to be cooled to room temperature before taking out from the moulds to avoid deformation.	13.The moulded articles can be taken out of the moulds even when they are still hot without any deformations.
14.Curing can be done by cooling.	14.Curing can be done by applying heat and pressure.
	15.Examples: Phenol-formalde-hyde resin (PF), urea-formaldehyde resin (UF), Melamine – formaldehyde

15.Examples: Polyethylene(PE), Polypropylene(PP), Poly Vinyl Chloride(PVC), Polystyrene(PS), POLytetrafluoroethylene (PTFE or Teflon), Polymethyl methacrylate (PMMA – Lucite or plexiglass) nylons, Polyesters.	resin (MF), epoxy resins, XLPE, bakelite.
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3.5 Compounding of plastics:

Definition: “The process of mechanical mixing of various additives with polymers (without chemical reaction) to impart some special properties to the end product is known as compounding of plastics”.

The additives get incorporated into the polymer to give a homogeneous mixture.

The functions of additives are

- To modify the properties of the polymer
- To introduce new properties into the fabricated articles.
- To assist polymer processing
- To make the polymer products more pleasing and colourful.
- They should be cheap and sufficient in their functions.
- They should be stable under processing and service conditions.
- They should not impart taste or odour.
- They should be non-toxic for food grade application of final compound after processing.
- They should not adversely affect the properties of polymer.

The principal additives used in compounding are

- a) Fillers b) Plasticizers c) Lubricants d) Flame retarders
- e) Colourants
- f) Stabilisers g) Activators, accelerators and cross-linking agents
- h) Nucleating agents i) Blowing agents.

3.6 Fabrication of plastics:

A variety of methods are used for fabricating plastic articles and products depending upon the nature of the resin used and the end use of the finished product. The methods are

- 1) Casting 2) Moulding 3) Extrusion 4) Blowing 5) Vacuum forming
- 6) Lamination 7) Surface coating

1)Casting: Casting is the simplest technique used for fabricating products of both thermoplastic and thermosetting resins. The molten compound mixture is poured into lead moulds and cured at about 70°C for several hours at atmospheric pressure to give finished products free from internal stress and amenable for polishing.

Ex: The curing time for phenolic resins is about 50 hours.

2)Moulding: Moulding is the most widely used method for fabricating plastic products. The different moulding methods used are –

- a) Injection moulding b) compression moulding c) cold moulding
- d) Transfer moulding

a)Injection moulding:

The method is mainly used for thermoplastic resins. The compounded mixture in the form of a powder/granules is fed into the heated cylinder (temperature range is 90-260°C) of the injection moulding machine. The softened plastic mass in the cylinder is injected at a controlled rate by a screw or, piston, plunger under high pressure into a cold mould. Curing of the softened plastic into rigid product occurs during cooling in the mould. The mould is opened after sufficient curing to remove the finished product.

b)Compression moulding:

The method is useful for fabricating thermoplastic and thermosetting resins. The required amount of a compounded mixture is placed in the mould and the mould is closed carefully. Then the mould is subjected simultaneously to high temperatures (in the range 100-200°C) as well as high pressures (100-500kg/cm²). Thermosetting resins undergo curing during heating while thermoplastic resins undergo curing during cooling of the mould.

c)Cold moulding:

In this method, the object is formed in the mould by the application of high pressure in the cold. Then it is taken out of the mould, heated (cured) to remove excess solvent and to promote further condensation and hardening.

d)Transfer moulding:

The method is a modification of injection moulding suitable for use with thermo setting plastics. The moulding composition is first plasticized by applying minimum heat and pressure in a chamber outside of the mould and

then it is injected into the mould where curing takes place under the influence of heat and pressure. The method is used for more complicated shapes and permits the use of delicate inserts.

3)Extrusion:

The method is also known as extrusion moulding. The method is used for fabricating thermoplastics having uniform cross-section such as sheets, rods, tubes, insulated electric cables etc., The compounded mixture is heated to a plastic condition and forced through a die of the required shape by a screw conveyor. The extruded product is cooled as it emerges out of the die on a conveyor by blowing air or spraying water.

