

Chapter 11. Applications and Processing of Polymers

Polymers play a very important role in human life. In fact, our body is made of lot of polymers, e.g. Proteins, enzymes, etc. Other naturally occurring polymers like wood, rubber, leather and silk are serving the humankind for many centuries now. Modern scientific tools revolutionized the processing of polymers thus available synthetic polymers like useful plastics, rubbers and fiber materials. As with other engineering materials (metals and ceramics), the properties of polymers are related their constituent structural elements and their arrangement. The suffix in polymer 'mer' is originated from Greek word *meros* – which means part. The word polymer is thus coined to mean material consisting of many parts/meros. Most of the polymers are basically organic compounds, however they can be inorganic (e.g. silicones based on Si-O network). This chapter introduces classification of polymers, processing and synthesis of polymers, followed by mechanism of deformation and mechanical behavior of polymers.

11.1 Polymer types and Polymer synthesis & processing

Polymers are classified in several ways – by how the molecules are synthesized, by their molecular structure, or by their chemical family. For example, linear polymers consist of long molecular chains, while the branched polymers consist of primary long chains and secondary chains that stem from these main chains. However, linear does not mean straight lines. The better way to classify polymers is according to their mechanical and thermal behavior. Industrially polymers are classified into two main classes – *plastics* and *elastomers*.

Plastics are moldable organic resins. These are either natural or synthetic, and are processed by forming or molding into shapes. Plastics are important engineering materials for many reasons. They have a wide range of properties, some of which are unattainable from any other materials, and in most cases they are relatively low in cost. Following is the brief list of properties of plastics: light weight, wide range of colors, low thermal and electrical conductivity, less brittle, good toughness, good resistance to acids, bases and moisture, high dielectric strength (use in electrical insulation), etc. Plastics are

again classified in two groups depending on their mechanical and thermal behavior as *thermoplasts* (thermoplastic polymers) and *thermosets* (thermosetting polymers).

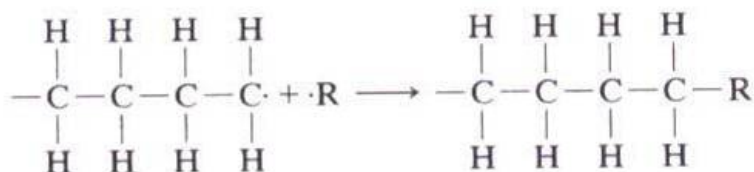
Thermoplasts: These plastics soften when heated and harden when cooled – processes that are totally reversible and may be repeated. These materials are normally fabricated by the simultaneous application of heat and pressure. They are linear polymers without any cross-linking in structure where long molecular chains are bonded to each other by secondary bonds and/or inter-wined. They have the property of increasing plasticity with increasing temperature which breaks the secondary bonds between individual chains. Common thermoplasts are: acrylics, PVC, nylons, polypropylene, polystyrene, polymethyl methacrylate (plastic lenses or perspex), etc.

Thermosets: These plastics require heat and pressure to mold them into shape. They are formed into a permanent shape and cured or ‘set’ by chemical reactions such as extensive cross-linking. They cannot be re-melted or reformed into another shape but decompose upon being heated to too high a temperature. Thus thermosets cannot be recycled, whereas thermoplasts can be recycled. The term thermoset implies that heat is required to permanently set the plastic. Most thermosets composed of long chains that are strongly cross-linked (and/or covalently bonded) to one another to form 3-D network structures to form a rigid solid. Thermosets are generally stronger, but more brittle than thermoplasts. Advantages of thermosets for engineering design applications include one or more of the following: high thermal stability, high dimensional stability, high rigidity, light weight, high electrical and thermal insulating properties and resistance to creep and deformation under load. There are two methods whereby cross-linking reaction can be initiated – cross-linking can be accomplished by heating the resin in a suitable mold (e.g. bakelite), or resins such as epoxies (araldite) are cured at low temperature by the addition of a suitable cross-linking agent, an amine. Epoxies, vulcanized rubbers, phenolics, unsaturated polyester resins, and amino resins (ureas and melamines) are examples of thermosets.

Elastomers: Also known as rubbers, these are polymers which can undergo large elongations under load, at room temperature, and return to their original shape when the load is released. There are number of man-made elastomers in addition to natural rubber. These consist of coil-like polymer chains those can reversibly stretch by applying a force.

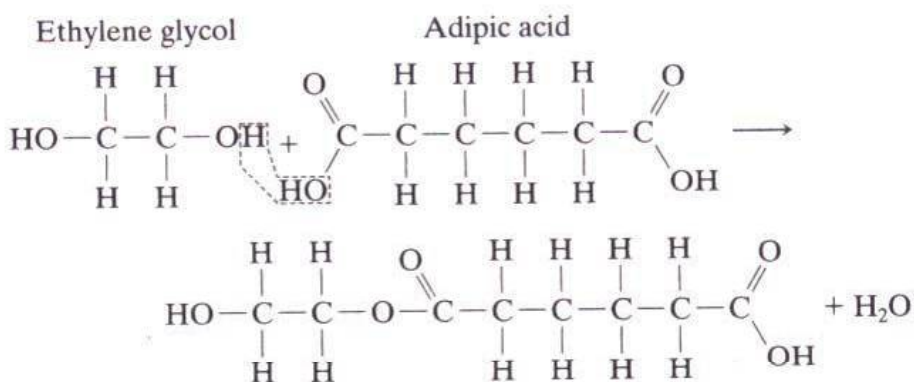
Processing of polymers mainly involves preparing a particular polymer by synthesis of available raw materials, followed by forming into various shapes. Raw materials for polymerization are usually derived from coal and petroleum products. The large molecules of many commercially useful polymers must be synthesized from substances having smaller molecules. The synthesis of the large molecule polymers is known as polymerization in which monomer units are joined over and over to become a large molecule. More upon, properties of a polymer can be enhanced or modified with the addition of special materials. This is followed by forming operation. Addition polymerization and condensation polymerization are the two main ways of polymerization.

thus terminating the growth of each chain or an active chain end may react with an initiator or other chemical species having a single active bond, as follows:



with the resultant cessation of chain growth. Polyethylene, polypropylene, PVC, and polystyrene are synthesized using addition polymerization.

Condensation polymerization, also known as step growth polymerization, involves more than one monomer species; and there is usually a small molecular weight by-product such as water, which is eliminated. The repeat unit here forms from original monomers, and no product has the chemical formula of mere one mer repeat unit. The polymerization of dimethyl terephthalate and ethylene glycol to produce polyester is an important example. The by-product, methyl alcohol, is condensed off and the two monomers combine to produce a larger molecule (mer repeat unit). Another example, consider the formation of a polyester from the reaction between ethylene glycol and adipic acid; the intermolecular reaction is as follows:



This stepwise process is successively repeated, producing, in this case, a linear molecule. The intermolecular reaction occurs every time a mer repeat unit is formed. Reaction times for condensation are generally longer than for addition polymerization. Polyesters, phenol-formaldehyde, nylons, polycarbonates etc are produced by condensation polymerization. Condensation polymerization reactions also occur in sol-gel processing of ceramic materials. Some polymers such as nylon may be polymerized by either technique.

Polymers, unlike organic/inorganic compounds, do not have a fixed molecular weight. It is specified in terms of *degree of polymerization* – number of repeat units in the chain or ratio of average molecular weight of polymer to molecular weight of repeat unit. Average molecular weight is however defined in two ways. *Weight average molecular*

weight is obtained by dividing the chains into size ranges and determining the fraction of chains having molecular weights within that range. *Number average molecular weight* is based on the number fraction, rather than the weight fraction, of the chains within each size range. It is always smaller than the weight average molecular weight.

Most of polymer properties are intrinsic i.e. characteristic of a specific polymer. Foreign substances called additives are intentionally introduced to enhance or modify these properties. These include – fillers, plasticizers, stabilizers, colorants, and flame retardants. Fillers are used to improve tensile and compressive strength, abrasion resistance, dimensional stability etc. wood flour, sand, clay, talc etc are example for fillers. Plasticizers aid in improving flexibility, ductility and toughness of polymers by lowering glass transition temperature of a polymer. These are generally liquids of low molecular weight. Stabilizers are additives which counteract deteriorative processes such as oxidation, radiation, and environmental deterioration. Colorants impart a specific color to a polymer, added in form of either dyes (dissolves) or pigments (remains as a separate phase). Flame retardants are used to enhance flammability resistance of combustible polymers. They serve the purpose by interfering with the combustion through the gas phase or chemical reaction.

Polymeric materials are formed by quite many different techniques depending on (a) whether the material is thermoplast or thermoset, (b) melting/degradation temperature, (c) atmospheric stability, and (d) shape and intricacy of the product. Polymers are often formed at elevated temperatures under pressure. Thermoplasts are formed above their glass transition temperatures while applied pressure ensures that the product retain its shape. Thermosets are formed in two stages – making liquid polymer, then molding it.

Different molding techniques are employed in fabrication of polymers. *Compression molding* involves placing appropriate amount of polymer with additives between heated male and female mold parts. After pouring polymer, mold is closed, and heat and pressure are applied, causing viscous plastic to attain the mold shape. *Figure-11.1* shows a typical mould employed for compression molding.

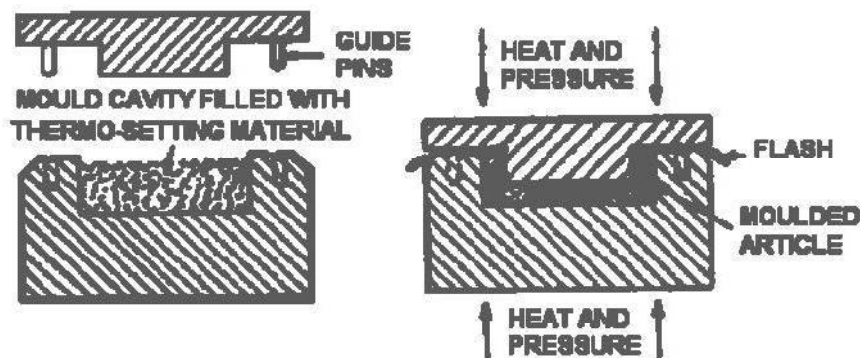


Figure 11.1: Schematic diagram of a mould employed for compression molding

Transfer molding differs from compression molding in how the materials is introduced into the mold cavities. In transfer molding the plastic resin is not fed directly into the mold cavity but into a chamber outside the mold cavities. When the mold is closed, a plunger forces the plastic resin into the mold cavities, where and molded material cures. In *injection molding*, palletized materials is fed with use of hopper into a cylinder where charge is pushed towards heating chamber where plastic material melts, and then molten plastic is impelled through nozzle into the enclosed mold cavity where product attains its shape. Most outstanding characteristic of this process is the cycle time which is very short. The schematic diagram of injection-molding machine is shown in *figure-11.2*

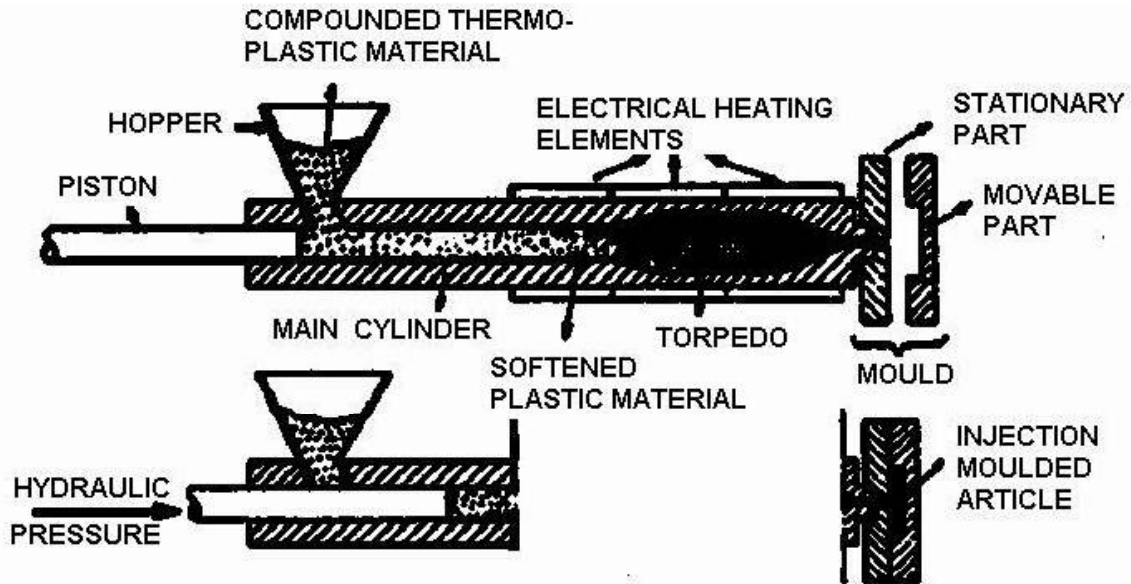


Figure 11.2: Schematic diagram of injection-molding machine

Extrusion is another kind of injection molding, in which a thermoplastic material is forced through a die orifice, similar to the extrusion of metals. This technique is especially adapted to produce continuous lengths with constant cross-section. The schematic diagram of a simple extrusion machine is shown in *figure- 11.3*

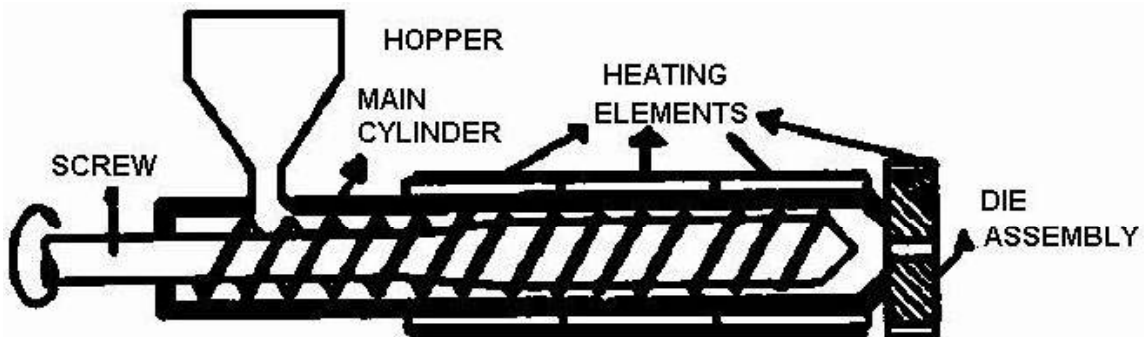


Figure 11.3: Schematic diagram of a simple extrusion machine

Blow molding of plastics is similar to blowing of glass bottles. Polymeric materials may be cast similar to metals and ceramics.

11.2 Crystallization, melting and glass transition

Polymers are known by their high sensitivity of mechanical and/or thermal properties. This section explains their thermal behavior. During processing of polymers, they are cooled with/without presence of presence from liquid state to form final product. During cooling, an ordered solid phase may be formed having a highly random molecular structure. This process is called crystallization. The melting occurs when a polymer is heated. If the polymer during cooling retains amorphous or non-crystalline state i.e. disordered molecular structure, rigid solid may be considered as frozen liquid resulting from glass transition. Thus, enhancement of either mechanical and/or thermal properties needs to consider crystallization, melting, and the glass transition.

Crystallization and the mechanism involved play an important role as it influences the properties of plastics. As in solidification of metals, polymer crystallization involves nucleation and growth. Near to solidification temperature at favorable places, nuclei forms, and then nuclei grow by the continued ordering and alignment of additional molecular segments. Extent of crystallization is measured by volume change as there will be a considerable change in volume during solidification of a polymer. Crystallization rate is dependent on crystallization temperature and also on the molecular weight of the polymer. Crystallization rate decreases with increasing molecular weight.

Melting of polymer involves transformation of solid polymer to viscous liquid upon heating at melting temperature, T_m . Polymer melting is distinctive from that of metals in many respects – melting takes place over a temperature range; melting behavior depends on history of the polymer; melting behavior is a function of rate of heating, where increasing rate results in an elevation of melting temperature. During melting there occurs rearrangement of the molecules from ordered state to disordered state. This is influenced by molecular chemistry and structure (degree of branching) along with chain stiffness and molecular weight.

Glass transition occurs in amorphous and semi-crystalline polymers. Upon cooling, this transformation corresponds to gradual change of liquid to rubbery material, and then rigid solid. The temperature range at which the transition from rubbery to rigid state occurs is termed as glass transition temperature, T_g . This temperature has its significance as abrupt changes in other physical properties occur at this temperature. Glass transition temperature is also influenced by molecular weight, with increase of which glass transition temperature increases. Degree of cross-linking also influences the glass transition such that polymers with very high degree of cross-linking do not experience a glass transition. The glass transition temperature is typically 0.5 to 0.75 times the absolute melting temperature. Above the glass transition, non-crystalline polymers show viscous behavior, and below the glass transition they show glass-brittle behavior (as chain motion is very restricted), hence the name glass transition.

Melting involves breaking of the inter-chain bonds, so the glass- and melting-temperatures depend on:

- chain stiffness (e.g., single vs. double bonds)
- size, shape of side groups
- size of molecule
- side branches, defects
- cross-linking

11.3 Mechanical behavior of polymers

Polymer mechanical properties can be specified with many of the same parameters that are used for metals such as modulus of elasticity, tensile/impact/fatigue strengths, etc. However, polymers are, in many respects, mechanically dissimilar to metals. To a much greater extent than either metals or ceramics, both thermal and mechanical properties of polymers show a marked dependence on parameters namely temperature, strain rate, and morphology. In addition, molecular weight and temperature relative to the glass transition play an important role that are absent for other type of materials.

A simple stress- strain curve can describe different mechanical behavior of various polymers. As shown in *figure – 11.4*, the stress-strain behavior can be brittle, plastic and highly elastic (elastomeric or rubber-like). Mechanical properties of polymers change dramatically with temperature, going from glass-like brittle behavior at low temperatures to a rubber-like behavior at high temperatures. Highly crystalline polymers behave in a brittle manner, whereas amorphous polymers can exhibit plastic deformation. These phenomena are highly temperature dependent, even more so with polymers than they are with metals and ceramics. Due to unique structures of cross-linked polymers, recoverable deformations up to very high strains / point of rupture are also observed with polymers (elastomers). Tensile modulus (modulus) and tensile strengths are orders of magnitude smaller than those of metals, but elongation can be up to 1000 % in some cases. The tensile strength is defined at the fracture point and can be lower than the yield strength.