4)Blowing:

In this method, the softened thermoplastic resin is blown by air or steam into a closed mould, just like industrial glass-blowing. The method is used for making bottles, toys etc.

5)Vacuum forming:

The method is useful for making boxes and complicated shapes from thermoplastic resins, it has 2 steps.

a)The thermoplastic material is made into a sheet by a process known as calendaring by passing the compound mixture between heated rollers and again between cooled rollers.

b)The sheet is held firmly in a frame and heated to soften it. The softened material is drawn into the mould by a vacuum pump and cured to form the finished product.

6)Lamination:

Lamination of sheets of cloth, paper or wood is carried out by impregnating then with a solution of the resin, piled one over the other to get a desired thickness and subjected to heat as well as pressure by pressing between polished sheets of steel to expel the solvent and heat to cure the resin. Usually thermosetting resins are used for lamination. The finished product has a high tensile and impact strength.

7)Surface coating:

Surface coating of a finished product made of metal and alloys or other materials by polymeric resins is adopted for protective or decorative purposes.

Ex: 1) Polyethylene is used to coat refrigerator parts, soap boxes and steering wheels.

2) Polytetrafluoroethylene (PTFE) or, Teflon, is coated on the surface of kitchen utensils for providing a non-sticky surface.

Surface coatings are carried out by coating the polymer powder on the hot degreased and cleaned surface of the article.

3.8. preparation, properties, engineering applications of polyethene and PVC:

1) Polyethylene:

Polyethylene is the simplest homo polymer and a thermoplastic. The structure of polyethylene is $(CH_2 - CH_2)_n$

There are two commercial grades of polyethylene. They are

- i) Low density polyethylene (LDPE)
- ii) High density polyethylene (HDPE)

i) Low density polyethylene (LDPE):

Preparation:

LDPE is prepared by polymerisation of ethylene under high pressure (1500 – 50,000 Psi) and high temperature (350°C) using a trace of oxygen or any peroxide such as benzoyl peroxide as initiator.

Properties:

- LDPE has a linear structure with extensive branching
- It has a low degree of crystallinity (40%)
- It has a low density (0.912 – 0.935)
- It has a low melting point (110°C)
- It has lower tensile strength, stiffness and hardness
- Its chemical resistance is also poor

ii) High Density polyethylene (HDPE):

Preparation:

HDPE is prepared by coordination polymerisation of ethylene using Ziegler natta catalyst $[TiCl_4 + Al(C_2H_5)_3]$ in hydrocarbon solvent

Properties:

- HDPE is a linear polymer with no branching.

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- It has relatively high degree of crystallinity (90%)
- It has high density (0.96)
- It has high melting point (140°C)
- It has high tensile strength, stiffness and hardness.
- It is not attacked by chemicals.

Distinguishing properties of LDPE and HDPE

LDPE	HDPE
1) Produced by chain polymerisation using oxygen (or) peroxides like benzoyl peroxide.	1) Produced by coordination polymerisation using Ziegler-Natta Catalyst $[\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3]$
2) Linear polymer with extensive branching.	2) Linear polymer with practically no branching.
3) Relatively lower degree of crystallinity (40%).	3) Relatively higher degree of crystallinity (90%)
4) Lower density (0.912 – 0.935)	4) Higher density (0.96)
5) Lower melting point (110°C)	5) Higher melting point (140°C)
6) Lower tensile strength, stiffness, hardness	6) Higher tensile strength, stiffness and hardness.
7) Chemical resistance is low	7) Chemical resistance is high
8) It is a white, waxy, translucent material.	
9) It does not dissolve in any solvent at room temperature.	

Applications:

- 1) Films and sheets: A large amount of polyethylene produced is used as packing materials for food and textile.
- 2) Molded articles: It is used for the manufacture of molded articles such as bottles, cans, buckets, toys, tubs, pipes, squeeze bottles etc.,
- 3) Insulating material: It is used for wire and cable coating because of its excellent electrical insulation properties.