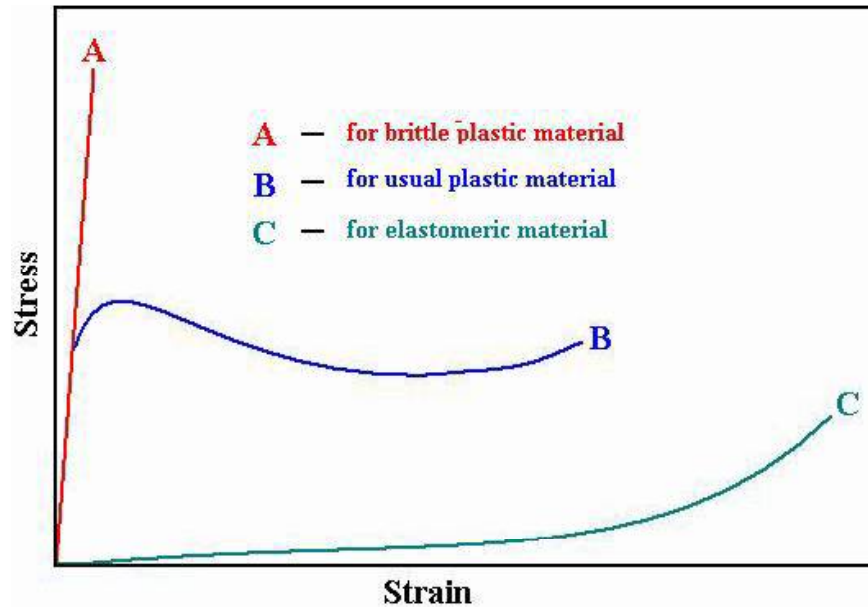


Figure-11.4: *Typical stress-strain curves for polymers.*

As the temperature increases, both the rigidity and the yield strength decrease, while the elongation increases. Thus, if high rigidity and toughness are the requirements, the temperature consideration is important. In general, decreasing the strain rate has the same influence on the strain-strength characteristics as increasing the temperature: the material becomes softer and more ductile. Despite the similarities in yield behavior with temperature and strain rate between polymers, metals, and ceramics, the mechanisms are quite different. Specifically, the necking of polymers is affected by two physical factors that are not significant in metals: dissipation of mechanical energy as heat, causing softening magnitude of which increases with strain rate; deformation resistance of the neck, resulting in strain-rate dependence of yield strength. The relative importance of these two factors depends on materials, specimen dimensions and strain rate. The effect of temperature relative to the glass transition is depicted in terms of decline in modulus values. Shallow decline of modulus is attributed to thermal expansion, whereas abrupt changes are attributable to viscoelastic relaxation processes.

Together molecular weight and crystallinity influence a great number of mechanical properties of polymers including hardness, fatigue resistance, elongation at neck, and even impact strength. The chance of brittle failure is reduced by raising molecular weight, which increases brittle strength, and by reducing crystallinity. As the degree of crystallinity decreases with temperature close to melting point, stiffness, hardness and yield strength decrease. These factors often set limits on the temperature at which a polymer is useful for mechanical purposes.

Elastomers, however, exhibit some unique mechanical behavior when compared to conventional plastics. The most notable characteristics are the low modulus and high deformations as elastomers exhibit large, reversible elongations under small applied stresses. Elastomers exhibit this behavior due to their unique, cross-linked structure.

Elastic modulus of elastomers (resistance to the uncoiling of randomly orientated chains) increases as with increase in temperature. Unlike non-cross-linked polymers, elastomers exhibit an increase inelastic modulus with cross-link density.

11.4 Mechanisms of deformation and strengthening of polymers

An understanding of deformation mechanisms of polymers is important in order to be able to manage the optimal use of these materials, a class of materials that continues to grow in terms of use in structural applications. Despite the similarities in ductile and brittle behavior with to metals and ceramics respectively, elastic and plastic deformation mechanisms in polymers are quite different. This is mainly due to (a) difference in structure they made of and (b) size of the entities responsible for deformation. Plastic deformation in metals and ceramics can be described in terms of dislocations and slip planes, whereas polymer chains must undergo deformation in polymers leading to different mechanism of permanent deformation. Unique to most of the polymers is the viscoelasticity – means when an external force is applied, both elastic and plastic (viscous) deformation occur. For viscoelastic materials, the rate of strain determines whether the deformation in elastic or viscous. The viscoelastic behavior of polymeric materials is dependent on both time and temperature.

Plastic polymers deform elastically by elongation of the chain molecules from their stable conformations in the direction of the applied stress by the bending and stretching of the strong covalent bonds. In addition, there is a possibility for slight displacement of adjacent molecules, which is resisted by weak secondary / van der Waals bonds. Plastic deformation in polymers is not a consequence of dislocation movement as in metals. Instead, chains rotate, stretch, slide and disentangle under load to cause permanent deformation. This permanent deformation in polymers might occur in several stages of interaction between lamellar and intervening amorphous regions. Initial stages involve elongation of amorphous tie chains, and eventual alignment in the loading direction. Continues deformation in second stage occurs by the tilting of the lamellar blocks. Next, crystalline block segments separate before blocks and tie chains become orientated in the direction of tensile axis in final stage. This leads to highly orientated structure in deformed polymers.

Elastomers, on the other hand, deform elastically by simple uncoiling, and straightening of molecular chains that are highly twisted, kinked, and coiled in unstressed state. The driving force for elastic deformation is change in entropy, which is a measure of degree of disorder in a system. When an elastomer is stretched, the system's order increases. If elastomer is released from the applied load, its entropy increases. This entropy effect results in a rise in temperature of an elastomer when stretched. It also causes the modulus of elasticity to increase with increasing temperature, which is opposite to the behavior of other materials.

Fracture of polymers is again dependent on morphology of a polymer. As a thumb rule, thermosets fracture in brittle mode. It involves formation of cracks at regions where there is a localized stress concentration. Covalent bonds are severed during the fracture.

However, both ductile and brittle modes are possible mode of fracture for thermoplasts. Many of thermoplasts can exhibit ductile-to-brittle transition assisted by reduction in temperature, increase in strain rate, presence of notch, increased specimen thickness and a modification of the polymer structure. Unique to polymer fracture is crazing – presence of regions of very localized yielding, which lead to formation of small and interconnected microvoids. Crazes form at highly stressed regions associated with scratches, flaws and molecular inhomogeneties; and they propagate perpendicular to the applied tensile stress and typically are 5 μm or less thick. A craze is different from a crack as it can support a load across its face.

The deformation of plastic materials can be primarily elastic, plastic, or a combination of both types. The deformation mode and resistance of deformation depends on many parameters for different plastics. The following factors influence the strength of a thermoplast: average molecular mass, degree of crystallization, presence of side groups, presence of polar and other specific atoms, presence of phenyl rings in main chains and addition of reinforcements. Effect of every one of these factor can be used to strengthen a thermoplast. Thermosets are, however, strengthened by reinforcement methods.

Strength of a thermoplast is directly dependent on its average molecular mass since polymerization up to a certain molecular-mass range is necessary to produce a stable solid. This method is not used so often as after a critical mass range, increasing the average molecular mass does not greatly increase its strength. In general, as the degree of crystallinity increases, the strength, modulus and density all increase for a thermoplast. Another method to increase the strength is to create more resistance to chain slippage. This can be achieved by addition of bulky side groups on main chains, which results in increase of strength but reduces the ductility. Increased resistance to chain slippage can be achieved by increasing the molecular bonding forces between the polymer chains. E.g.: introducing a chlorine atom on every other carbon atom of main chain to make polyvinylchloride (PVC). Introducing an ether linkage (i.e. introduction of oxygen atom) or amide linkage (i.e. introduction of oxygen and nitrogen atoms) into the main chain can increase the rigidity of thermoplasts. One of the most important strengthening methods for thermoplasts is the introduction of phenylene rings in the main chain. It is commonly used for high-strength engineering plastics. The phenylene rings cause steric hindrance to rotation within the polymer chain and electronic attraction of resonating electrons between adjacent molecules. Another method of strengthening is introduction of reinforcements like glass fibers. Glass content ranges from 20 to 40%, depending on trade-off between desired strength, ease of processing and economics.

Thermosets are strengthened by reinforcements again. Different reinforcements are in use according to the necessity. Glass fibers are most commonly used to form structural and molding plastic compounds. Two most important types of glass fibers are E (electrical)- and S (high strength)- glasses. *E-glass* (lime-aluminium-borosilicate glass with zero or low sodium and potassium levels) is often used for continuous fibers. *S-glass* (65% SiO_2 , 25% Al_2O_3 and 10% MgO) has higher strength-to-weight ratio and is more expansive thus primary applications include military and aerospace applications. Carbon fiber reinforced plastics are also often used in aerospace applications. However they are very expensive.

The other classes of reinforcements include aramid (aromatic polyamide) fibers. They are popularly known as *Kevlar*. Presently two commercial variants of Kevlar are available – Kevlar29 and Kevlar49. Kevlar29 is a low-density, high strength aramid fiber designed for applications such as ballistic protection, ropes and cables. Kevlar49 is characterized by a low density and high strength/modulus; is used in aerospace, marine, automotive and other industrial applications. Thermosets without reinforcements are strengthened by creation of network of covalent bonds throughout the structure of the material. Covalent bonds can be developed during casting or pressing under heat and pressure.

11.5 Characteristics and typical applications of few plastic materials.

a) Thermo plastics

1. Acrylonitrile-butadiene-styrene (ABS):

Characteristics: Outstanding strength and toughness, resistance to heat distortion; good electrical properties; flammable and soluble in some organic solvents.

Application: Refrigerator lining, lawn and garden equipment, toys, highway safety devices.

2. Acrylics (poly-methyl-methacrylate)

Characteristics: Outstanding light transmission and resistance to weathering; only fair mechanical properties.

Application: Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs

3. Fluorocarbons (PTFE or TFE)

Characteristics: Chemically inert in almost all environments, excellent electrical properties; low coefficient of friction; may be used to 260° C; relatively weak and poor cold-flow properties.

Application: Anticorrosive seals, chemical pipes and valves, bearings, anti adhesive coatings, high temperature electronic parts.

4. Polyamides (nylons)

Characteristics: Good mechanical strength, abrasion resistance, and toughness; low coefficient of friction; absorbs water and some other liquids.

Application: Bearings, gears, cams, bushings, handles, and jacketing for wires and cables

5. Polycarbonates

Characteristics: Dimensionally stable: low water absorption; transparent; very good impact resistance and ductility.

Application: Safety helmets, lenses light globes, base for photographic film

6. Polyethylene

Characteristics: Chemically resistant and electrically insulating; tough and relatively low coefficient of friction; low strength and poor resistance to weathering.

Application: Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials.

7. Polypropylene

Characteristics: Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to UV light.

Application: Sterilizable bottles, packaging film, TV cabinets, luggage

8. Polystyrene

Characteristics: Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive

Application: Wall tile, battery cases, toys, indoor lighting panels, appliance housings.

9. Polyester (PET or PETE)

Characteristics: One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity acids, greases, oils and solvents

Application: Magnetic recording tapes, clothing, automotive tire cords, beverage containers.

b) Thermo setting polymers

1. Epoxies

Characteristics: Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties.

Application: Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates.

2. Phenolics

Characteristics: Excellent thermal stability to over 150° C; may be compounded with a large number of resins, fillers, etc.; inexpensive.

Application: Motor housing, telephones, auto distributors, electrical fixtures.

Lecture 2

**Polymers: Polyolefins:
Polyethylene, Poly Propylene
And Polystyrene**

POLYMERS: POLYOLEFINS: POLYETHYLENE, POLY PROPYLENE AND POLYSTYRENE, STYRENE COPOLYMERS

Polyolefins family of polymers derived from a particular group of base materials known as olefins, are the world's fastest growing polymer family. Polyolefins such as polyethylene (PE) and polypropylene (PP) are commodity plastics found in applications varying from house hold items such as grocery bags, containers, carpets, toys and appliances, to high tech products such as engineering plastics, industrial pipes, automotive parts, medical appliances and even prosthetic implants [Kapur et al., 2008]. Ethylene and propylene are monomers for polyethylene and polypropylene respectively. Global polyolefin market is likely to be 150 million tones by 2015 and 200 million tones by the year 2020. In India, the domestic polymer industry (like global industry) is dominated by polyolefins (polyethylene, polypropylene) [Shashi Kant & Kapur, 2011]. Market coverage of polyethylene, polypropylene is given in Table M-VIII 2.1. Polystyrene is another important polyolefin and find wide application in manufacture of all sorts of packaging material. Styrene co-polymerised with acrylonitrile resulting in SAN polymer is characterized with high tensile strength than polystyrene. Another important styrene copolymer is Acrylonitrile Butadiene styrene (ABS) plastic find use in engineering plastic and is characterized with special mechanical properties.

Table M-VIII 2.1: Polyethylene/Polypropylene Market Coverage

Polymer Types	Grade	Market Coverage
HDPE	Film grade	Blown film with paper like quality, suitable for counter bags, carrier bags & wrapping films
	Pipe grade	Pipes PE-80/100 class, drinking water & gas pipes, waste pipes & sewer pipes their fitting etc.
	Large BM grade	Universal container grade, vol. approx. 1,500lit;heating oil storage tanks, transport containers
	Small BM grade	Disinfectant bottles, up to 2 lit, tubes for the cosmetics, containers from few ml up to 10 lit.
	Raffia grade	Stretched films and tapes for production of high strength knitted & woven sacks/bags/nets etc.

	Injection Molding	For transport and stacking crates, particularly bottle crates
LLDPE	Films	Garment bags, grocery sacks, liner, blends, trash bags, cast like film diapers etc.
	Rotomolding	Large industrial parts used indoors, large industrial /agricultural tanks, shipping drums, toys etc.
	Injection Molding	House wares, crates, master batches, pails, food container etc.
PP	Homo polymer	Injection molding (Battery cases, crates, furniture, house ware, luggage, sports/toys), Blow molding, Sheets, Tape/Raffia, FIBC, TQPP/BOPP films(food packaging, bottle labels etc.) Extrusion coatings etc.
	Random Copolymer	Thin walled injection moulding, low heat seal & high transparency films, Blow moulding, packaging parts, automotive parts etc.
	Impact Copolymer	Automotive parts (bumper, exterior trims, instrument panels, interior trims), Appliances, House wares, rigid packaging, thermoforming etc.

Source: Kapur et. al., 2008, courtesy: Journal of the petrotech society

CATALYST FOR POLYOLEFIN

There are four major families of catalyst used for olefin polymerization. Characteristics of catalyst is given in [Table M-VIII 2.2](#).

- Ziegler Natta
- Phillips(chrome)
- Metallocene
- Late transition metal catalyst

Table M-VIII 2.2: Characteristics of Polyolefin Catalyst

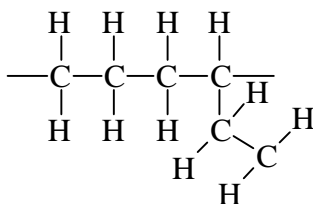
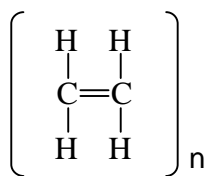
Type	State	Typical examples
Ziegler/ Ziegler-Natta	Heterogeneous Heterogeneous	$TiCl_3, TiCl_4 / MgCl_2$ $VCl_4, VOCl_3$
Phillips(chrome)	Heterogeneous	CrO_3 / SiO_2
Metallocene	Homogeneous Heterogeneous	Cp_2ZrCl_2 $Cp_2ZrCl_2/MgCl_2$
Late transition metalabsed	Homogeneous	Ni, Pd, Co, Fe, with diimine, and other ligands

Source: Kapur et al. 2008

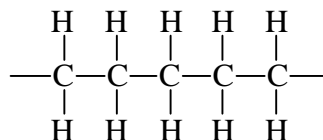
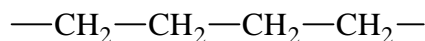
POLYETHYLENE

Polyethylene is one of the most widely used thermoplastic and its ever increasing demand is due to availability of monomer ethylene from naphtha and Gas cracker plant. First polyethylene plant in India was based on ethylene from molasses. Some of the other deriving force for fast growth and use of polyethylene are ease of processing the polymer, its relative cost, resistance to chemicals and its flexibility [Hatch & Matar, 1979]. A wide variety of polyethylene varying intensity and characteristics for wide range of application is available.

- Low density polyethylene (Branched) produced by high pressure
- LDPE 0.910 – 925 M.P. 105-110°C Crystallinity 60-70%
- Medium density MDPE 0.920 – 940
- High density HDPE 0.941 – 0.959 M.P. 125-130°C
- Crystallinity 75-90%
- Very few side chains. Produced by low pressure
- Linear High density to Ultra high density homopolymers
- Linear low density polyethylene (LLDPE) 0.916-0.940 a-olefin as comonomer density 70.941
- High molecular weight – High density P.E. (HMW-HDPE)



Branched



Linear

Molecular mass 200,000 – 500,000

Advantage: Low cost, excellent dielectric properties, moisture resistance, very good chemical resistance, available in food grade, processed by all thermoplastic methods.

Process Technology for Polyethylene: Several processes has been commercialised for the manufacture of polyethylene with varying densities. Various processes for manufacture of polyethylene are given in [Table M-VIII 2.3](#).

Table M-VIII 2.3: Various Polyethylene Processes

Process	Licensor	Process	Product
Innovene Process	B.P.Chemicals	Polymerisation in Fluidised bed reactor using Ziegler Natta catalyst or Chromium catalyst Temperature 75°C -110°C	LDPE,HDPE
Broster Process	BorealisA/S	Uses gas phase low pressure reactor. Ziegler Natta catalyst Comonomer hydrogen. Prepolymerisation in slurry loop reactor and fluidised bed reactor. Temperature 75°C -100°C	Bimodal and unimodal LLDPE, MDPE
High pressure free radicals process	Exxon Chemicals Co	Polymerisation occurs in autoclave reactors or Tubular reactor	LLDPE,
Speriline gas phase Process	Montell Technology Co	Polymerisation in Gas phase reactor using Ziegler natta catalyst	LLDPE, HDPE
Phillips Co, LPE process	Phillip Petroleum Co.	Polymerisation takes place in an isobutene slurry using very high activity proprietary catalyst in loop reactor.	Lineal polyethylene
UNIPOL PE process	Union carbide Corp	Low pressure polymerization in fluidised bed reactor at 25kg/cm ² and 100°C	LLDPE to HDPE
Sclairtech Process	Dupont	Polyethylene is produced by solution polymerization using ethylene gas and cyclohexane as solvent. Comonomer butane or Octane or both) Catalyst: Ziegler Natta catalyst	HDPE, MDPE, LLDPE

Source: Hydrocarbon processing petrochemical process 2003

UNIPOL Process

The process produces low density polyethylene and high density polyethylene using low pressure in gas phase. Wide range of polyethylene is produced using proprietary solid and slurry catalyst. The process produces wide range of polyethylene in a gas phase, fluidised bed reactor using proprietary solid and slurry catalyst. Gaseous ethylene, comonomer and catalyst are fed to fluidised bed reactor containing a fluidized bed of growing polymer particles operating at 25kg/cm^2 and 100°C . Polymer density is easily controlled from 0.915 to 0.97 g/cm^3 . Process flow diagram for polyethylene manufacture is given in [Figure M-VIII 2.1](#).

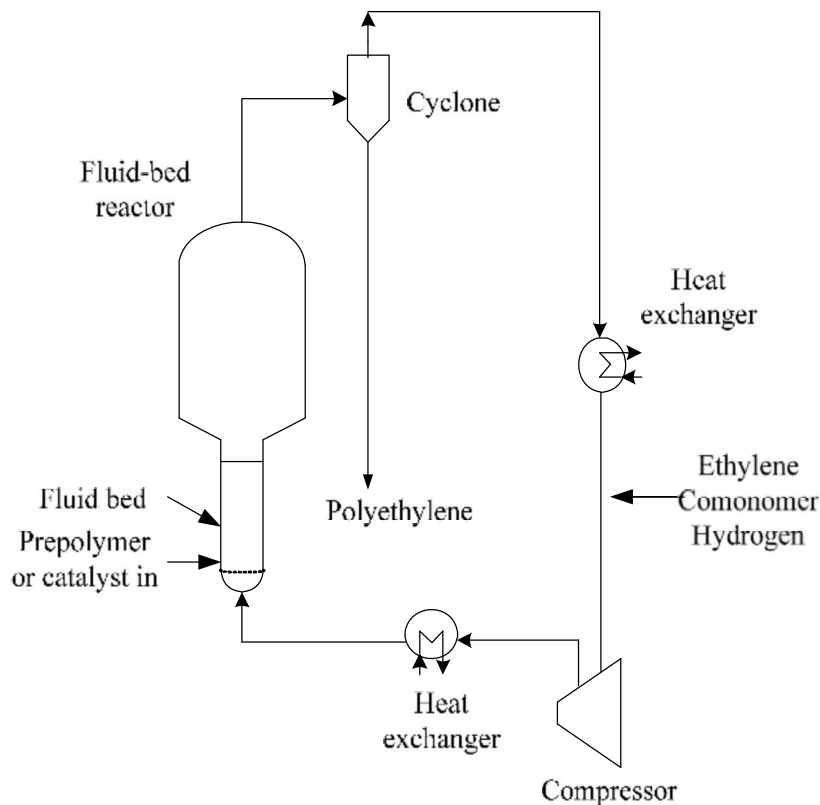






Figure M-VIII 2.1: Fluidized-bed Gas Phase PE Process.

DUPONT SCLAIRTECH Process

A broad range of polyethylene with density varying from 0.919 to 0.9605 g/cm^3 with varying melt index can be made by this process. The process can be divided into three major areas

-  Reaction area
-  Recycle/recovery Area,

-  Extrusion and Finishing
-  Dowtherm Vaporiser

The process involves solution polymerization of gaseous ethylene using cyclohexane solvent and comonomer butene or octane comonomer (incase of low density polymers). Zigler catalyst is used to polymerise ethylene using cyclohexane as solvent. A chain terminator is used to control the molecular weight at the reactor outlet a catalyst deactivator is added to terminate the reaction. The polymer is depressurized to flash off solvent, unreacted ethylene and comonomer from the molten polyethylene which are separated and recovered using distillation. The polymer after stripping the residual solvents fed to main extruder and resulting polymer pellets are dried and send to blender for homogenizing and finally conveyed to storage silo. In the process Dowtherm is added as heating media. Process flow diagram for the manufacture of polyethylene by sclairtech Process is given in [Figure M-VIII 2.2](#).

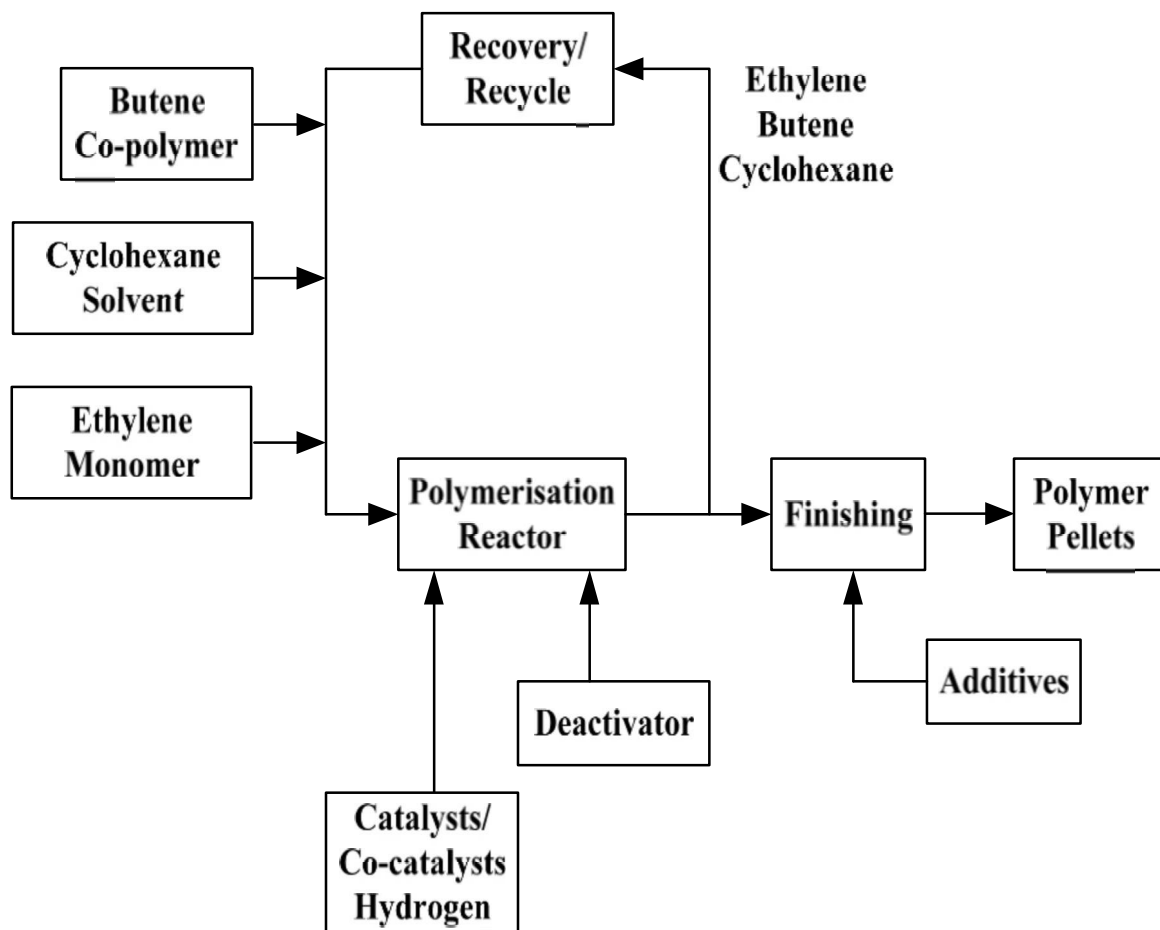


Figure M-VIII 2.2: LLDPE Process by SCLAIRTECH Process

POLYPROPYLENE

Polypropylene is a low density semi-crystalline stereo-regular polymer which exists in three forms- isotactic, syndiotactic and atactic. Polypropylene was discovered in March 1954 by Professor Giulio Natta demand of polypropylene is growing at a much faster rate due to its strong demand per capita consumption of polypropylene is given in [Figure M-VIII 2.3](#).

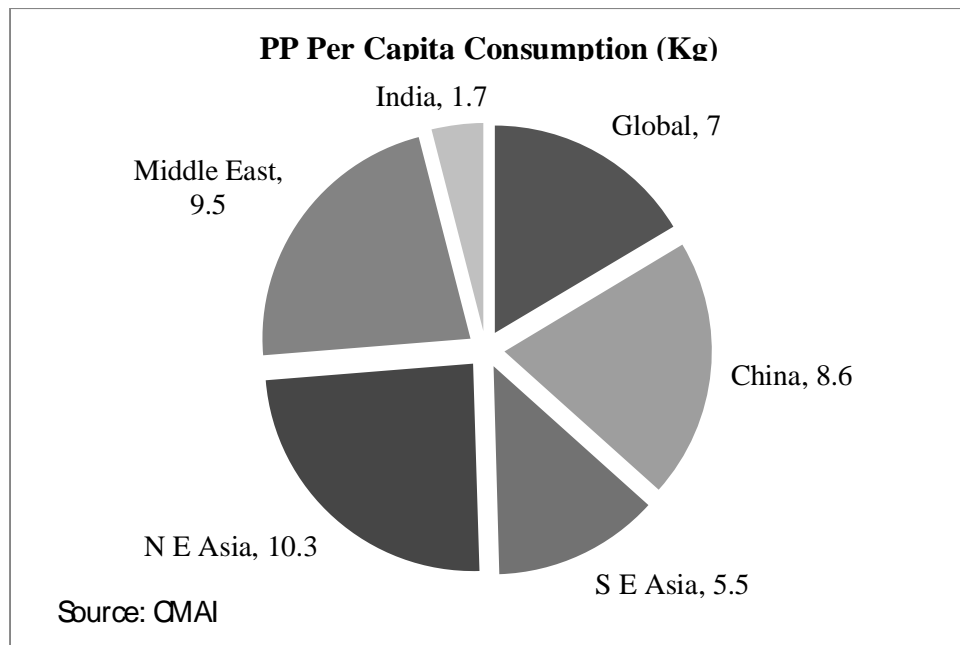


Figure M-VIII 2.3: Per capita Consumption of Polypropylene

Source: Shah,A., Indian propylene markets (India Petrochem 09)

Process Technology for Polypropylene

Polypropylene polymerisation process have undergone a number of revolutionary changes since the production of crystalline polypropylene were commercialised in 1957 by Motecatini in Italy and Hercules in U.S. Commercial polypropylene processes are based on low pressure processes using Ziegler-Natta catalyst that produces a product with an isotactic content of 90percent or more. Various processes for polypropylene manufacturing are given in [Table M-VIII 2.4](#). A typical polypropylene process is given in [Figure M-VIII 2.4](#).

Table M-VIII 2.4: Polypropylene Manufacturing Process

Process and licensor	Summary of process	Product
Borstar Polypropylene process Licensor Borealis A/S	Produced by bulk Polymerisation in loop reactor followed by final gas phase a fluidised bed reactor(temp. 80-90°C and 25-35 bar.	A versatile process and through the choice of reactor combinations, homopolymer, random copolymers, heterophasic copolymers and a very high rubber content heterophasic copolymers can be produced
Spheripol Process Montell technology	Homopolymer and Random copolymer polymerisation takes place in liquid propylene in a loop reactor. Heterophasic impact copolymerisation is done by adding a gas phase reactor.	Process produces propylene based polymers including homopolymer PP, random and heterophasic impact and specialty impact copolymers
Novolen Process Krupp Uhde GmbH	Polymerization is conducted in one or two gas phase reactors connected in series.	Polypropylene homopolymer, random copolymer and impact copolymer including Metallocene PP
Union carbide gas phase UNIPOL PP process	A wide range of polypropylene is made in a gas phase, fluidised bed reactor using proprietary catalyst	Homopolymer, random polymer and impact copolymer polypropylene
Sperizone Process Technology owner: Basell polyolefins	Sperizone Process is new proprietary gaseous technology based on a multi-zone circulating concept reactor	A broad range of propylene based polymer can be produced including mono and bimodal (medium/wide, very wide MWD)

Source: Petrochemical Processes 2003, Hydrocarbon Processing March 2003

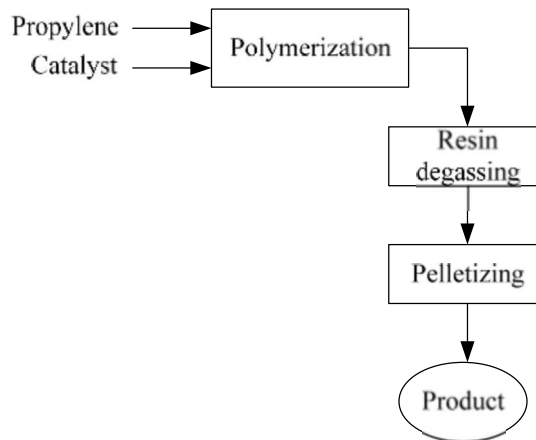


Figure M-VIII 2.4: Polypropylene Process

UNIPOL Process: The process produces homopolymer, random copolymer and impact copolymer polypropylene. Polymerisation takes place in a fluidized bed reactor using slurry reactor (TiCl_4 supported on MgCl_2 in slurry form in mineral oil. Co-catalyst TEAL, purified propylene and ethylene in case of random PP), purified H_2 and selectivity control agent is continuously fed to the reactor. Temperature 35°C and pressure 33 kg/cm^2 is maintained in the reactor. Figure M-VIII 2.5 illustrate the Unipol process for manufacturing of polypropylene.

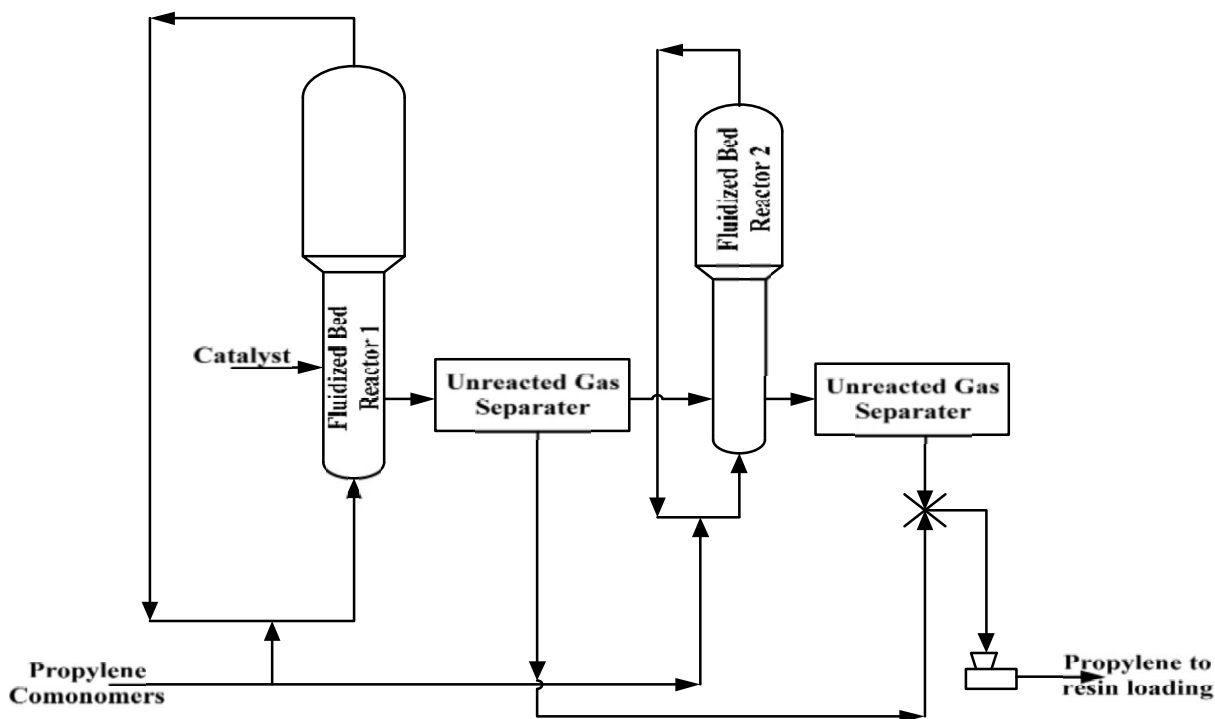


Figure M-VIII 2.5: Polypropylene by Unipol process

Sources: Petrochemical Processes” Hydrocarbon Processing, March 2003, Page 124

POLYSTYRENE

Polystyrene is an important thermoplastic. Polystyrene because of its ease of fabrication, low specific gravity, thermal stability and low cost, find wide applications in consumer durable goods, electronics, packaging toys, structural foams, wall tiles, shoe soles, blister packages, lenses, bottle caps, wire and cable sheathing, small jars, vacuum formed refrigerator liners,

containers of all kinds, transparent display boxes and automobile interior parts. When styrene is copolymerized with acrylonitrile, the polymer Styrene Acrylonitrile (SAN) resin has a higher tensile strength than polystyrene. Acrylonitrile butadiene styrene (ABS) polymer has special mechanical properties and find application as engineering plastics.

Styrene is produced by dehydrogenation of ethyl benzene which is made by alkylation of benzene. Ethylbenzene by UOP EB One process is produced by liquid phase alkylation of benzene using proprietary zeolite catalyst which can be regenerated repeatedly thereby avoiding significant catalyst disposal problems associated with other aluminium chloride catalyst. The process offers better product quality, better heat integration, low investment and a more rugged and reliable catalyst system.[<http://www.uop.com/aromatics/3020.html>]

Lumus/UOP Classic SM process: in this process styrene is made by catalytically dehydrogenating ethylbenzene in presence of steam in multistage reactor system. The reaction is carried out at high temperature under vacuum. The process uses a oxidative rehet technology. Polystyrene is clear transparent resin with a wide range of melting points and good flow properties which make it suitable for injection moulding [[Hatch & Matar,1979](#)]

Process Technology

There are two major processes for the production of polystyrene are NOVA's Polystyrene Technology and UOP Polystyrene Technology

NOVA's Polystyrene Technology: The process produces a complete range of general purpose (crystal) and impact resistant polystyrene. This is based on bulk continuous polymerization technology.

UOP Polystyrene Technology: this process is based on continuous bulk polymerization to produce a wide range of general purpose polystyrene, high impact polystyrene and SAN resin. A typical plant includes feed preparation, reactor section, devolatilisation section, monomer recovery section, water removal, product pelletizing and bulk resin handling.

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**Acrylonitrile, Acrylic Fibre,
Modified Acrylic Fibre,
Polyurethane**

ACRYLONITRILE, ACRYLIC FIBRE, MODIFIED ACRYLIC FIBRE, POLYURETHANE

Acrylic fibres are third largest class of synthetic fibre after polyester and nylons. Commercial acrylic fibre was developed by Dupont in US as Orlon while modified acrylic fibre was developed by Union carbide as Dynel. In acrylic fibre monomer is acrylonitrile while in case of modified acrylic fibre acrylonitrile is co polymerised with Vinylidene chloride vinyl chloride. The halogenated monomers impart flame resistance and are suitable for home furnishing, protective coatings, sleepwear, and hospital blankets. Characteristics of acrylic fibre and modified acrylic fibre are mention in [Table M-VIII 7.1](#).

Acrylic fibres are soft, light weight, durable strong, high crease recovery, color fastness to both washing & sunlight, easy care- easy laundry & low maintenance cost, high abrasion resistance, good aesthetics-high lustre, good wicking action- helps in quick transfer of moisture & sweat resulting in quick drying, no allergic and non toxic, resistance to mild & insects, oils, chemicals. It is very resistant to deterioration from sunlight exposure.