II) Poly vinyl chloride (PVC):

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Polyvinyl chloride is obtained by heating a water emulsion of the vinyl chloride in an autoclave under pressure in the presence of benzoyl peroxide or hydrogen peroxide.

Properties:

- 1) PVC is a colourless and odourless powder.
- 2) It is chemically inert and non-inflammable and exhibits high resistance to light, atmospheric oxygen, acids and alkalis.
- 3) It is soluble in chlorinated hydrocarbons, tetrahydrofuran (THF) and cyclohexanone.
- 4) Pure resin possesses a high softening point (148°C) and a greater stiffness and rigidity compared to polyethylene, but is brittle.
- 5) It is the most widely used synthetic plastic.

Applications:

1) Rigid PVC unplasticized PVC have superior chemical resistance and high rigidity but is brittle. It is used for making sheets, that are employed for tank – linings, light-fittings, safety, helmets, refrigerator components, tyres, cycle and motor cycle mudguards. It is also extruded in strip and tube form for use in the place of non-ferrous metals.

2) Plasticized PVC is used for making continuous sheets of different thicknesses from 0.1mm to 8mm. It is employed for packing rain coats, table-clothes and curtains, electrical insulation like coverings of electric cables, injection moulding of articles like toys, tool-handles, toiled-goods, radio-components, plastic-coated cloth, chemical containers, thermal insulating foam, conveyor belts etc.,

Plasticized PVC is obtained by adding plasticizers like dibutyl phthalate, dioctyl phthalate, tricresyl phosphate etc.

II) Polyvinyl chloride (PVC):

PVC is made by addition polymerization. It is of two types.

i) Rigid PVC : (Unplasticized PVC):

Preparation: Rigid PVC is made by heating vinyl chloride (in the form of emulsion of it in water) in the presence of small amount of benzoyl peroxide or H_2O_2 as catalyst under pressure in an autoclave.

Properties:

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- a) Presence of chlorine atoms on the alternate carbon atoms of PVC causes an increase in the interchange attraction. This increases the hardness and stiffness of polymer. Its softening point is also high (148°C)
- b) The Cl-Cl dipole makes PVC a polymeric polar molecule, but because of the immobility of the dipole at room temperature, power factor of PVC is comparatively low.
- c) PVC is colourless, odourless and non-inflammable.
- d) It has superior chemical resistance but is soluble in ethyl chloride and tetrahydrofuran (THF).
- e) It has excellent oil resistance and resistance to weathering.

Applications:

- a) It is used in acid recovery plants and in plants for handling hydrocarbons, many of which adversely affect the polyolefins. This is due to its very good resistance to chemicals.
- b) Rigid PVC has great potential importance to building industry since it has excellent resistance to weathering. When considered regarding initial cost, installation and maintenance cost, it is found to be very economical. Hence, it is used for making pipes for drainage and guttering. It is also replacing wood for making window frames that neither corrodes or not.
- c) Rigid PVC is also used for making bottles –

i) For consumable liquids (like edible oils, fruit squashes, table wine and vinegar).

ii) For liquids of household use (like bisleri mineral water, cosmetics and detergents).

ii) Plasticized PVC:

Preparation: plasticized PVC is obtained by adding plasticizers such as DOP (dioctyl phthalate), dibutyl phthalate, tricresyl phosphate etc., to rigid PVC.

Properties:

Plasticized PVC is a very good insulator for direct current and low frequency AC current.

Applications:

a) Plasticized PVC is completely replaced rubber insulated wire for domestic flex and is used widely industrially.

b) It is used for sheathing in cables where polyethylene is employed as insulators.

c) Plasticized PVC is used for making leather cloth which is used in

i) Car applications in upholstery and trim,

ii) Kitchen upholstery

iii) Bathroom curtaining

iv) Ladies handbags.

Compared to leather, PVC-leather cloth has greater abrasion resistance, flex resistance and washability. Its cost is very low.

d) It is also used for making

i) Plastic rain wear ii) Baby pants iii) All PVC-shoes for beach wear &

iv) Garden hose.