Polyurethane are another important polymer which find application in manufacture of flexible, high resilience foam seating; rigid foam insulation panels, microcellular foam seals and gaskets; durable elastomeric wheels tires; automotive suspension bushings, electrical potting compounds; high performance adhesives; surface coatings and surface sealants; synthetic fibre

Table M-VIII 7.1: Major Synthetic Fibers and Their Characteristics

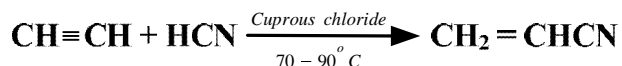
Name of the synthetic fiber	Monomer	Basic chemicals	Properties of the synthetic fiber			Characteristics
			Density	Moisture regain	Melting point	
Acrylic Fiber	Acrylonitrile	Propylene, ammonia	1.17	1.5-2.5	Sticking point= 235 °C	Silk like lustre, good resistance to weathering, alkalies and acids, high bulking, tensile strength 2-3 gm/denier. Elongations at break 16-21%.
Modified Acrylics	Acrylonitrile, vinyl chloride, vinylidene chloride	Propylene, ammonia, ethylene	-	1.5-2.5	Sticking point= 235 °C	Good resistance to weathering, alkalies and acids, high bulking, good resistance to combustion.
Polypropylene	Propylene	Propylene	0.85-0.94	< 0.1	168-171 °C	Good resistance to bacteria, chemical and water.

ACRYLONITRILE(CH₂=CH-CN)

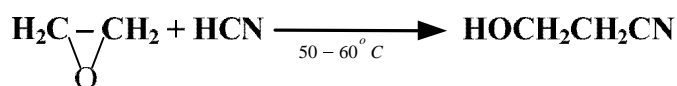
Acrylic nitrile is one of the important monomer for manufacture of acrylic fibres, however, earlier routes of acrylonitrile manufacture by acetylene, ethylene oxide or acetaldehyde route has being replaced by propylene route due to availability of cheaper propylene from steam cracker plant. This involves ammono-oxidation of propylene. Other uses of acrylonitrile are in the manufacture of nitrile rubber, ABS and SAN plastics, adiponitrile and acrylamide. In addition it

is also used in the manufacture of acrylates, intermediates for flocculants, pharmaceuticals, antioxidants, dyes and surface active agents [Chemical Industry digest March 1996, p. 22]. Various route of acrylonitrile manufacturing shown in Figure M-VIII 7.1.

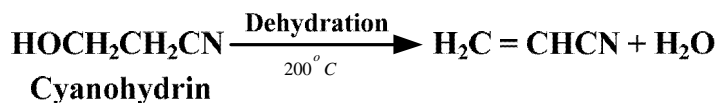
Acetylene Route



Ethylene Oxide Route

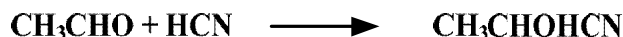


Epoxide



Acrylonitrile (CH₂=CH-CN)

Acetaldehyde Route



Propylene Route

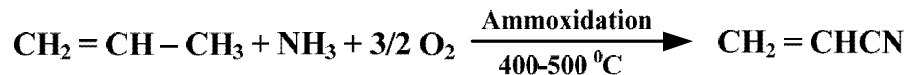


Figure M-VIII 7.1: Various Routes for the Manufacture of Acrylonitrile

Acrylonitrile by Ammoxidation of Propylene

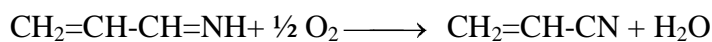
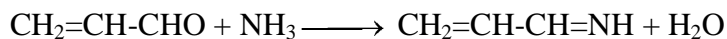
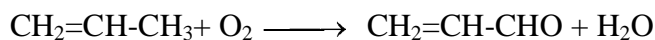
A typical acrylonitrile plant consists of reactor section, acrylonitrile recovery section, acrylonitrile purification section and HCN purification section. Propylene, ammonia and air are fed to fluidised bed catalytic reactor where ammoxidation of propylene – a highly exothermic reaction occurs. Manufacturing process technology shown in [Figure M-VIII 7.2](#).

Process steps involve are

- Catalyst preparation: bismuth and molybdenum
- Mixing of propylene, ammonia and oxygen in 1:1:6
- Reaction section: Acrylonitrile, acetonitrile, hydrogen cyanide, unreacted mixture of propylene, ammonia and oxygen are fed to fluidised bed reactor. Various products from reactor are ammonia and oxygen. Reaction is highly exothermic.
- Removal of ammonia
- Absorption of absorbable component from ammonia free gas in water to separate the non-condensable and unconverted propylene, propane, nitrogen, CO and CO₂.
- Stripping of organic components and separation of HCN
- Separation of Acrylonitrile and acetonitrile which are close boiling compounds. And are separated by extractive distillation using water as solvent. A dilute solution of acrylonitrile is separated which is recovered and concentrated
- Purification of acetonitrile
- Final purification of acrylonitrile

Reactions:

Formation of acrylonitrile occurs by the following reaction:



Overall reaction:



Side reactions:

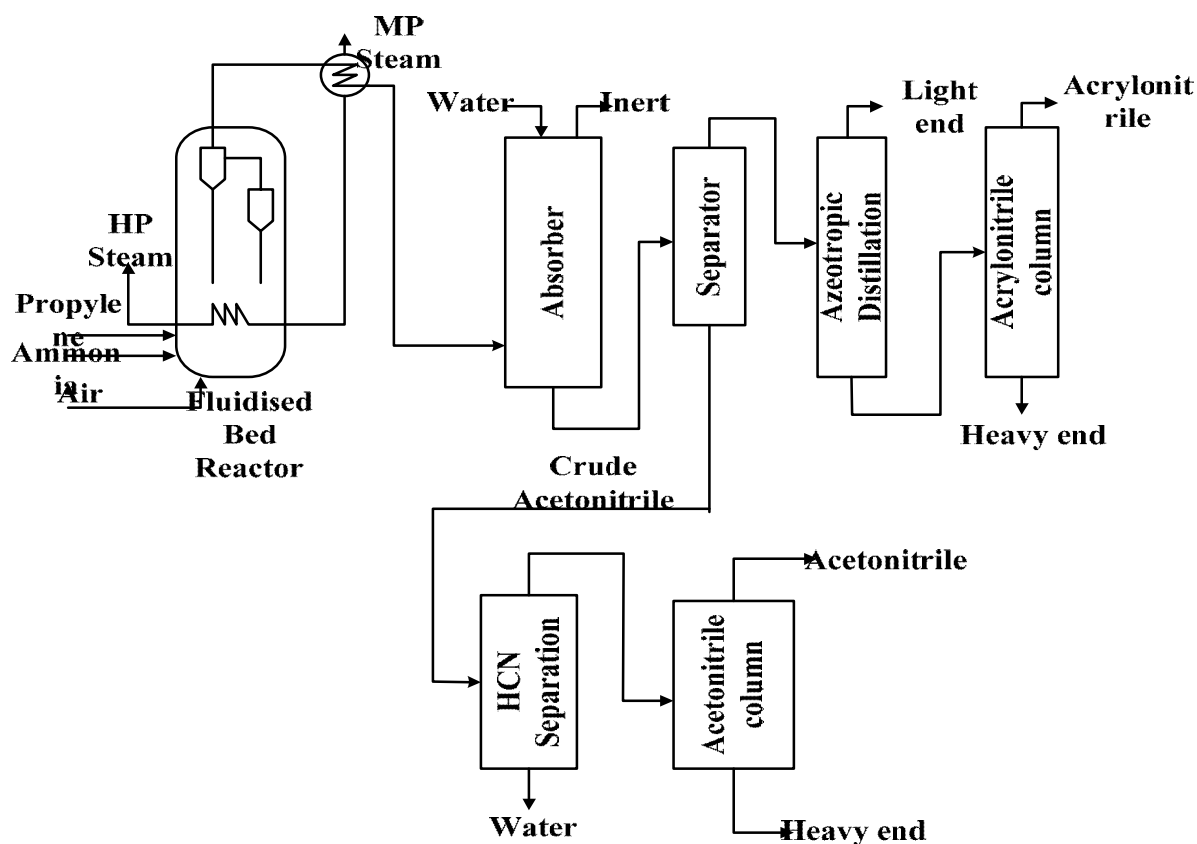
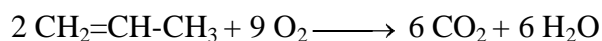
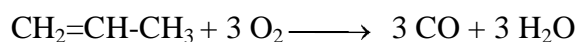
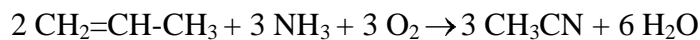


Figure M-VIII 7.2: Process Technology of Acrylonitrile Manufacture

ACRYLIC FIBRE MANUFACTURE

Acrylic fibres are third largest class of synthetic fibre after polyester and nylons. Commercial acrylic fibre was developed by Dupont in US as Orlon while modified acrylic fibre was developed by Union carbide as Dynel.

Process Technology

Manufacturing process shown in [Figure M-VIII 7.3](#). The manufacturing process can be broadly divided into two parts:

Polymerisation: Polymerisation includes copolymer composition, catalyst system, polymerisation reaction and monomer recovery. Major polymerisation processes are bulk polymerisation, suspension polymerisation, emulsion polymerisation and solution polymerisation. Most of the acrylic polymers manufactured for fiber grade are made through suspension polymerisation that gives high percentage of conversion, better product whiteness, shorter residence time and easy control of polymerisation. Emulsion polymerization is used in case of modified acrylic fibre. Inorganic compounds such as persulphate, chlorates or hydrogen peroxide are used as radical generators.

Redox initiation is normally used in production of acrylic fibre. The most common redox system consists of ammonium or potassium persulphate (oxidizer), sodium bisulphate (reducing agent) and ferric or ferrous ion (catalyst) [[Capone, G.J., Masson, J.C. Fibre Acrylic in “ Kirk-Othmer encyclopedia of Chemical technology, Fifth edition Volume 11 Wiley Intersciences](#)]

Spinning: Spinning includes solution/dope preparation, spinning techniques and finishing operation including after treatment, cutting and bailing.

Dry Spinning: In dry spinning of acrylic fibre dimethyl formamide (DMF) is used. The DMF spin dope contains the polymer in the DMF, thermal stabilizers, delustrant. It passed through spinnerette placed at top of the solvent removal tower. The DMF evaporated by circulating inert gas through tower at about 300-35 °C to remove the solvent

Wet Spinning: In wet spinning sodium thiocyanate are commonly used as solvent. Wet spinning fiber is spun into a liquid bath containing a solvent non-solvent mixture called coagulant. Non-solvent is usually water. The fibre emerging from spin bath are washed and dried followed by cutting and bailing.

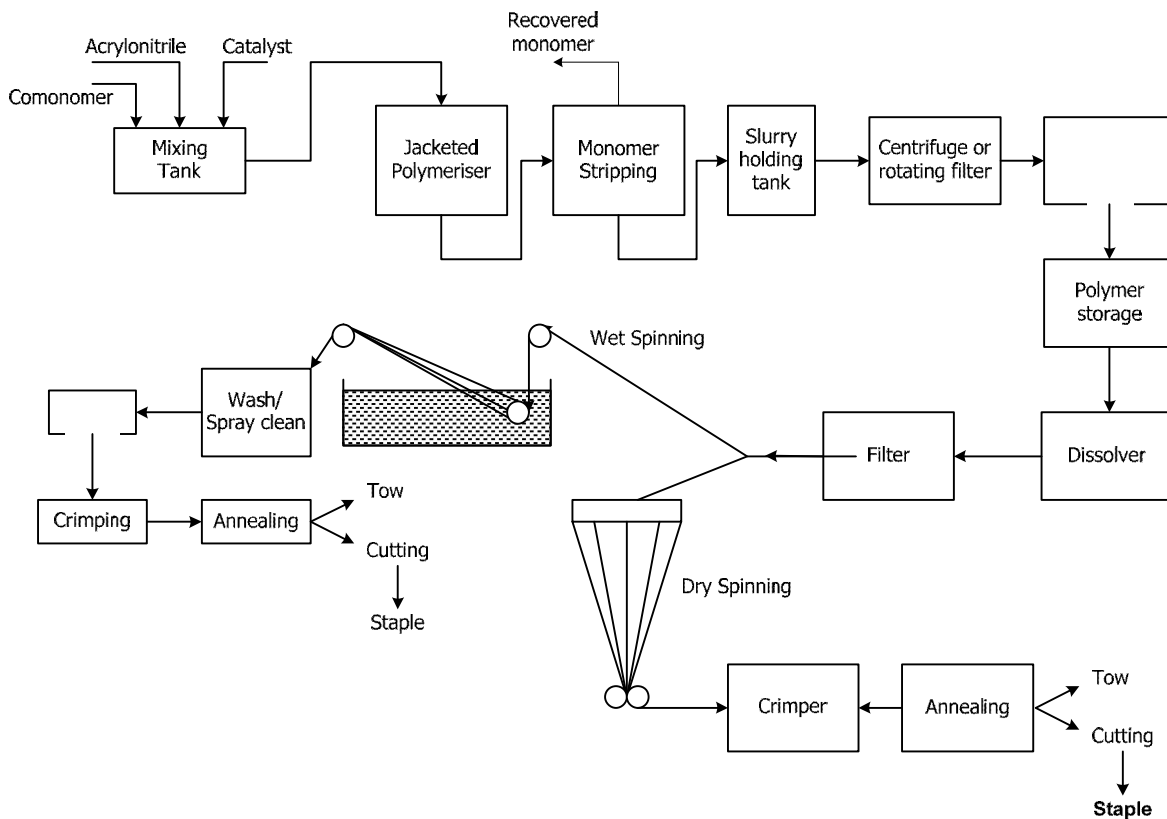


Figure M-VIII 7.3: Process Flow Diagram of Manufacture of Acrylic Fiber
 Source: Mall, I.D, Petrochemical Process technology, 2007

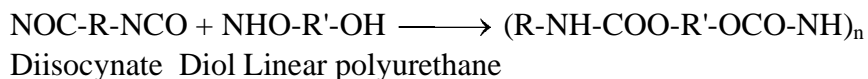
POLYURETHANE

The polyurethanes which were discovered by Otto Bayer and co-workers in 1937 [Riegel, 1997] are versatile class of thermosetting polymers and offer the elasticity of rubber combined with toughness and durability of metal. Worldwide demand for polyurethane expected to grow at CAGR of 5.8percent from 12.0 million tones tones in 2010 to 116.88 million tones in 2016, with Asia pacific region accounting for over 60percent of this figure, according to GBI research. The global market value of polyurethane will rise in the coming years, with thermal insulation becoming a key material application. According to GBI research flexible and rigid polyurethane foams made up the bulk of the total endues segment in 2010, accounting for 60percent of the full amount [Chemical Industry Digest July 2012, p.29].

Polyurethane is polymer formed by combining two or more isocyanate functional group and two or more hydroxyl groups. The alcohol and isocyanate groups combine to form a urethane linkage. Polyurethanes made by addition of polyols and polyfunctional isocyanates. Commonly

used isocyanates are toluene di-isocyanate (TDI), diphenyl methane diisocyanate (MDI), Hexamethylene di-isocyanate (HDI).

Polyols may be either polyether polyols or polyester polyols. However, polyether polyols are more commonly used. Catalyst used in polyurethane manufacture are—aliphatic and cycloaliphatic tertiary amines and organic tin compounds. Typical reaction involved by reaction of poly isocyanates and poly hydroxy compounds is:



POLYURETHANE FOAM

Poloyuretane rigid foam are characterized by good structural strength, excellent adhesion to most substance, processing flexibility and long life. Rigid polyurethane foams are most widely preferred insulation and find application in refrigerator, manufacture of thermo-ware, cold sore panel, refrigerated trucks and wagons. A rigid polyurethane foam is a cellular polymer in which the individual small cells are filled with a gaseous blowing agent which imparts the remarkably low thermal conductivity to these foams [Fonseca, 1993].

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7. Riegel, 1997

1. POLYMERS

1.1 GENERAL INTRODUCTION AND ITS SCOPE

Polymers form a very important class of materials without which the life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, and in adhesives and adhesives tapes. The word polymer is derived from greek words, poly= many and mers= parts or units of high molecular mass each molecule of which consist of a very large number of single structural units joined together in a regular manner. In other words polymers are giant molecules of high molecular weight, called macromolecules, which are build up by linking together of a large number of small molecules, called monomers. The reaction by which the monomers combine to form polymer is known as polymerization [1]. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer.

1.2 HISTORICAL DEVELOPMENT OF POLYMERS

Polymers have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharides play crucial roles in plant and animal life. From the earliest times, man has exploited naturally-occurring polymers as materials for providing clothing, decoration, shelter, tools, weapons, writing materials and other requirements. However, the origin of today's polymer industry is commonly accepted as being the nineteenth century when important discoveries were made concerning the modification of certain natural polymers. In eighteenth century, Thomas Hancock gave an idea of modification of natural rubber through blending with ceatrain additives. Later on, Charles Goodyear improved the properties of natural rubber through vulcanization process with sulfur. The Bakelite was the first synthetic polymer produced in 1909 and was soon followed by the synthetic fiber, rayon, which was developed in 1911. The systematic study of polymer science started only about a century back with the pioneering work of Herman Staudinger. Staudinger has given a

new definition of polymer. He in 1919 first published this concept that high molecular mass compounds were composed of long covalently bonded molecules.

1.3 CLASSIFICATION OF POLYMERS

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless forms and numbers because of very large number and type of atoms present in their molecule. Polymer can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymer can be classified in different ways, which are summarized in Table 1.1, whereas, important and broad classification of polymers are described in the next section.

Table 1.1: Classification of Polymers

Basis of Classification	Polymer Type
Origin	- Natural, Semi synthetic, Synthetic
Thermal Response	- Thermoplastic, Thermosetting
Mode of formation	- Addition, Condensation
Line structure	- Linear, Branched, Cross-linked
Application and Physical Properties	- Rubber, Plastic, Fibers
Tacticity	- Isotactic, Syndiotactic, Atactic
Crystallinity	- Non crystalline(amorphous), Semi-crystalline, Crystalline
Polarity	- Polar, Non polar
Chain	- Hetro, Homo-chain

1.3.1 Origin

On the basis of their occurrence in nature, polymers have been classified in three types [2]:-

A. Natural polymer:- The polymers, which occur in nature are called natural polymer also known as biopolymers. Examples of such polymers are natural rubber, natural silk, cellulose, starch, proteins, etc..

B. Semi synthetic polymer:- They are the chemically modified natural polymers such as hydrogenated, natural rubber, cellulosic, cellulose nitrate, methyl cellulose, etc.

C. Synthetic polymer:- The polymer which has been synthesized in the laboratory is known as synthetic polymer. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone, etc..