These applications are due to flexibility and water-proof nature of plasticized PVC. It is also more economical and better aesthetically.

3.9 preparation, properties and engineering applications of PS and Teflon:

Polystyrene (PS):

Polystyrene (PS) is an addition polymer of styrene. It is a thermoplastic and has the following structure.

The monomer styrene is obtained by the alkylation of benzene followed by catalytic dehydrogenation.

Preparation: Polystyrene is prepared by free radical addition polymerization of styrene in the presence of benzoyl peroxide as catalyst.

Properties:

Polystyrene is a white, amorphous, linear thermoplastic.

It is chemically inert.

Because of the presence of bulky phenyl groups, packing of polystyrene chains is not efficient and hence it is amorphous polymer. Its specific gravity (1.054) is also low.

Polystyrene can be nitrated by fuming nitric acid

- It can be sulphonated by conc. H_2SO_4 .
- It yields water-soluble emulsion at about 100°C .
- It is highly electric insulating, highly resistant to acids.
- It has relatively low softening range ($90 - 100^\circ\text{C}$) and is brittle.
- It has the unique property of transmitting light through curved sections.
- It is readily attacked by a number of solvents.
- Its optical properties are excellent and its refractive index (1.60) is quite high.
- Its tensile strength is about 8000Psi.

Applications:

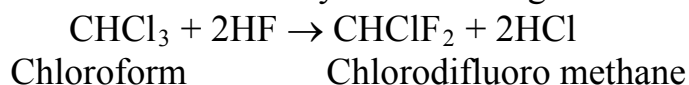
- 1) Moulded articles: A large amount of polystyrene is used for the manufacture of household articles such as containers, jars, lids, bottles, cabinets for TV, radio and washing machines, combs, toys, brush handles etc.
- 2) Optical objects: Because of its refractive index and clarity, it is used for the manufacture of lenses, fluorescent light diffuser etc.,
- 3) Insulating material: Because of its excellent electrical resistant properties, it is used for wire and cable coatings.
- 4) It is used for the production of a variety of foamed products.
- 5) The sulfonated polystyrene is used as an ion-exchange resin.

Polytetrafluoro ethylene (PTFE) : (Teflon):

Teflon is the trade name for polytetrafluoro ethylene. The linear structure of Teflon is $(\text{CF}_2 - \text{CF}_2)_n$

The monomer used is tetrafluoro ethylene which is a non-toxic gas.

The monomer is obtained by the following reactions:



Pyrolysis



Preparation:

Teflon is usually prepared by emulsion polymerisation of tetrafluoroethylene, under pressure in the presence of benzoyl peroxide as catalyst.

Properties:

- Teflon is essentially a linear polymer with no branching
- It is a thermoplastic
- Teflon has the following unique properties:
 - High degree of crystallinity (93-98%)
 - High melting point (327°C)
 - High density (2.30g/cm³)
 - Chemical inertness over a wide range of temperature
 - Excellent electrical insulation properties.
 - Non-adhesive characteristics
 - Very-low coefficient of friction
 - Excellent toughness and heat resistant.

Applications: Teflon is used for

- Wire and cable insulation
- Laminates for printed circuitry
- Coatings of frying pans.
- Non-lubricating bearings.
- Variety of seals, gaskets, packings valve and pump parts and stop-cocks for burettes.
- Insulators for motors, generators, coil transformers and capacitors.

Bakelite:

Properties:

- Phenolic resins are hard, rigid and strong materials
- They have excellent heat and moisture resistance.
- They have good chemical resistance.
- They have good abrasion resistance.
- They have electrical insulation characteristics
- They are usually dark coloured.
- Lower molecular weight grades have excellent bonding strength and adhesive properties.