1.3.2 Thermal Response

On the basis of thermal response, polymers can be classified into two groups [3]:-

A. Thermoplastic polymers:- They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions. Example of such polymers are Polyolefins, nylons, linear polyesters and polyethers, PVC, sealing wax etc..

B. Thermosetting polymers:- Some polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. For example, Phenolic, resins, urea, epoxy resins, diene rubbers, etc.

1.3.3 Mode of Formation

On the basis of mode of formation, polymers can be classified as [2]:-

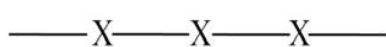
A. Addition polymers:- They are formed from olefinic, diolefinic, vinyl and related monomers. They are formed from simple addition of monomer molecules to each other in a quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers are polyethylene, polypropylene, polystyrene.

B. Condensation polymer:- They are formed from intermolecular reactions between bifunctional or polyfunctional monomer molecules having reactive functional groups such as $-OH$, $-COOH$, $-NH_2$, $-NCO$, etc..

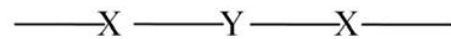
1.3.4 Line Structure

On the basis of structure, polymers are of three types.

A. Linear polymer:- If the monomer units are joined in a linear fashion, polymer is said to be linear polymer.

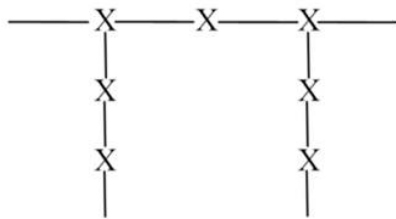


Linear Homopolymer

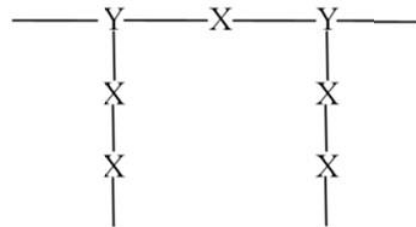


Linear Copolymer

B. Branched polymer:- When monomer units are joined in branched manner, it is called branched polymer.

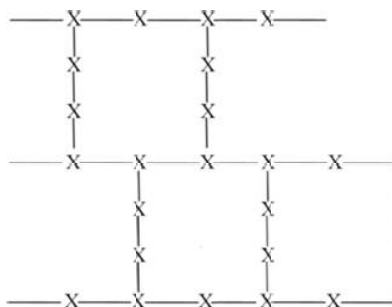


Branched Homopolymer

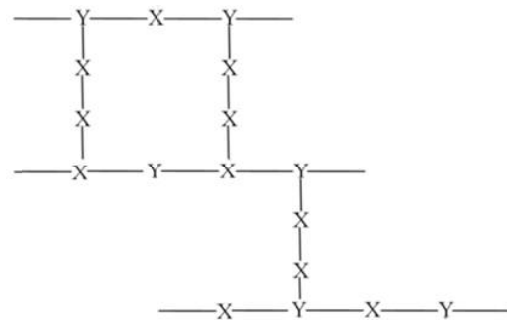


Branched Copolymer

C. Cross linked polymer:- A polymer is said to be a cross linked polymer, if the monomer units are joined together in a chain fashion.



Cross linked Homopolymer



Cross linked Copolymer

1.3.5 Application and Physical Properties

Depending on its ultimate form and use a polymer can be classified as [2]:-

A. Rubber (Elastomers):- Rubber is high molecular weight polymer with long flexible chains and weak intermolecular forces. They exhibit tensile strength in the range of 300-3000 psi and elongation at break ranging between 300-1000% . Examples are natural and synthetic rubber.

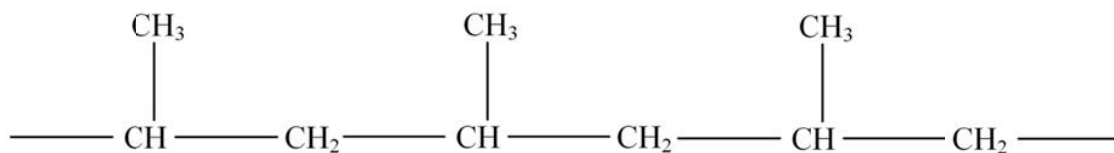
B. Plastics:- Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. These are usually much stronger than rubbers. They exhibit tensile strength ranging between 4000-15000 psi and elongation at break ranging usually from 20 to 200% or even higher. The examples of plastics are, polyethylene, polypropylene, PVC, polystyrene, etc.

C. Fibers:- Fibers are long- chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They also have high tensile strength ranging between 20,000- 150,000 psi., are light weight and possess moisture absorption properties.

1.3.6 Tacticity:-

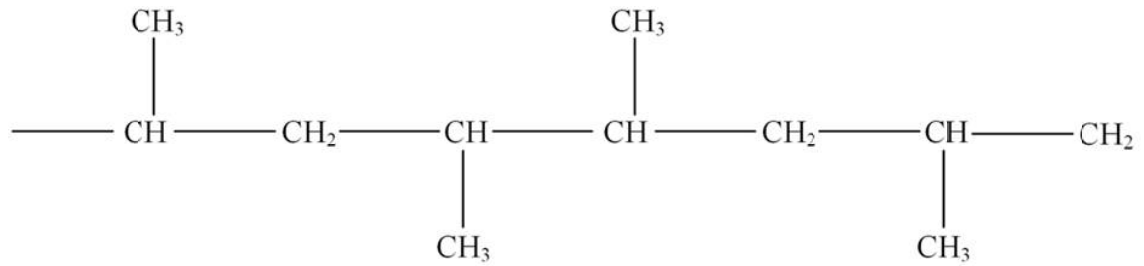
It may be defined as the geometric arrangement (orientation) of the characteristic group of monomer unit with respect to the main chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups:-

A. Isotactic polymer:- It is the type of polymer in which the characteristic group are arranged on the same side of the main chain.



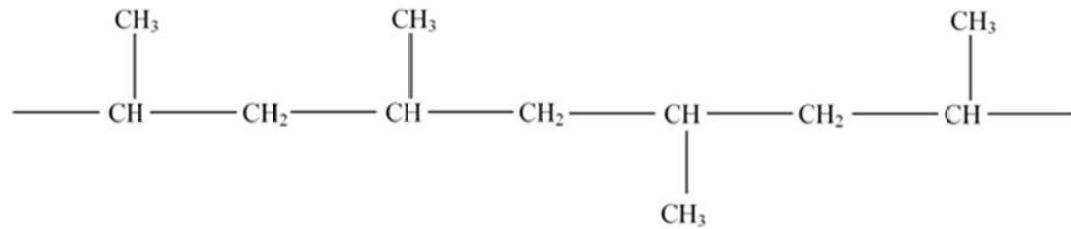
Isotactic Polypropene

B. Syndiotactic polymer:- A polymer is said to be syndiotactic if the side group (characteristic group) are arranged in an alternate fashion.



Syndiotactic Polypropene

C. Atactic polymer:- A polymer is said to be atactic, if the characteristic groups (side group) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and more elasticity.



Atactic Polypropene

1.4 BIOCOMPOSITES

Composite are attractive materials because they combine material properties in ways not found in nature. Such materials often result in lightweight structures having high stiffness and tailored properties for specific applications, thereby saving weight and reducing energy needs [4-6]. Fiber-reinforced plastic composites began with cellulose fiber in phenolics in 1908, later extending to urea and melamine, and reaching commodity status in the 1940s with glass fiber in unsaturated polyesters. From guitars, tennis racquets, and cars to microlight aircrafts, electronic components, and artificial joints, composites are finding use in diverse fields.

Composite materials derived from biopolymer and synthetic fibers such as glass and carbon also come under biocomposites. Biocomposites derived from plant-derived fiber (natural/biofiber) and crop/bioderived plastic (biopolymer/bioplastic) are

likely to be more ecofriendly, and such biocomposites are sometimes termed “green composites” [4].

1.4.1 Natural/Biofibers as Reinforcements in Biocomposites

The world’s supply of natural resources is decreasing and the demand for sustainable and renewable raw materials continues to rise. Biofiber-reinforced composites represent a potential nontraditional, value-added source of income to the agricultural community.

Jute is from India and Bangladesh; coir is produced in the tropical countries of the world, with India accounting for 20% of the total world production; sisal is also widely grown in tropical countries of Africa, the West Indies, and the Far East, with Tanzania and Brazil being the two main producing countries; kenaf is grown commercially in the United States; flax is a commodity crop grown in the European Union as well as in many diverse agricultural systems and environment throughout the world, including Canada, Argentina, India, and Russia. Flax fiber accounts for less than 2% of world consumption of apparel and industrial textiles, despite the fact that it has a number of unique and beneficial properties. Hemp originated in Central Asia, from which it spread to China, and is now cultivated in many countries in the temperate zone. Ramie fibers are the longest and one of the strongest fine textile fibers mostly available and used in China, Japan, and Malaysia.

Most of the polymers by themselves are not suitable for load-bearing applications due to their lack of sufficient strength, stiffness, and dimensional stability. However, fibers possess high strength and stiffness. Unfortunately, they are not suitable for use in load-bearing applications by themselves because of their fibrous structure. In fiber-reinforced composites, the fibers serve as reinforcement by giving strength and stiffness to the structure while the plastic matrix serves as the adhesive to hold the fibers in place so that suitable structural components can be made. A broad classification (nonwood and wood fibers) of natural fibers is represented schematically in Fig. 1.1.

Currently several nonwood fibers (e.g., hemp, kenaf, flax, and sisal) are being utilized commercially in biocomposites in combination with polypropylene for

automotive applications. Now from need of society and research point of view it is much important to work on leaf based nonwood fibers [4].

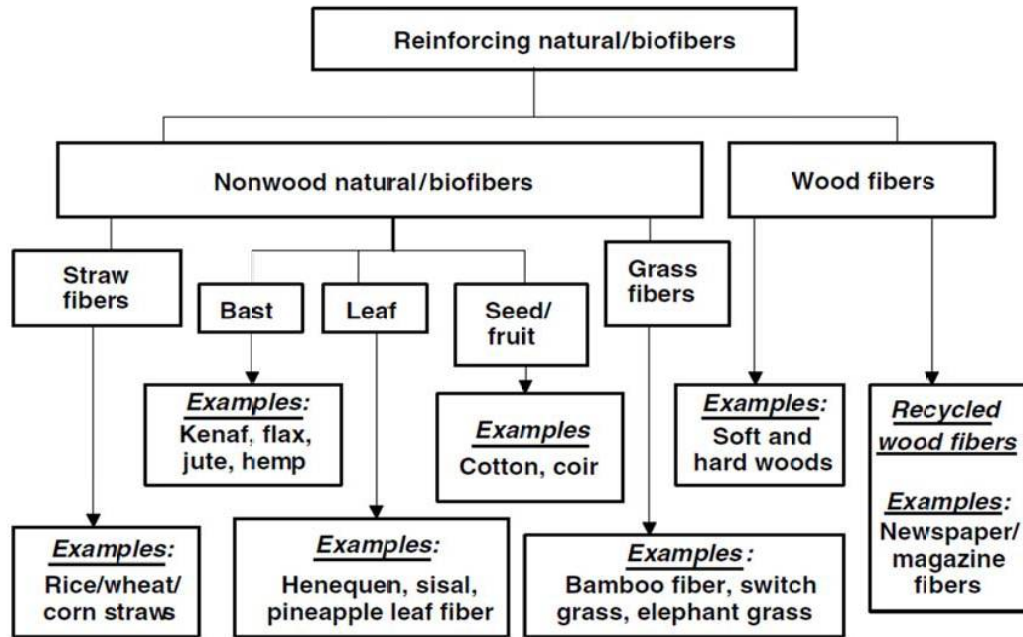


Fig 1.1: Schematic representation of reinforcing natural/biofibers classification [4]

1.5 MECHANISM OF POLYMERIZATION

The linking together of a large number of small molecules termed as monomers with each other to form a macromolecule or polymer molecule through chemical reactions is termed as polymerization. It can also be defined as the fundamental process by which low molecular weight compounds are converted into high molecular weight compounds. In addition to the structural and compositional differences between polymers Flory stressed the very significant difference in the mechanism by which polymer molecules are build up. Although Flory continued to use the terms "addition polymerization" (polymerization by repeated addition processes) and "condensation polymerization" (polymerization by repeated condensation processes, i. e., with the elimination of small molecules) in his discussion of polymerization mechanism. The current terminology classifies polymerization into step growth polymerization and chain growth polymerization [7].

The degree of polymerization is related to the molecular mass (M) of the polymer and is given by the equation,

$$D_p = \frac{M}{m} \quad 1.1$$

where, m is the mass of the monomeric unit.

1.5.1 Condensation Polymerization or Step-growth Polymerization

Condensation Polymerization is a chemical reaction in which polymer is formed and a small molecule of by-product with a lower molecular weight is released. The by-product eliminated is called as condensate. The reaction can take place between two similar or different monomers. It is also called as step-growth polymerization [8-9].

1.5.2 Addition Polymerization or Chain Polymerization

In addition polymerization, two or more molecules of monomers attach together to form a polymer. In this polymerization, there is no elimination of any molecule. It is a chain reaction and no by product is released. It is obtained by linking together the monomer molecules by a chain reaction to give a polymer whose molecular weight is exactly an integral multiple of that of the monomer as in the case of polyethylene obtained by polymerization of ethylene. Only a single monomer is involved in addition polymerization and hence the polymer is homopolymer and contains the same monomer units. Addition polymerization reaction is usually induced by light, heat or a catalyst for opening the double bond of the monomer and creating the reactive sites [9].

1.6 CHARACTERIZATION OF POLYMERS

It is comparable to the synthesis of organic compound, composites, biocomposites without a subsequent characterization of its various properties. Synthesized material characterization is therefore of very great importance. Some of the important aspects related to characterizations have been described in this section.

1.6.1 Molecular Weight and its Distribution

The molecular weight of a polymer is of prime importance in the polymer's synthesis and application. It is important because it determines many physical properties. The term molecular weight is a ratio of the average mass per formula unit of substance to 1/12 th of an atom of ^{12}C . Molecular weight (MW) and its distribution (MWD) has a considerable effect on macroscopic properties of polymer such as toughness, tensile strength, adherence and environmental resistance, etc. [10]. A simple chemical has fixed molecular weight but when we discuss about the molecular weight of polymer, we mean something different from that which applies to small sized compounds. Since polymers are mixture of molecules of different molecular weight, the molecular weight is expressed in the term of "average" value. This average molecular weight is basically based on either average number of repeating units, known as number average molecular weight, or average weight, known as weight average molecular weight. The number average molecular weight is obtained from the number n_i of macromolecules for each degree of polymerization P_i by taking for each degree of polymerization the product of the number of polymer molecules and their degree of polymerization $n_i p_i$ and dividing the sum of these product by the total number of monomers N_o :

$$\overline{M}_n = \frac{\sum_{i=1}^{\infty} n_i P_i}{N_o} \quad 1.2$$

The weight average molecular weight \overline{M}_w is obtained in a similar manner from mass m_i of each degree of polymerization P_i according to the following equation:

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} m_i P_i}{M_o} \quad 1.3$$

When the molecular weight distribution is very narrow, the number average and weight average molecular weights are essentially equal. When the distribution is broad, the weight average molecular weight is considerably greater than the number

average molecular weight and broader the distribution, the greater the difference between them as shown in Figure 1.2. From these molecular averages the molecular weight distribution is represented by their ratio $\frac{\overline{M}_w}{\overline{M}_n}$

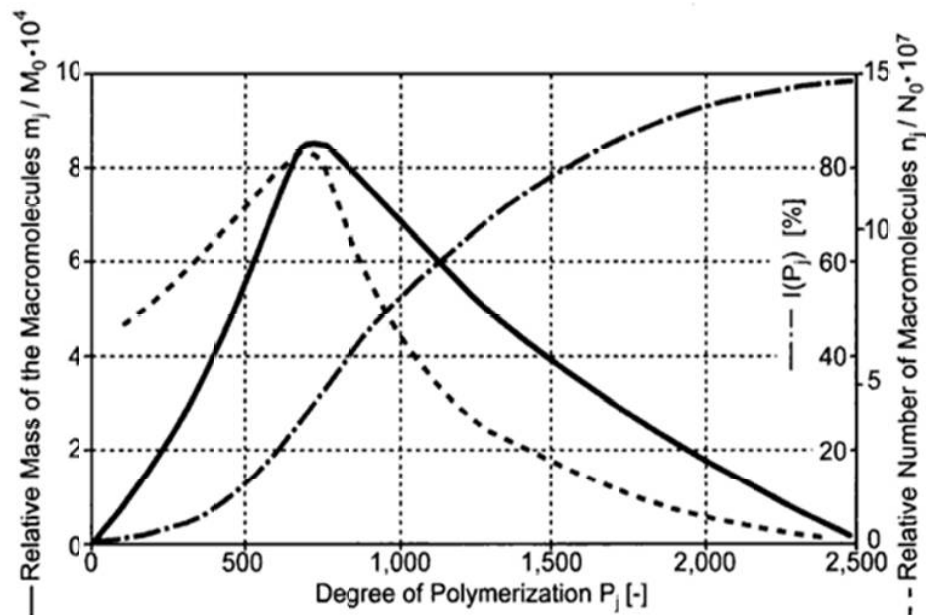


Fig1.2: Schematic representation of the weight average and number average molecular weight distribution as a function of the degree of polymerization [11].

Tensile and impact strengths increase with molecular weight. The melt viscosity of the polymer, however, shows a different trend. At very high molecular weights, the melt viscosity rises more steeply than at low molecular weights. Molecular weight distribution also affects properties of polymers. To know of a polymer properly, we must have a good knowledge of both the average molecular weight as well as its dispersion patterns.

1.6.2 Crystallization

Crystallization in polymer has always been the subject of great scientific and academic interest, since polymers are known to exhibit a variety of structures at various length scales, such as unit cell, lamella, and spherulites. It is an interesting property related to phase transition which determines the final properties of many technologically relevant and scientifically exciting systems [12, 13]. Polymer

crystallization controls the structural formation process of polymeric materials and thereby dominates the properties of final polymer product. Polymer crystallization is usually divided into two separate processes : primary nucleation and crystal growth [14].

In general, a crystalline phase must primarily nucleate. The fundamental kinetics of nucleation are often complicated to determine because the rate of heterogeneous nucleation at defects, impurities, and surfaces is much faster than the homogeneous rate of nucleation within the pure bulk liquid. After a nucleus forms, the kinetics of crystal growth determines the overall rate of the phase transformation. For growth from solid or liquid solutions, the rate limiting step in the kinetics is often mass diffusion. For crystal growth from a melt, heat transfer plays an important role for metals, ceramics, and semiconductors, but for large molecules and polymers, the microscopic kinetics associated with attaching a large molecule or polymer segment to the growing crystal are typically the most important consideration [14].