Applications: Phenol formaldehyde resins are used for

- Domestic plugs and switches
- Handles for cooker and saucepans.
- Distributor heads for cars

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- Adhesives for grinding wheels and brake linings.
- Varnishes, electrical insulation and protective coatings.
- The production of ion exchange resins.
- Impregnated paper, wood and other fillers, for producing decorative laminates and wall coverings and industrial laminates for electrical parts including printed circuits.

Nylon:

Synthetic fiber forming polyamides are termed as 'Nylons'.

Preparation:

- Nylon – 6 can be prepared by self-condensation of ϵ - amino caproic acid.
- Nylon-6 can be prepared by ring opening polymerisation of caprolactam.
- Nylon-6 can be synthesized from cyclohexane.

The steps involved are –

- Conversion of cyclohexane to cyclohexanone by oxidation.
- Treatment of cyclohexanone with hydroxyl amine to form an oxime.
- Conversion of cyclohexanone oxime into caprolactam by Beckmann rearrangement in the presence of H_2SO_4 .

Nylon 6.10:

- Nylon 6.10 is prepared by the condensation polymerisation of hexamethylene diamine and sebacic acid.

Properties:

- The structure of nylons are linear that permits side-by-side alignment. The molecular chains are held together by hydrogen bonds. Thus nylons have high crystallinity that imparts high strength, high melting point, elasticity,
- toughness, abrasion resistance and retention of good mechanical properties upto 125°C.
- They are also sterilisable.
- They have good hydrocarbon resistance since nylons are polar polymers. Larger the number of carbon atoms, greater will be ease of processing and hydrocarbon and moisture resistance.

Applications:

- Nylon 6.6 is primarily used for fibers that find use in making socks, undergarments, carpets etc.,

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- Nylon 6.6 is also used in mechanical engineering for well known applications like gears, bearings, bushes, cans etc.,
- Nylon 11 and Nylon 12 are used for making flexible tubing for conveying petrol.
- Mouldings have application in medicine and pharmacy because of sterilisability.
- Durable but costly hair combs.
- Nylon 6.6 is also used for facketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.
- Nylon 6 is mainly used for making tyre cords.
- Nylon 6.10 is suitable for monofilaments that are used for bristles, brushes etc.,
- Glass reinforced Nylon plastics are used in housings and cosings of domestic appliances, radiator parts of car and for relay coil formers.

Nylon – 11:

Nylon -11 can be prepared by the self-condensation of w –amino undecanoic acid.

Nylon 6,6:

i)Nylon 6.6 is prepared by the condensation polymerisation of hexamethylene diamine and adipic acid in 1:1 molor ratio without an external strong acid.

ii)Nylon 6.6 can be prepared starting form 1,3-butadiene

3.10 Conducting polymers:

Definition: A polymer that can conduct electricity is known as conducting polymer.

Classification: Conducting polymers can be classified as follows.

I) Intrinsically conducting polymers:

The polymers have extensive conjugation in the backbone which is responsible for conductance. These are of two types.

1)Conducting polymers having conjugated π - electrons in the backbone:

Such polymers contain conjugated π -electrons in the back bone which increases their conductivity to a large extent.

Explanation: Overlapping of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands that extends over the entire polymer molecule. The valence band and the conduction bands are separated by a significant band gap. Thus, electrical conduction occur only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band.

All the three forms of polyanilines have conductivities of the order of 10^{-10} Scm⁻¹. conductivity of these polymers having conjugated π -electrons in the backbone is not sufficient for their use in different applications.

2)Doped conducting polymers:

In comparison to conventional polymers, the conducting polymers having conjugated π -electrons in the backbone can be easily oxidized for reduced as they have low ionization potentials and high electron affinities. The conductivities can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. It is referred to as doping.

This is of two types.

- a)P-doping or oxidative doping
- b)n-doping or, reductive doping

a)p-doping:

It is done by oxidation process. P-doping involves treatment of an intrinsically conducting polymer with a lew's acid, thereby oxidation takes place and positive charges on the polymer backbone are created. The oxidation process leads to the formation of delocalized radical ion called 'Polaron'. A second oxidation of this polaron, followed by radical recombination yields two positive charge carriers on each chain which are mobile. These delocalized positive charges are current carriers for conduction.

The common p-dopants used are I_2 , Br_2 , ASF_5 , PF_6 , naphthyl amine.

b)n-doping: n-doping is done by reduction process. N-doping involves the treatment of an intrinsically conducting polymer with a lewis base like sodium naphthalide.

n-doping leads to the formation of polaron and bipolaron in two steps. This followed by recombination of radicals yields two negative charge carriers on each chain of polyacetylene which are responsible for conduction.

II) Extrinsicly conducting polymers:

These are the polymers whose conductivities due to the presence of externally added ingredients in them. These are of two types.

1) Conductive element filled polymer: In this type, the polymer acts as the binder to hold the conducting element such as carbon black, metallic fibres, metallic oxides together in the solid entity.

Minimum concentration of conductive filler which should be added so that the polymer starts conducting is known as 'percolation threshold'. Because at this concentration of filler, a conducting path is formed in polymeric material. Generally special conducting grade C-black is used as filler which has very high surface area, more porosity and more filamentous properties.

These polymers possess reasonably good bulk conductivity. They are generally low in cost, light in weight, mechanically durable and strong and are easily processable in different forms, shapes and sizes.

2) Blended conducting polymers: These polymers are obtained by blending a conventional polymer with a conducting polymer. These polymers possess better physical, chemical, electrical and mechanical process and they can be easily processed.

Ex: upto 40% polypyrrole will have a little effect on tensile strength and also give a much higher impact strength than obtained with a carbon-black filled compounds at only 10% loading.

Applications of Conducting Polymers:-

In rechargeable Light weight batteries based on perchlorate doped Polyacetylene-lithium Systems: These are about 10 times lighter than conventional lead storage batteries. These can produce current density up to 50mA/cm^2 .

- In electrochromic displays and optical filters: ICP's can absorb visible light to give coloured products so can be useful for electrochromic displays and optical filters. Thus the conducting polymers can be used as electro chromic materials i.e., the

materials that change colour reversibly during the electrochemical processes of charge and discharge.

- In wiring in aircrafts and aerospace components.
- Conducting polymers are also used for making sensors for pH, O_2 , NO_x , SO_2 , NH_3 and glucose.
- In telecommunication systems.
- In electromagnetic screening materials.
- In electronic devices such as transistors and diodes.
- IN solar cells, drug delivery system for human body etc.,
- In photovoltaic devices.
- In non-linear optical materials.
- In molecular wires and molecular switches.
- Membranes made up of conducting polymers can show boundary layer effects with selective permeability for ions, gases etc., Hence they are useful for ion-exchangers and controlled release of drugs.

3.11 Natural rubber:

Natural rubber is found in several species of rubber trees grown in tropical countries of these *Hevea brasiliensis* is the most important source of natural rubber and the rubber obtained from this is known as “Hevea” rubber. Rubber is stored in the form of white fluid called ‘latex’ behind the bark of the rubber tree.

Natural rubber is a high polymer of isoprene (2-methyl-1,3-butadiene). It is a hydrocarbon polymer having molecular formula $(C_5H_8)_n$.

Polyisoprene exists in two geometric isomers cis and trans. Natural rubber is soft and has cis-configuration while ‘Guttapercha’ or, ‘Ballata’ has trans configuration.

Deficiencies of natural rubber:

- Natural rubber as such has no practical utility value. It is because of many inherent deficiencies. They are –
- It is hard and brittle at low temperature and soft and sticky at high temperature.
- It is soft and soluble in many hydrocarbon solvents and carbon disulphide (CS_2).
- It has high water absorption power.
- It is a sticky substance, rather difficult to handle
- It is readily attacked by acids and alkalies.
- It has low tensile strength.

- It has poor abrasion resistance.
- It is sensitive to oxidative degradation

Vulcanization:

Vulcanization is a process of heating the raw rubber at 100 – 140°C with sulfur for

1 – 4 hours. The sulfur combines chemically at the double bonds of different rubber molecules and provides cross-linking between the chains.