The crystalline and amorphous components influence polymer properties. Actually, crystallinity of a polymer sample is expressed in terms of that fraction of the sample which is crystalline. The definition of degree of crystallinity is, of course, based on the premise that crystalline and non-crystalline components of a polymer can co-exist". The highest crystallinity is generally associated with polymers which have a simple unit cell structure and a relatively high degree of molecular order. The overall property (Q) of a partially crystalline polymer can be expressed as a sum of its two components as:

$$Q = Q_c + Q_a \quad 1.4$$

where Q_c and Q_a are contributions of the crystalline and amorphous components of the sample, respectively. A number of methods can be used to detect crystallinity and estimate its degree: X-ray diffraction, infrared-absorption spectroscopy, polarized light microscopy, density, differential thermal analysis and nuclear magnetic resonance spectroscopy, etc.. Accurate and undisputed measurement of the volume fraction of crystallinity in a polymer is not easily accomplished because each of the method of measurement mentioned above is concerned with a different physical aspect of material. Nevertheless, the great practical consequences of crystallinity and

orientation on mechanical properties dictate that at least relative changes in these factors be observed by whatever means are applicable, and that these be correlated with changes in processing and fabrication methods and with end-use behaviour. It was found that the preparation method of samples influence the morphology and crystallization behaviour of blends.

1.6.3 Glass Transition Temperature

In the study of polymers and their applications, it is important to understand the concept of the glass transition temperature T_g . The glass transition is a phenomenon observed in linear amorphous polymer. It occurs at fairly well defined temperature when the bulk material ceases to be brittle and glassy in character and become less rigid and more rubbery. The knowledge of T_g is essential in the selection of materials for various applications.

Many Physical properties change profoundly at the glass transition temperature, including mechanical properties and electrical properties. All of these are dependent on the relative degree of freedom for molecular motion within a given polymeric material and each can be used to monitor the point at which the glass transition occurs [15-17].

1.7 MECHANICAL PROPERTIES OF POLYMERS

To study the necessary set of valuable properties, polymers differing from one another by their chemical structure and properties are usually mixed together, either homogeneously or heterogeneously. The mechanical properties of inhomogeneous mixture are worse than those of individual polymers, while the mechanical properties of homogeneous mixture are good.

Polymers can exhibit the features of glassy, brittle solid or an elastic rubber, or that of a viscous liquid, depending on the temperature and time scale of measurement. The studies on mechanical properties of polymer can, therefore, be carried out by subjecting them to some form of mechanical stress either continuous or in a periodic manner at different rate. Some of the important properties of polymers with regard to their use as engineering material are tensile strength, compressive and flexural strength, hardness, creep, fatigue resistance and impact resistance.

Toughness of a polymer is the ability to absorb mechanical energy without fracturing. The property such as tensile strength is the maximum amount of tensile load per unit area a material can withstand, while the tensile elongation gives the measure of increase in length in response to a tensile load expressed as a percent of the original length. Elongation at break is the maximum elongation the plastic can undergo.

Engineering applications of polymers are governed to a great extent by strain hardening considerations. The designer using polymeric materials must, therefore, understand their mechanical behaviour with respect to the maximum permissible strains to avoid failure. As for most materials, a simple tensile stress-strain curve provides a good start towards understanding the mechanical behaviour of a particular polymer. This curve is usually established by continuously measuring the force developed as the sample is elongated at constant rate of extension until it breaks. Portions of the curve in Fig.1.3 represent the stress-strain behaviour of any polymer and are used to define several useful quantities. The initial slope provides a value for Young's modulus (or the modulus of elasticity) which is a measure of stiffness. The curve also gives yield stress, strength and elongation at break. The area under the curve or work to break is a rough indication of the toughness of the polymeric material. The stress at the knee in the curve (known as the yield point) is a measure of the strength of the material and resistance to permanent deformation. The stress at the breaking point, commonly known as ultimate strength, is a measure of the force required to fracture the material completely.

A hard, brittle material such as an amorphous polymer far below its T_g , usually has an initial slope indicative of very high modulus, moderate strength, a low elongation at break, and a low area under the stress-strain curve (Fig. 1.4). Polymeric materials showing hard brittle behaviour at room temperature or below are polystyrene, poly (methyl methacrylate) and many phenol-formaldehyde resins.

Hard and strong polymers have high modulus of elasticity, high strength, and elongation at break of approximately 5 percent. The shape of the curve often suggests that the material has broken where a yield point might be expected. This type of curve is characteristic of some rigid poly(vinyl chloride) formulations and polystyrene polyblends. Hard, tough behaviour is shown by polymers such as cellulose acetate,

cellulose nitrate and nylons; they have high yield points and high modulus, high strengths and large elongations. Most polymers of this group show cold-drawing or "necking" during the stretching process. Cold-drawing is important in synthetic fiber technology, and is used to develop strength. Polymeric materials that are soft and tough show low modulus and yield values, moderate strength at break, and very high elongation ranging from 20 to 100 per cent. This type of stress-strain curve is characteristic of plasticized PVC and rubbers (elastomers).

The two mechanical performances creep and stress relaxation are related to each other. In creep, elongation takes place under the application of constant stress, while in stress relaxation, decrease in stress occur when a specimen is held at constant and essentially instantaneously induced strain. The varying stress or strain is measured as a function of time. Repeated flexing of a sample through a given distance often causes a sample to fail at a lower stress than it could for a single flexure. This feature is referred to as fatigue.

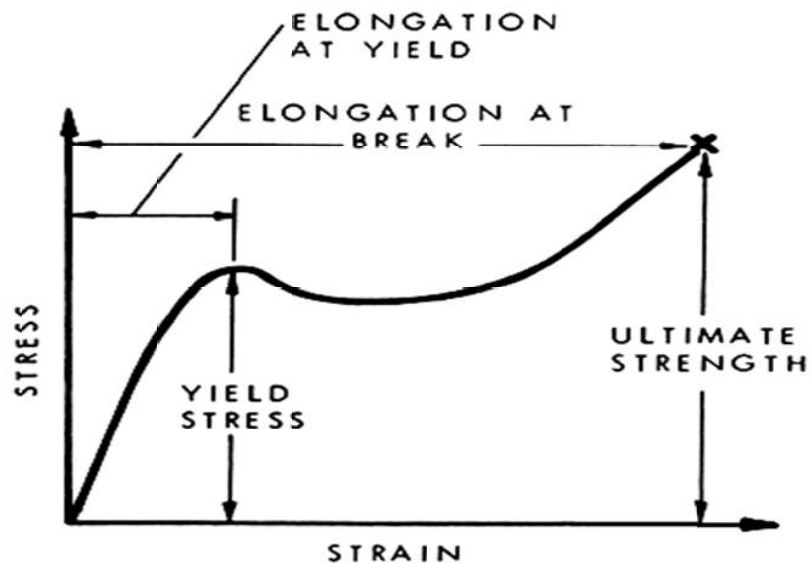


Fig 1.3: Generalized tensile stress-strain curve for some polymeric materials

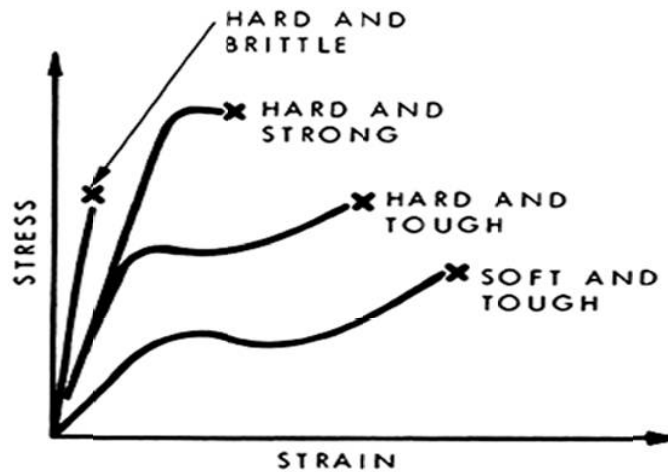


Fig 1.4: Tensile stress-strain curves for four types of polymeric material.

Fatigue testing may be carried out by subjecting the sample to alternating tensile and compressive stress. The fatigue resistance usually decreases with increase in rigidity.

Impact strength is a measure of toughness or resistance to breakage under high velocity impact conditions. From this point of view, polymeric materials under normal conditions of use are thought to be either brittle or tough. For example, polystyrene, poly(methyl methacrylate) and unmodified, non plasticized PVC are usually rated as brittle, breaking with a sharp fracture; plasticized PVC's are considered to be tough. In general, polymeric materials are either brittle or tough, depending on the temperature and rate of impact, i.e. rate of deformation. Impact strength of polymers and derived plastics depends on the position of the glass transition temperature (T_g) with respect to room temperature and ease of crystallization. Far below the glass-transition, amorphous polymers break with a brittle fracture, but they become tougher as the service temperature approaches T_g . Above T_g , amorphous polymers are in a rubbery state so that the term impact ceases to have any significance

1.7.1 Mechanical properties of a thin film Polymer

The mechanical properties of any polymer blend and composite also depend on its dimensional size whether it is thinner or thicker in appearance. The size of the blend makes it usable in various fields. Today polymers are used extensively in many applications in thin film form, like film coating, adherent epoxy under fills to localize

the stress concentration during thermal expansion, in electronic packaging etc.. The mechanical state within the polymer necessarily varies from point to point within the thin film, as can the strength of the adhesion between the polymer and the substrate. In most practical cases, even in thin film applications such as found in electronic packaging applications, the typical dimensions of the polymer component are much larger than the dimensions of individual molecules. At scales much larger than this, the material can be considered as continuum and the usual mechanics can be invoked to model the deformation behavior, and bulk tensile properties (which will vary with resin and processing) can accurately describe the time dependent properties of the thin film.

1.7.2 Microhardness of a Polymer

If we discuss the mechanical properties of polymer and biocomposites, hardness of the material is one of the most important aspects in its mechanical characterization; it is generally defined as “resistance of a material to plastic deformation, usually by indentation”. It is the property of a material, which gives it the ability to resist permanent deformation (bend, break, or have its shape changed), when a load is applied. The greater the hardness of the material, the greater is the resistance it has towards deformation. The one of the best available definition is given by Ashby [18], which states “hardness is a measure of the resistance to permanent deformation or damage”.

Microhardness is the hardness of a material measured at low loads as determined by forcing an indenter such as Vickers or Knoop into the surface of the material under 5 g to 160 g load. Usually the indentations are so small that they must be measured with a microscope. Micro indenters work by pressing a tip into a sample and continuously measuring applied load, penetration, depth and cycle time. Nano-indentation tests measure hardness by indenting with very small (of the order of 1 nano-Newton) indentation forces and measuring the depth of the indentation that is made.

The hardness test measures the mean contact pressure, when an indenter is pressed onto the surface of a flat specimen. It provides the simple and non-destructive means of assessing the resistance of material to plastic deformation. In this present work Vickers’s microhardness indentation testing has been utilized to

study various properties of polymer and polymer biocomposite blends, which has also been utilized by various workers. This typical hardness test involves applying a fixed load to the indenter, and measuring the resultant size of indentation. This has been related empirically to the yield stress of the material. This work presents the results of micro-indentation testing on electrically stressed polymer thin films [19-26].

1.8 ELECTRICAL PROPERTIES OF POLYMER

Materials such as glass, ceramics, polymers and biocomposites are non conducting materials. They prevent flow of current through them. When these types of non-conducting materials are placed in an electric field, they modify the electric field and they themselves undergo appreciable changes as a result of which they act as stores of electrical charges. When charge storage is the main function, the materials are called dielectrics. For a material to be a good dielectric, it must be an insulator. As good insulators, polymers possess excellent dielectric properties. Many authors have reported theoretical and experimental work related to these properties [29-52]. The common electrical properties of interest are discussed below:

1.8.1 Dielectric polarization

Polarization with the application of an electric field, due to the displacement of charge particles inside the material forming dipoles, is known as internal polarization. Some of the internal polarizations are electronic, orientational (dipolar), space charge and barrier polarization.

Dielectric can also be charged by direct injection of charge carriers, when high electric field ($\approx 10^5$ V/cm) is applied between the electrodes in intimate contact with it. Charges get sprayed or deposited due to corona discharge or dielectric breakdown in the thin air gap between the electrode and the dielectric. If the injected charge in the surface is of same sign as that of electrode in contact, it is called homo-charge; if it is opposite in sign then it is called hetero-charge.

The total polarization is the resultant of both internal and external polarization.

$$P = P_{\text{int}} + P_{\text{ext}} \quad 1.5$$

Polymers as dielectrics are known to store charge permanently when subjected to field - temperature treatment; such quasi permanently charged dielectrics are known as Electret.

1.8.2 Dielectric strength

It measures the highest current that can be applied to a plastic before it allows current to pass. It is expressed as the voltage just before this happens divided by the thickness of the sample (in volts/m). It is affected by temperature, thickness, how the sample was conditioned, rate of voltage increase, test duration and contamination etc.

1.8.3 Electrical conduction

The electrical conductivity of polymer, χ , measures the presence of free ions not connected chemically with the macromolecules. It also depends on presence of low molecular weight impurities that can serve as source of ions. The chemical constitution has only an indirect effect on the mobility of the ions.

In glassy state the conductivity of the polymer is approximately 10^{-13} to 10^{-19} ohm⁻¹. With increasing temperature, the conductivity of polymer increases according to the exponential law as,

$$\chi = A e^{-\Delta U/RT} \quad 1.6$$

where, A is a Coefficient mainly dependent on temperature, R is Universal gas constant, and ΔU is the Activation energy

1.8.4 Dielectric constant (or permittivity)

Dielectric constant, ϵ^l , indicates how easily a polymer/plastic can be polarized relative to vacuum. It is defined as the ratio of the capacity of an electric capacitor filled with the substance to that of the same capacitor in vacuum, at a definite external field frequency. This dimensionless number which is important in high frequency applications varies with temperature, moisture, frequency and thickness.

1.8.5 Dissipation factor

This measures the energy dissipated during rapid polarization reversals, as with an alternating current. It can be seen as the ratio of energy lost as heat to current

transmitted. It is usually measured at 1 MHz. This factor should be low when polymers are used as insulators in high-frequency applications such as radar and microwave equipments.

1.8.6 Dielectric loss

Dielectric loss, ϵ'' , measures the part of the energy of an electric field that is dissipated irrecoverably as heat in the dielectric. Dielectric loss in polymeric materials is due to the independent movement of chain sections consisting of large number of monomer units.

1.8.7 Volume resistance

A standard measure of conductivity when a direct current potential is applied across a material is volume resistivity (measured as ohm \times area of the smaller electrode/ specimen thickness). Materials measuring volume resistance above 10^8 ohm-cm are insulators.

1.8.8 Surface resistance

This expresses how well current flows over the surface of a material between electrodes placed on the same side of a specimen. While volume resistance is a property of the material, surface resistance measures how susceptible a plastic is to surface contamination, especially moisture. It is useful when surface leakage may be a problem but since it is not measurable exactly it should be used with wide margin of safety.

1.9 STATEMENT OF THE PROBLEM

Composite materials are attractive because they combine material properties in ways not found in nature. Such materials often result in lightweight structures having high stiffness and tailored properties for specific applications, thereby saving weight and reducing energy needs [4,54-55]. Typically, a manmade composite would consist of a reinforcement phase of stiff, strong material, frequently fibrous in nature, embedded in a continuous matrix phase. The advantage of such a coupling is that the high strength and stiffness of the fiber may be exploited.

Biocomposites are composite materials comprising one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include

plant fibers such as cotton, flax, hemp and fibers from recycled wood or waste paper, or even by-products from food crops. Biocomposites offer a significant non-food market for crop-derived fibers and resins.

Considerable growth has been seen in the use of biocomposites in the automotive and decking markets over the past decade or so, but application in other sectors has hitherto been limited. Nevertheless, with suitable development, the potential exists for biocomposites to enter new markets and thus stimulate an increase in demand for non-food crops. Fibers provide strength and stiffness and act as reinforcement in fiber-reinforced composite materials; ultimately the properties of a composite are governed by the inherent properties of these fibers. Natural fibers can be subdivided into vegetable, animal and mineral fibers [55].

Biodegradation is the process by which organic substances are broken. The term is often used in relation to ecology, waste management and environmental remediation (bioremediation). Biodegradable composite which can be easily degraded in natural environment are gaining public interest. Biodegradable plastics and biocomposites are being developed in number of research laboratories concerned about the persistence and ecological effect of synthetic plastic in the environment worldwide including applications such as waste management, recycling, sustainability, packing, automotive, construction, etc [54-56].

Wide range of bio-based biodegradable polymers which are utilized to prepare biodegradable polymer and biocomposite such as Polyhydroxyalkanoates (PHAs), Polylactides (PLA), Cellulose esters, Starch plastics which are Renewable resource-based and Aliphatic polyesters, Aliphatic-aromatic polyesters, Poly ester amide, Poly vinyl alcohol are Petroleum/fossil fuel-based. Poly vinyl alcohol (PVA) is one of the best biodegradable polymers and it is widely utilized to prepare the biocomposites.

The characterization of biocomposite can be made on the basis of structural, mechanical, electrical, thermal and biodegradation. The study of the surface structure of biocomposite can be made with the help of various characterization techniques like FTIR, XRD, SEM, TEM, AFM, STM, etc [56-62]. The surface structure is also responsible for the biodegradation of the biocomposites. The mechanical behavior of various types of biodegradable materials depends, mainly, on their chemical composition and the application conditions. Various additives are added into the bio-

blends to improve their properties, which sometimes even reach the levels of the conventional plastics. It is well known that the environmental conditions during production, storage, and usage of these materials influence their mechanical properties. The mechanical characterization can be made with the help of Microhardness and Tensile Stress, tensile strength [56,58,59,63]. The study of thermal properties like thermal stability, thermal expansion of biocomposites can be made with the DSC and TGA [64-66]. Biodegradation of polymeric materials affect a wide range of industries; information on degradability can provide fundamental information facilitating design and life-time analysis of materials. The common tests to check the Biodegradability of biocomposites are Weight Loss Test, FT-IR Technique and ¹H NMR Spectroscopy [67]. The TSDC technique is a basic tool to identify and evaluate the polarization and charge storage and decay phenomena, so it can be utilized to check the electrical behavior of biocomposite films [29-52].

With the view to have a sufficiently good knowledge of structural, mechanical, electrical, and thermal behaviour and to characterize the material for such applications a detailed investigation has been under taken on biocomposite of PVA and palm leaf. The measurement techniques employed include:

1. IR/XRD/DSC/AFM and SEM studies on samples to investigate the structural, morphological, thermal aspects of the film specimens.
2. Microhardness measurement to study the effect of composition and load on the pure PVA film and PVA incorporated palm leaf biocomposite film specimens.
3. Tensile strength and elongation studies on samples to investigate the mechanical properties of the specimens.
4. Short circuit thermally stimulated depolarization current measurement on samples polarized under varying field and temperature conditions.