The degree of vulcanization 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.

Advantages of vulcanization:

- The tensile strength of vulcanized rubber is very good. It is 10 times the tensile strength of raw rubber.
- It has excellent resilience i.e., articles made from it returns to the original shape when the deforming load is removed.
- It has better resistance to moisture, oxidation, abrasion.
- It has much higher resistance to wear and tear compared to raw rubber.
- It has broader useful temperature range (-40 to 100°C) compared to raw rubber's useful temperature range (10 – 60°C).
- It is a better electrical insulator Ex: Ebonite
- It is resistant to i) Organic solvents like petrol, benzene, CCl₄, ii) Fats and oils, but it swells in them.
- It has only slight tackiness.
- It has low elasticity. This property depends on the extent of vulcanization. Ebonite has practically no elasticity.
- It is very easy to manipulate the vulcanized rubber to produce the desired shapes.

3.12 Elastomers:

Definition: Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on released of stress.

The property of elastomers is known as elasticity. This arises due to the coiled structure of elastomers.

Characteristics of Elastomers:

- Elastomers have linear but highly coiled structure.

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- Inter chain cohesive forces are negligible because these are hydrocarbons.
- They have high degree of elasticity.
- They can retract rapidly.

BuNa – S : [Styrene rubber or, SBR (Styrene – butadiene rubber) or GRS (Government controlled styrene rubber)]

Preparation:

Buna – S is prepared by the copolymerization of butadiene (75%) and styrene (25%) in an emulsion system at 50°C in the presence of cumene hydroperoxide as catalyst.

If the emulsion polymerisation is carried out at low temperatures (-18° to 5°C) in the presence of redox catalyst like cumene hydroperoxide + dextrose in the presence of iron salt, the resultant SBR is known as cold SBR.

Vulcanization can be done either by sulfur or sulfur monochloride (S₂Cl₂). Less sulfur and more accelerators are required for vulcanization.

Properties:

- High abrasion resistance
- High load-bearing capacity
- Resilience (regaining original shape after removal of applied force)
- It swells in oils and solvents.
- Low oxidation resistance, as it gets readily oxidized, especially in the presence of traces of ozone present in the atmosphere.
- Vulcanized and compounded cold rubber has a greater tensile strength and greater abrasion resistance than the SBR or natural rubbers.

Applications:

SBR is used in the following applications.

- | | | |
|----------------------------------|----------------|-------------------------|
| 1) Motor tyres | 2) Shoes soles | 3) Foot wear components |
| 4) Insulation of wire and cables | | 5) Carpet backing |
| 6) Gaskets | 7) Adhesives | 8) Tank-lining |

Butyl rubber:

Preparation:

Butyl rubber is prepared by the aluminum chloride initiated cationic copolymerisation of isobutene with small amount (1-5%) of isoprene.

Properties:

- Under normal conditions, it is amorphous but it crystallizes on stretching.
- It is quite resistant to oxidation due to low degree of unsaturation.
- Due to very low unsaturation, it can be vulcanized but it cannot be hardened much.
- It can be degraded by heat or light to sticky low-molecular weight products so stabilization is must.
- Being non-polar, it has good electrical insulation properties.
- Compared to natural rubber it possesses outstanding low permeability to air and other gases.
- It does not crystallize on cooling and hence remains flexible down to -50°C .
- Because of its hydrocarbon nature, butyl rubber is soluble in hydrocarbon solvents like benzene but has excellent resistance to polar solvents like alcohol, acetone and ageing chemicals (ex: HCl, HF, HNO_3 , H_2SO_4 etc.)

Applications: It is used for

- Insulation of high voltage wires and cables
- Inner tubes of automobile tyres.
- Conveyor belts for food and other materials.
- Lining of tanks
- Hoses

Thiokol rubbers:**Preparation:**

Thiokol is prepared by the condensation polymerisation of sodium polysulfide (Na_2S_x) and ethylene dichloride ($\text{ClCH}_2\text{CH}_2\text{Cl}$). In these elastomers, sulfur forms a part of the polymer chain.

Properties:

- They have excellent resistance to swelling and disintegration by organic solvents and gasoline, kerosene, lubricating oils.
- Outstanding resistance to oxygen ozone, sun light.
- It undergo swelling by benzene and derivatives of benzene.
- It has lower tensile strength and modulus than natural rubber. It tends to lose shape under continuous pressure.
- It has offensive-mercaptan-like odour, that restricts its use.

Applications:

- Manufacture of oil hoses, chemically resistant tubing and engine gaskets.
- Diaphragms and seals in contact with solvents.
- Printing rolls
- Containers for transporting solvents and
- Solid propellant fuels for rockets.

3.13 Fibers:

Fibers are a class of materials that are continuous filaments or discrete elongated pieces. They are highly crystalline form of polymers.

The requisite properties for a natural or synthetic polymer molecule to function as a fiber for use in textile are –

- 1) High tensile strength
- 2) Flexibility
- 3) Abrasion resistance
- 4) Amenability of dyeing
- 5) Chemical stability in terms of resistance to hydrolysis under washing conditions.
- 6) Resistance to degradation on exposure to light

Classification:

Fibers are classified into two types. They are

- 1) Natural fibers
- 2) Artificial fibers (Synthetic fibers)

1) Natural fibers: Natural fibers include the fibers produced by plants, animals and geological material. They are environment friendly and biodegradable. They are –

i) Vegetable fibers: They are cellulosic material like cotton, jute, plant fibers are used for making textiles, ropes, mats, paper bags etc.,

ii) Wood fibers: The strength of a plant is due to the presence of wood fiber. Wood pulp is used in making paper. Wood fibers like jute are used for making bags.

iii) Animal fibers: They are made of protein. Pure silk, wool, hair are animal fibers.

iv) Mineral fibers: Ex: Asbestos, Mica etc.,

2) Synthetic fibers:

Synthetic fibers can be produced in large quantities and cheaper than some of the natural fibers. Fiber forming synthetic polymers include polyamides (nylon6 and nylon – 6,6), polyesters (ex. polyethylene terephthalate, terylene or, Dacron), Polyolefins (Polyacrylo nitrile). Polyethylene, polypropylene are also produced in the form of fibers which are hydrophobic, chemically resistant and difficult to dye and hence used for making ropes.

Polyester:

Synthesis of polyester is achieved by poly condensation of purified terephthalic acid (1,4 – benzene carboxylic acid) and monoethylene glycol.

The esterification is catalysed by the presence of mineral acid like HCl.

Fiber reinforced plastics: (FRP):

The fiber polymers impregnated with solids / fillers to impart mechanical strength and hardness without losing elasticity are known as fiber reinforced plastics (FRP).

Various fillers are known to impart characteristic property to the plastic material.

Ex – 1: Fillers like carborundum, quartz and mica are added to impart hardness and strength.

2) Barium salt fillers are impervious to X-rays.

3) Asbestos fillers added to plastic provide heat and corrosion resistant.

Nature of polymers used for FRP: Both thermoplastics and thermoset plastics are used such as polyethylene, polypropylene, Nylon-6, polyester, melamine.

Applications:

- For making door handles, battery cases, exhaust fans engine cooling fans etc., in automobiles using the base polymers like polyethene, polypropylene, nylon – 6.
- For making nose cones, pistol grips and rifle bullets in defense industries using the base polymers nylon-6 and polystyrene.

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- For making shuttle and textiles using nylon-6 as base polymer in textile industries.
- For making the consumer goods like doors, windows, tables, chairs, almyrahs, cameras, housings etc., using polypropylene and acrylobutadiene styrene blended plastics.
- For making computer tape, insulators, wires and cable insulation, switch, gear parts exhaust fans as electrical appliances using the base polymers like polypropylene nylon and styrene acrylonitrile copolymer.
- For making the items like water meters and chemical pump housings, tubings, seat coverings etc., using the base polymers like polypropylene, m PVC and nylon – 6.

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