1.10 SELECTION OF MATERIAL

1.10.1 Polyvinyl Alcohol (PVA)

Many authors have studied biocomposites; some of the studies are based on the composition of PVA with agro-industrial waste, corn fiber starch, glycerol, cellulose.

The sample has been prepared with different techniques. The structural, thermal and mechanical characterization has been carried out. The effect of various types of thermal pretreatment on the properties of biocomposites has been investigated.

Chiellini et al have studied composite films based on biorelated agro-industrial waste with PVA and reported that the mechanical properties of prepared agro-industrial based biocomposite films were found to be dependent upon the nature and environmental conditions [56]. Cinelli et al have studied the properties of injection molded composition containing corn fiber and PVA and reported that the addition of starch moderately reduces tensile properties of composite, lowering the elongation and increasing Young's modulus while tensile strength remains constant. Yun et al have studied the mechanical properties with the functional group of additives for starch/ PVA films and reported increase in flexibility and strength of films and degree of swelling (DS) of films[68].

Mao et al have studied the mechanical properties, morphology and biodegradability of Extruded Cornstarch- Glycerol PVA blends and reported that addition of PVOH to blends slows down the biodegradation process and improves physical and mechanical properties[59]. Jayshekara et al have studied biodegradation by composting of surface modified starch and PVA blended films and reported that PVA can be facilitate as biodegradation of composite films[69].

Imam et al have widely studied the composites based on PVA and reported that the FTIR based biodegradation and hexamethoxymethyl-melamine (HMMM) based composite for improving water resistance of PVA based biocomposite[64]. Rudnik has studied the thermal properties of biocomposite and reported increase in thermal stability of modified starch[70]. The thermal stimulated discharge current in polymer composite films has been reported by many authors on polymeric films [29-52,71,72].

PVA is one of the most important polymeric materials to prepare composites of biomaterials. The chemical structure of Polyvinyl alcohol is shown in Fig 1.5. The general properties of PVA are appearance as white granule or powder, specific gravity of 1.25~ 1.32, bulk density of above about 0.4 ~ 0.7, ph value is about to 5 ~ 7 with glass transition temperature (Tg) = 85⁰C, melting point of 210 ~ 230⁰C, thermally stable, gradual discoloration at about 100⁰C, darkens rapidly above 160⁰C, gradual

decomposition above 180⁰C as melting point is similar to decomposing temperature and is soluble in water and resist to oil, animal, plant and grease oils. The different type of biocomposites of PVA have been studied with corn-starch, lingo-cellulosic fiber, agro-industrial waste, starch, glycerol with different aspect of study like mechanical, surface structure and thermal properties.

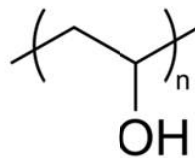


Fig 1.5: Chemical Structure of PVA.

The different types of biodegradable biocomposites have been prepared for various biological applications including packing, agriculture, waste management, recycling, sustainability, automotive, construction, contact lenses, bio-medical field, etc[55-60]. Application of hexamethoxymethyl-melamine (HMMM) with PVA reduces its water sensitivity[56].

1.10.2 Alexander Palm Leaf

The other names of this palm are; Alexandra palm, Kind palm, King Alexander palm, Aalexandrae palm. It has a medium sized, gray trunk (1 – 1.5 feet in diameter). Crownshaft is a bright green colour (a woody shaft at the top of the trunk composed of tightly wrapped leaf base). The type of the leaf is pinnate. It is a fast growing solitary single trunk palm of height of near about 40 feet. Palm leaf contains fibers inside the leaf and it has many potential applications in agriculture and villages.

1.10.3 Bio Composites of PVA and Palm Leaf

The world's supply of natural resources is decreasing and the demand for sustainable and renewable raw materials continues to increase. Biofiber-reinforced composites represent a potential nontraditional, value-added source of income to the agricultural community. Due to the above mentioned properties of Polyvinyl Alcohol and Palm leaf powder the biocomposite of PVA and Palm Leaf can be developed. In present study the biocomposite of PVA and Palm leaf powder has been successfully prepared and this biocomposite can be the potential material with conducive

structural, mechanical and electrical properties for various applications like automobile, agriculture and industries sectors.

1.11 Possible Outcome

The developed biocomposite may definitely exhibit the properties incorporating the individual qualities of PVA and Palm Leaf powder. It may lead to develop a green material with higher mechanical properties, improved microhardness, improved structural morphology, improved thermal properties and improved charge storage properties, providing high strength to weight ratio, for various applications as biodegradable and environmental friendly material.

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Ceramics: Properties and processing

A warm welcome to all of you in this module on ceramics. As you well aware that we have been discussing our course on processing of non-metals, which has been divided into seven different modules. We have completed two modules - in which, we have seen the different aspects of material, we have seen manufacturing aspects of engineering materials. And we have seen the second module, we have seen the glasses. As the title of the course is processing of non-metals our focus is two important aspects that is the non-metals and they processing techniques. And in this particular course, the processing of non-metals we would be covering different types of non-metals, such as we are today going to start our discussion on ceramics. And at a later stage in the module number six we would be covering ceramics matrix composite, which would be and advanced stage of basics ceramics or monolithic ceramics, where the materials has been modified in order to take advantage of the properties of the ceramics.

And in order to overcome the limitations of the ceramics, so that is a late at later stage that is in module number six, and we are going to cover the polymers and well as the polymer matrix composites. So, now, we are at a stage where we are going to start module number three, in module number four our focus will be on polymers; in module number five, our focus will be on polymer matrix composites; and in module number six, again we will discuss about the ceramic matrix composites. And finally, in module number seven, our focus would be on the secondary processing aspects of this composite materials or advance materials or non-metals or non-metallic materials.

So, today we are going to start a new module that is ceramics. In ceramics, our focus will primarily be to understand the basic aspects of ceramics that what are ceramics, how the ceramics can be classified, what are the various criteria on the basics of which ceramics can be classified, what are the distinct features of ceramics, what type of bonding exists in ceramics, what are the different types of ceramics raw materials, and finally, we are

going to see what are the application of ceramics. So, this is something related to the materials aspects of ceramics that is the materials science aspects of ceramics.

Then we would shift our focus from the materials aspects of ceramics towards the processing aspects of ceramics. In which, we would be seen different process which are used for processing of ceramics like powder processing technique is there slip casting is there. They are number of techniques, which are used for processing of ceramics. So, we will see one by one all the techniques which are used for processing of ceramics. But in the first two lectures, that is lecture number one and lecture number two, our focus is primarily to understand the basics aspects of ceramics. So, we would be covering this fundamentals aspects in two lectures, that is ceramics one and that is ceramics two.

Introduction

- The word ceramic is derived from the greek term *keramos*, means “potter’s clay” and *keramikos* means “clay products”.
- Till 1950s, the most important types of ceramics were the traditional clays, made into pottery, bricks, tiles etc.
- Ceramic artefacts play an important role in historical understanding of the technology and culture of the people who lived many years ago.

So, today we are going to start our decision in module three, that is ceramics. And we are going to start the discussion with basics aspects of ceramics. So, with this introduction, let us start our discussion on the basic aspects of ceramics. So, this is the introduction to the word ceramics the word ceramics is derived from Greek term *Keramos* which means potters clay, and *Keramikos* which means clay products. So, basically they are two important points that are coming in this particular words that is ceramic that is potters clay and clay products. So, basically the traditional used for ceramics started with the use of clay and converting this raw materials that is clay into some tangible product that is pottery and some other products of made up of clay.

So, basically, the word ceramic is very clearly mentioned it is derived from Greek work keramos, which means potters clay. Basically it is the concept of or science and engineering of ceramics started with the potters clay, and the clay products. So, basically ceramics deals with the name of the process also as well as the product also. So, the product also product is also a ceramic and the ceramic making it also a process. So, basically first important point is to understand the origin from where this particular branch of science and engineering is started. This important aspects of material science started that is from potters clay, when the raw materials clay was converted into the final useable tangible product.

Then from the historical point of view till 1950, the most important types of ceramics was traditional clays, made into pottery, bricks, tiles etcetera. So, the application aspects are also given and the raw material aspect is also given. If you also have a look the raw material or the traditional clays, so clay is material and the product is pottery the different type of pottery items bricks, tiles, etcetera. So, traditionally, the clays were classified into the ceramics category, but later on different types of ceramics have been invented that would be seen in the application of ceramics like bio-ceramics, ceramics for electronics industries, and they are ceramics for space shutter application. So, these days, we have different sophisticated advance ceramics available which are used for specific design requirements, but traditionally the ceramics that were used in engineering application or in house hold application were made from traditional clay.

Next point, ceramics artefacts that is the products made by ceramics play an important role in historical understanding of the technology and culture of the people who lived many years ago. If you remember during the excavation many times pottery shreds are found out, some ceramics products are found out. Then from the kind of we can say the art work done on those ceramics product, the culture is estimated that what was the culture or what type of people used to live and what was the cultural we can say the heritage related to that particular era. So, important point to note here is that, this is an important type of material which not only have engineering relevance, but also has historical relevance. And it is we can say house hold items which dictates or which helps us to understand the culture has well as the historical developments of a particular civilization or of a particular time domain.

So, basically this particular slide highlights the important aspects of ceramics that somebody whose listening to this word ceramics for the very first time, should be able to understand that what is a ceramics from where it has got its origin, and what are the traditional application of this particular material and what is its relevance in society. So, this particular points give us a idea that is an important material which is in use for a long long time. And particularly now gained substantial application spectrum in different engineering application that we are going to study in our subsequent slides. So, basically the focus is on the word ceramic and we are going to understand the basic fundamental aspects of ceramics, and then we will see what are the latest application of these materials.

Introduction

- A ceramic material is an inorganic, non-metallic material and is often crystalline
- Traditional ceramics are clays
- The earliest application was in pottery
- Most recently, different types of ceramics used are alumina, silicon carbide etc.
- Latest advancements are in the bio-ceramics with examples being dental implants and synthetic bones

A ceramic material is an inorganic, non-metallic material and is often crystalline. So, this important point highlights three important aspects of ceramics that is a ceramics is inorganic - that is point number one; it is non metallic is point number two, and is often crystalline. In our previous model, if you remember we have discussed upon glasses and we have seen that glasses are usually amorphous. So, ceramics materials is a crystalline material and we have also seen the distinguish between the crystalline material and the amorphous material.

So, ceramic material is inorganic, it is non-metallic, and it is often crystalline. Second important point is very important that is non-metallic, because now we have discussing

the course on processing of non-metals. So, ceramics is one of the important non-metals and we should know the tools and techniques for high quality good cost effective processing of ceramic material. So, basically again I am highlighting and revising, because it is a simple definition of a ceramic material and anybody who is attending to this particular discussion should be able to remember that what actually a ceramic a ceramic is an inorganic material a non-metallic material.

Moreover the most of the ceramic is mostly crystalline second traditional ceramics are clays as we are already understood in the very first slide that the very basic origin of the word ceramic is from potters clay. So, basically the traditional ceramics are clay the earliest application was in pottery that we have also seen in the previous slide most recently different types of ceramics are used are alumina silicon carbide extra.

So, these are just two examples of the latest use of ceramic material, they are different types of ceramics ceramics is a very huge family and there are a large number of materials which fall under this category and are used in different engineering applications. So, just to make the things simple and easily understandable, I have taken two very simple examples of the latest materials which fall under the category of ceramics. Most recently different types of ceramics have been used that is alumina and silicon carbide. So, the latest advancements are now, these are two examples of the ceramics then the latest advancements are in the fields of bio ceramics that is sometimes bio-medical implants are being made up of ceramic materials and dental implants as well as synthetic bones.

So, basically now we are trying to understand that what basically a ceramic is, what is the historical perspective of the ceramic material, and we are trying to understand the application point of view of the ceramic material that what are the latest applications like in the last point. We can see artificial bones or synthetic bones dental implants as well as the bio ceramics. These are some of the applications of ceramics in today's scenario and to examples of ceramic material latest ceramics that we have seen that is alumina and silicon carbide. We would have seen a large number of we can say applications of the ceramic material in today's lecture and in the subsequent lectures.

So, by now if we have, if we revise what we have covered, we have just seen what basically a ceramic is it is an inorganic non-metallic material which are mostly crystalline, then we have seen two important examples of a ceramic material that is

alumina and silicon carbide. Then we have seen some of the latest applications of the ceramic materials like the bio medical implants, the dental implants or the synthetic bones. So, now, we will carry forward our discussion and have a comparative analysis of the ceramics with the other important engineering materials like metals and polymers.

Basically, the purpose of showing this particular slide is that we want to compare the ceramic with the metal basically our focus core focus is on processing of non-metals. So, polymers and ceramics both are non-metals. So, we have to compare the characteristics of these two particular materials in reference to the properties of the metals, because these properties only would dictate the processing techniques for these materials. So, one by one we can try to understand the difference that what are the good properties of ceramics which are not present in the metals or what are the danger area or limitations in ceramics where metals have got an edge.

Property	Ceramic	Metal	Polymer
Density	Low	High	Lowest
Hardness	Highest	Low	Lowest
Ductility	Low	High	High
Wear resistance	High	Low	Low
Corrosion resistance	High	Low	Low
Thermal conductivity	Mostly low	High	Low
Electrical conductivity	Mostly low	High	Low

So, first important property on your screen is density. So, density, you can see ceramics have the low density; metals have high density, and polymers have lowest density. Now from the density point of view, if we take the application spectrum that what type of applications are relevant to the density then we can say low weight applications are particularly relevant to the density of the material. So, metals have high density therefore, the use of metals for light weight applications is not usually feasible or is not usually advisable. Whereas, in case of ceramics, the density is low; in case of polymers

the density is lowest therefore for light weight for light applications there are large variety of materials which have been developed using ceramics and polymers and are been used for light weight applications specifically in aerospace industries, in marine industries, in sports goods and equipments. There are large number of applications where light weight is the prime design criteria and in those cases ceramics and polymers have an edge over the metals. So, the first important property that the ceramics have an edge is the light weight characteristics that is the density of ceramics is less as compared to that of metals.

Property numbers two that is hardness. Ceramics have high hardness that is the highest hardness metals have low hardness and polymers have the lowest hardness. So, if we compare the metals with ceramics the hardness of ceramics is much much higher compared to most of the metals. So, the hardness is an important property where we are focusing the use of wear resistance materials. So, when we want to have the wear resistance, we tried we tend to increase the hardness. So, hardness is good for ceramics; it is higher for ceramics, but for metals it is lower. So, hardness also if high hardness is required ceramics have an edge ductility which is another important property, it is low for ceramics and it is high for metals. So, plastic deformation or bending or any other process to give a shape to the metal it is easier in case of metals, but in case of ceramics it is difficult, because they do not have the property of ductility.

So, ceramics the ductility is low; whereas, in metals the ductility is high therefore, the metals can be drawn into thin wires metals can be plastically deformed whereas ceramics cannot be drawn into thin wires even if possible then very very precise control over the processing parameters is required. So, therefore, the ductility of the ceramics is lower as compared to that of metals. The next property as I have already highlighted along with point number two that is hardness is wear resistance. So, wear resistance in case of ceramics is high; whereas, in case of metals is low. So, we can say wherever we want to have an application of a particular material where wear resistance is a design requirement there we would advocate the use of ceramic materials as compared to the metals because the wear resistance of ceramics is higher as compared to that of metals.

Coming on to the corrosion resistance. So, corrosion resistance is also higher for ceramics as compared to that for metals. Thermal conductivity is mostly low for ceramics in most of the cases, although there can be some ceramics which may have a

temperature dependent conductivity and may go into superconductivity range at an elevated temperature. But those are specific examples or exceptional cases, but in most of the ceramics we will see that the thermal conductivity would be low as compared to that of metals and the electrical conductivity would also be low as compared to that for metals. So, we have seen in this particular table, the comparison between the ceramics and the metals. The other comparison between the metals and the polymers we will see. When we will start discussing the module on polymers, but if we compare the two important class of materials that is the metal and the ceramic we can see that for lightweight application, for high temperature applications, for wear resistance corrosion resistance applications. Where wear resistance and corrosion resistance is desired we should certainly use the ceramic material, but wherever we want high electrical conductivity or we want a good thermal conductivity in those cases we should go for metals as our alternative.

So, basically ceramics have got certain advantages and metals have got their own advantages, but apart from the advantages that the ceramics have there are few limitations also, because ceramics have the major advantage of high temperature suitability for high temperature applications ceramics can be used. Then they have good corrosion resistance also, therefore, in some applications we may love to advocate the use of ceramics where high temperature is there corrosion resistance is also there. So, we may be initiated or we may be motivated to advocate the use of ceramics, but one of the important points to note is the brittle nature of the ceramics.

So, whenever we are going to advocate the use of ceramics for a particular engineering application, we should take into account the type of loads that are going to come on that particular component. So, if impact load is going to come then we should not advocate or we should not initiate the use of ceramic material for that particular application. So, although ceramic materials have got a wide variety of properties like high hardness, we can say low density. So, for light weight applications high hardness for wear resistance we can say low density. So, for light weight applications high hardness for wear resistance applications, corrosion resistance applications we may be tempted to promote the ceramic materials, but one of the major limitations is the brittle nature. So, that particular aspect has to be addressed and that we will try to address when we will study our module on ceramic matrix composites.

Where the ceramic matrix is reinforced with the reinforcing phase and some of the properties of ceramics which are lacking are improved with the help of reinforcing phase, although the advantageous properties of ceramics are taken care of. They are usually adopted in to the ceramic matrix composite, but the limiting properties of ceramics are addressed by the reinforcing phase and we get a good quality material which over comes the limitations of the monolithic ceramics. So, the important point in this particular slide is to have a comparative analysis of the metals and the ceramics, and we should be able to understand that what is the application spectrum as an engineer we should know that whenever we are designing a product. We have to specify the material, we would be used to fabricate or process that final product.

So, basically we before advocating the use of a particular material, we should know that what are the strengths of that material and what are the weaknesses of that material and this particular slide gives us overview of the comparison between the metals and the ceramics. And we have been able to understand that what are the properties, which are good for ceramics as compared to metals, and what are the important challenges for ceramics which have to be overcome with the blending of other phases or other materials with the ceramic materials.

Applications

- Pottery products, sanitary ware, floor and roof tiles
- Crucibles, kiln linings, other refractories
- High end applications such as in ceramic matrix composites, tiles in space shuttle, bullet proof jackets, disk brakes, ball bearing applications, bio-ceramics

Let us see what are the important applications we can have pottery products, sanitary ware floor, and roof tiles. It is one spectrum of applications then crucibles kiln linings

and other refractory. Refractory means high temperature application then high end applications are there. So, we started from the very basic application or household applications like pottery products or sanitary ware which is weir in very household floor and roof tiles also. So, we are starting from the consumer goods then slightly high end applications like the crucibles kiln linings and other refractories that are high temperature applications then high end application such as ceramic matrix composite.

So, ceramic matrix composites, we are going to cover in our module number six. We will see that what are the various types of toughening mechanism, we will try to understand that what are the various types of manufacturing processing or processing techniques which are used for ceramic matrix composites. So, this is another class of materials, which is finding substantial application in various engineering requirements then the tiles in space shuttle this is also high-end application bulletproof jackets, disk brakes, ball bearing applications bio ceramics. So, these are some of the latest applications of the ceramic materials. So, starting from the very basic application household applications, we can see the ceramics have now graduated into a very important class of engineering material, and is finding diverse applications in the fields ranging from aerospace to bio ceramics.

Now, till now what we have discussed, let us just have brief overview of what we have tried to understand till now. Now we have tried to understand the brief origin of the ceramic materials, the ceramic clays which have been used for a long long time that initially the ceramic materials were used as clays. Then we have tried to understand the basic concept of the ceramics, we have tried to compare the ceramics with the metals and then we have seen what are the various applications of ceramic materials. So, having this introduction that what do we mean by a ceramic, how the ceramic materials compared with the metallic materials, and finally, the applications where we can see the ceramics around us because all of us, can see the ceramic materials all around us. We can see the roof tiles, we can see some decorative pottery items which are usually kept in the houses. So, basically, we can till now, we can just visualize that what are the various applications of ceramic materials.

Classification of ceramics materials

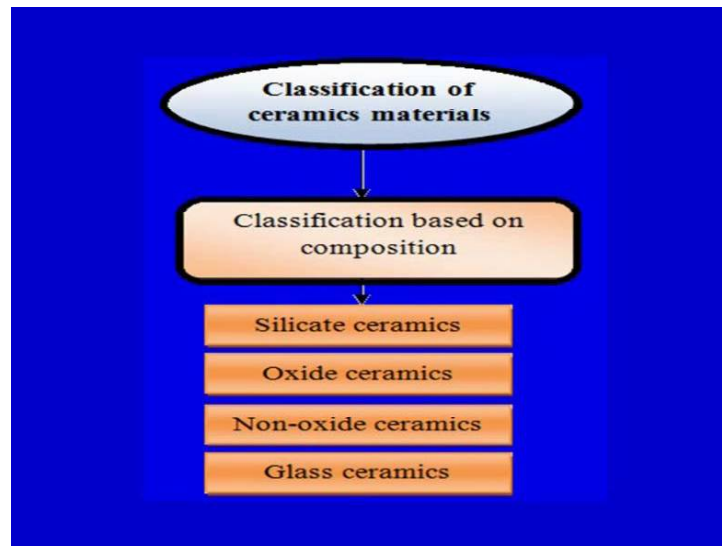
- Ceramics can be classified in diverse ways i.e. there are number of ways to classify the ceramic materials.
- Most commonly, the ceramics can be classified on the following basis:
 - Classification based on composition
 - Classification based on applications

Now, let us see how the ceramic materials can be classified. So, the classification can be based on two important criteria. So, the ceramics can be classified in a large number of ways we can we can choose different types of criteria for classifying the ceramic materials, but broadly there two important criteria that have been widely accepted as the classifying criteria. So, mostly the ceramics can be classified by the following basis. So, two important classifying criteria are classification based on the composition of the ceramic materials and the classification based on applications of the ceramic materials that is why in the previous slide we have seen that starting from the very basic application from household application the applications of ceramics may range to bio ceramics and the bullet proof armour.

So, on the basis of the applications the ceramics can be classified as well as the ceramics can be classified on the basis of composition of the base material. So, the composition in this particular ceramic, we will see in our subsequent lecture that that the ceramics is made up of two or three elements. And therefore, the structure of the ceramics is also very very complex as compared to the metallic materials, but that we will come to at a later stage, but let us first see the broad classification of the ceramic materials.

Now, classification of ceramic materials on the basis of composition, we can broadly classify them into four categories silicate ceramics which is one of the most commonly used ceramic material. Oxide ceramic like a lumina one example, I have given. We will

just see some other examples of the oxide ceramics also in the subsequent slides, non oxide ceramics and the glass ceramics. So, glass ceramics is also a very very important class of ceramic material which is finding a wide variety of applications in today's engineering world.



So, basically on the basis of composition we can classify the ceramics into four categories. So, all the four categories have been highlighted on your screen and one by one, we will try to see that which particular type of ceramics falls under which categories. So, again we can see that in this particular diagram, we have been able to classify the ceramics into four broad categories, there is based on the composition. Now one by one, we will try to understand that silicate ceramics, oxide ceramics, non-oxide ceramics and glass ceramics.

The main types of silicate ceramics are:

- Clay-based ceramic
- Talc-based technical ceramics
- Special groups are zircon- and mullite based fine ceramics

The main types of silicate ceramics are these are the most commonly used type of ceramic materials. They are clay based ceramics, talc based technical ceramics, special groups such as zircon and mullite based fine ceramics, but we can try to understand here that one of the broad categories based on the composition of the material is the silicate ceramic. So, major type of this ceramic products are made by the silicate ceramics and they can further be sub divided into clay based ceramics talc based technical ceramics as well as special groups or fine ceramics. So, basically first important category on the basis of the composition is the silicate ceramics. We should try to remember that on the basis of composition, there are four types of categories of ceramics or four types of we can say sub divisions of the ceramic materials on the basis of composition that is first one silicate ceramics, which is most widely used second is the oxide ceramics non oxide ceramics and the glass ceramics. So, the first one is the silicate ceramics different types is already mentioned on your screen.

Oxide ceramics

- Oxide ceramics include alumina, zirconia
- Properties : High melting points and a wide range of electrical properties.
- For example, glazes and protective coatings seal porosity, improve water or chemical resistance, and enhance joining to metals or other materials.

Next is the oxide ceramics. So, coming on to the oxide ceramics the oxide ceramics basically include alumina zirconia and their other types of oxide ceramics also. Now, what are the important properties of the oxide ceramics we can have a high melting point, and a wide range of wide variety of electrical properties now there are different examples like glazes and protective coatings seal porosity improve water or chemical resistance and enhance joining to metals or other materials. So, the we can say the application areas of oxide ceramics are also given. So, we have seen the two examples of oxide ceramics since two specific properties of oxide ceramics and we have seen the application that they can be used for glazes and protective coatings for sealing the porosity as we have seen and we can say important application ceramics are porous in nature.

So, sometimes we need to reduce or seal the porosity. So, there the oxide ceramics can be used improve water or chemical resistance, it is also very very important as we know that corrosion resistance and chemical resistance of oxide ceramics is good and they can enhance joining to the metals or other materials. So, oxide ceramics is one category on the basis of composition which is falling under the ceramics category.

Then non-oxide ceramics, there are large number of we can say material related problems and difficulties and limitations. As we know that whatever properties, we desire from a particular material, all those properties we cannot achieve with one specific

materials. For example, for a very high temperature application at that particular application we require high strength of the material also the mechanical properties should not deteriorate at an elevated temperature. So, this is just one example of a very specific requirements. So, there are very diverse requirements from the engineering materials in today's day, in today's world.

Non-oxide ceramics

- In past three to four decades, many severe material problems and difficulties.
- Problems: corrosion, erosion, wear, temperature, electrical insulation etc.
- It can be overcome by the correct selection from a range of materials categorized as oxide or non-oxide ceramics.

So, basically in past three to four decades, many severe problems and difficulties are there. So, problem such as corrosion erosion wear temperature electrical insulation etcetera. These are some of the problems that exists. So, these can be overcome by the correct selection of range of materials categorized as oxide and non-oxide ceramics. So, non-oxide ceramics, this is just giving you an highlight that in which particular application spectrum the non oxide ceramics can be used, but what are the exactly non oxide ceramics that also we should try to understand.

In oxide ceramics, we have seen two important examples are alumina and zirconia. So, in case of non oxide ceramics we can have carbides we can have nitrides. So, carbides nitrides fall under the category of non-oxide ceramics, and within carbides we can have silicon carbides we can have titanium carbide tungsten carbide. So, we can have different types of carbides we can have different types of nitrides and these will fall under non-oxide ceramics. So, carbides and nitrides will fall under non-oxide ceramics, alumina zirconia are the oxide ceramics. Till now on the basis of the composition of the basic

material, we can classify the ceramics into four categories - that is first one is the silicates; second is the oxide ceramics, and the third one is the non oxide ceramics and the fourth category is the glass ceramics. But before going to the glass ceramics, let us see the examples of non oxide ceramics, I have already told non-oxide ceramics basically are carbides and nitrides, and they have got their own specific set of applications.

Glass ceramics

- A material processed through the controlled crystallization of base glass.
- Amorphous phase and more than one crystalline phases and are produced by a controlled crystallization procedure.
- 30% to 90% crystallinity, and yield an array of materials.

Now, coming on to the glass ceramics, a material processed through the controlled crystallization of the base glass. So, we have seen in our previous module that was on glass that what is difference between amorphous and crystalline material. So, glass is basically amorphous material, but a glass ceramic is a material which is processed through the controlled crystallization of the glass. So, we will have certain degree of crystalline and that would add a specific dimension to the material and would make it applicable in certain application areas. So, amorphous phase and more than one crystalline phase is and are produced by a controlled crystallization procedure. So, the glass ceramic exist in amorphous phase and more than one crystalline phases, and how it will be processed by the controlled crystallization.

We know that we have to undertake this much amount of crystallization. So, 30 to 90 percent crystalline, and an yield array of materials. So, we will get different types of materials. So, basically glass ceramics are we will process the glass, and later on add

certain degree of crystalline nature into that base glass, and we will get a glass ceramic why do we need to do this let us try to understand this.

Glass ceramics

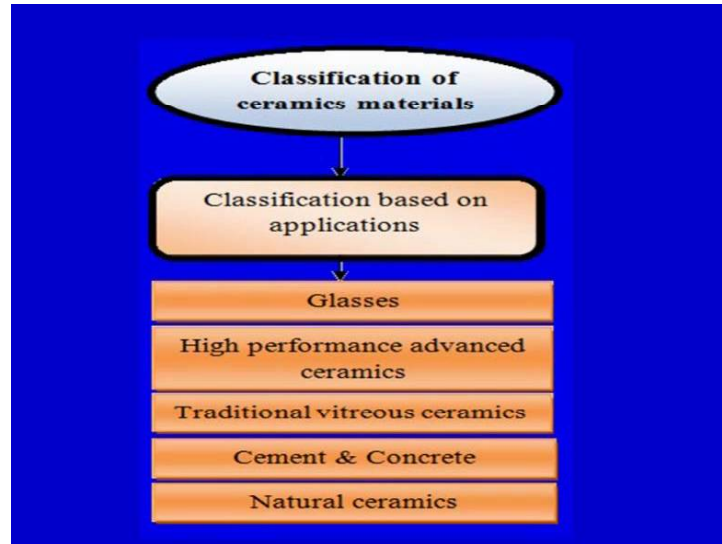
- Glass-ceramics holds the processing advantage of glass and has special characteristics of ceramics.
- Properties of material zero porosity, high strength, toughness, translucency or opacity, superconductivity etc.
- Properties can be altered by controlling composition and by controlled heat treatment of the base glass.

Glass ceramics hold the processing advantage of glass and has special characteristics of ceramics. So, basically a question can be asked that what is the need, when we have a glass has an engineering material and ceramics is another category of engineering material, what is the need to blend this two characteristics together or blend this two materials together. So, first important point is on your screen, you can see the glass ceramics. They hold the processing advantage of glass, because it is easier to process glass as compared to ceramics and has a special characteristics of the ceramics.

So, ceramics have got certain specific properties that we have already understood in one of the previous slides where we have paired the ceramics with the metals. We want to take the advantages of those properties take advantages of processing is of the glass then we combine this two important characteristics together. The processing characteristics of glass and the other properties of ceramics and we get a glass ceramic. So, that is one of the important points why we want to blend the two together properties of material zero porosity, may be this properties of the material that glass ceramics what type of properties they process possess zero porosity porosity is very less high strength. So, strength is improved toughness is good translucency or opacity we can have whatever we want or design accordingly and superconductivity.

So, basically glass ceramics have got certain special characteristics. Now what are those special characteristics that is mentioned on your screen. Again we want to revise the porosity is less strength, is good toughness, is good, we can have a range from translucency to opacity and the superconductivity. So, we can see that although ceramics are poor conductors of electricity, but glass ceramics can be made superconductive at specific operating conditions. So, basically when we blend the two things together that this particular concept we are also going to see in case of polymer matrix composite and ceramic matrix composite in later modules of this particular of this course. But here also we have combined the characteristics of two things together or two materials together glasses and ceramics and we have been able to make a resultant material which is giving a certain special characteristics as mentioned.

On your screen, you can see porosity, low porosity, high strength, toughness and super conductivity properties can be altered by controlling composition and by controlled heat treatment of the base glass. So, this is not, these are not the only properties or this is not the only characteristics that these materials possess. There are other types properties which can be achieved with the controlled heat treatment or by controlling the composition of the material that we are forming. So, just take a revision of what we have seen in the classification of the ceramics, we have seen on the basis of composition. We can classify the ceramics into four broad categories that first one is the silicate, second one is the oxide ceramics, third one is the non-oxide ceramics, and the forth one is the special category of glass ceramics.



Now, second characterization or second classification is on the basis of applications. So, we have seen that although there are number of ways to classify the ceramic materials, but we are basically focusing on two important criteria that is on the basis of composition of the materials. And on the basis of the application of the materials, so on the basis of the composition, we have already seen that there are four subcategory in case in case of applications. Now we can see, we can have glasses, high performance advanced ceramics such as bio ceramics or for ceramic tiles for space shuttles, traditional vitreous ceramics, that is the most commonly used clays cement and concrete. And finally, the naturally occurring ceramics such as our bones.

Glasses

- Glasses are based on Silicate (SiO_2) along with other additives to shrink the melting point and to impart special characteristic properties.
- Mainly used in the manufacturing of the following products;
 - (a) containers
 - (b) households
 - (c) optical glasses etc.

Now, glasses, glasses are based on silicate along with other additives to shrink the melting point and the impart special characteristic properties. We just give revision of what we have already covered in our module number two mainly used in the manufacturing of following products like containers household equipments and optical glasses as we have seen. There are number of other applications of glasses for the detailed discussion on glasses, you can refer to the discussions on module two or discussions held in module two in which we have seen the different types of glasses.

High performance advanced ceramics

- They are basically special ceramics having outstanding measures in terms of toughness, wear resistance, electrical properties, etc.
- Their applicative demand has rose to a larger extent in the last decade & they find their need in cutting tool, grinding, bearing, sensor, laser, superconductor etc.

High performance advanced ceramics that is the next category on the basis of the application. They are usually special ceramics having outstanding measures in terms of toughness, wear resistance and electrical properties. Their applicative demand has to the large extent in the last decade and they find their need in cutting tools like wigs sometimes we use carbide tools for machining purpose. So, we can have different types of hard tools which can be used for machining grinding, bearing, ball bearing applications also are the latest applications of ceramics they have used for sensors also lasers superconductors. So, we can see that high performance applications for ceramics also are there and the ceramics can be classified into category where they have used for high performance applications. Some of the applications which are not mentioned here in case of bio ceramics or in space shuttles or or our body armour, bulletproof body armour. So, we can see high performance advanced ceramics is one category although few examples are listed on your screen there are other examples as well.

Traditional vitreous ceramics

- All the clay-based products within ceramics comes under this category.
- Applications are easily noticeable in porcelain, sanitary ware, tiles, bricks, refractories etc.

Traditional vitreous ceramics you can see all the clay-based products within ceramics comes under this category. So, clay based ceramics usually are traditional ceramics applications are easily noticeable in porcelain, sanitary ware, tiles. Bricks, refractories which we have already seen covered in this lecture. Only in the very beginning, we have seen that what are the typical applications of ceramic materials. Now we are classifying the ceramic material into different categories on the basis of the applications.

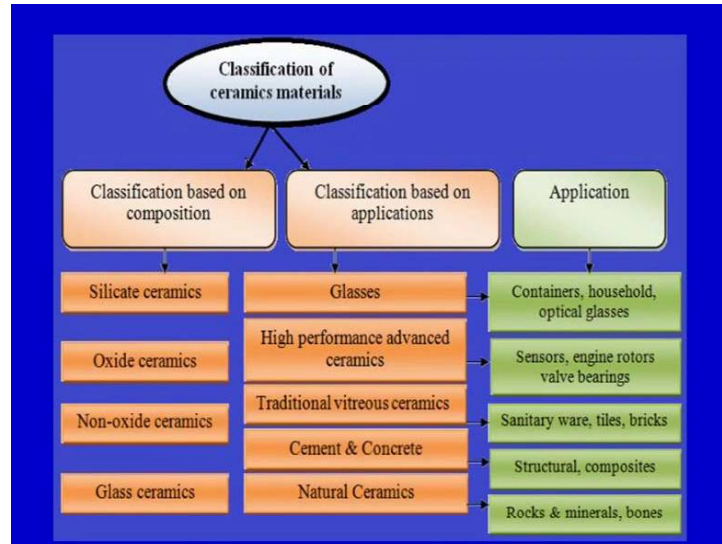
Cement and concrete

- Which are multiphase in nature i.e. they exist in more than one phase.

Natural ceramics

- This includes rocks, minerals, ores that are extracted from the earth and are produced by the laws of nature.
- They also include bones.

Then cement and concrete is another, we can say sub category of the ceramics based on the application. These are multiphase in nature. They exist in more than one phase multiphase means they exist in more than one phase concrete and cement is well known commodity. I think all engineers know about this natural ceramics, this include rocks minerals ores that are extracted from the earth and are produced by the laws of nature they also include the bones. So, basically there are natural ceramics also which can be used for certain application, there are we can say cement and concrete category for the ceramics on the basis of the application. Then are high performance ceramics then there are traditional then there are clays etcetera. Glasses, glass ceramics on the basis of the application also we have got a wide variety of ceramic materials. So, whatever we have discussed.



Let us now try to highlight or try to summarize with the help of this diagram. Classification of ceramic materials, classification based on composition. We can have silicate ceramics, oxide ceramics, non-oxide ceramics, and glass ceramics. We have seen the examples of all four types of these classification based on application. We can have glasses high performance advanced ceramics traditional vitreous ceramics, cement and concrete and natural ceramics and the examples we have seen in each and every case. So, with this, we come to the end of lecture number one in our module three that is ceramics.

In our subsequent lectures, our focus would be to further investigate or further study the basic aspects of ceramic to understand what is the type of bonding that exists in ceramics and how that bonding affects the properties. And finally seen what are the mechanical properties of the different types of ceramic materials and then we will shift our attention to the major focus of this particular course that is the processing of nonmetals. So, then our subsequent lectures would be focusing on the processing aspects of ceramics. In our next lecture, our focus would be on the basic aspects of ceramics.