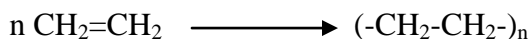


UNIT IV
POLYMERS AND COMPOSITES

Polymers

Polymers are macromolecules (giant molecules of higher molecular weight) formed by the repeated linking of large number of small molecules called monomers.

Eg: Polyethylene is a polymer formed by the repeated linking of large number of ethylene molecule.



Monomer

Monomer is a micro molecule having at least two bonding sites (small molecule) which combines with each other to form a polymer.

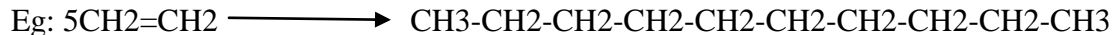
Polymerization

Polymerization is a process in which large number of small molecules (called monomers) combines to give a big molecule (called a polymer) with or without elimination of small molecules.

Degree of Polymerization (DP)

The number of repeating units (n) in a polymer chain is known as the degree of polymerization. It is represented by the following relationship.

$$\text{Degree of polymerization} = \frac{\text{Molecular weight of the polymeric network}}{\text{Molecular weight of the repeating unit}}$$



In this example, five repeating units are present in the polymer chain.

$$\text{Degree of polymerization} = 5.$$

Glass transition temperature:

When an amorphous polymer is heated, it gets converted from hard brittle state (glassy state) to a soft flexible state (rubbery state). The temperature at which a polymer transforms from a hard glassy state to soft rubbery state is called glass transition temperature.

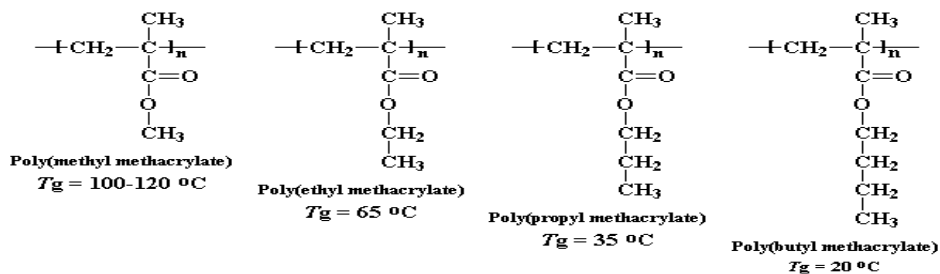
i). **Flexibility:** Higher flexibility of a polymeric chain leads to higher segmental mobility and hence lower will be T_g . More is the flexibility of the polymeric chain less is the T_g value. Linear polymeric chains containing C-C, C-O or C-N single bonds have high degree of freedom of rotation and hence more flexible. Rigid groups, bulky side groups or cyclic rings in polymeric chain reduce flexibility of the chain by restricting the free rotation and hence thus increasing the T_g value.

Example: Polyethylene polymer has T_g value - 110°C because it is having less crystallinity, molecules are more flexible. Whereas nylon 6 having high crystallinity, where molecules are less flexible for movement, therefore T_g value of nylon 6 is 57°C

ii). **Inter molecular forces:** Presence of larger number of polar groups in the molecular chain lead to strong inter molecular cohesive forces which restrict the molecular mobility. This leads to an increase in T_g value. Eg- T_g value of poly propylene is -18°C , where as that of nylon 6 containing polyamide (polar) groups is 57°C .

iii). **Effect of branching and cross linking:** The polymers having side groups have high T_g value, whereas the polymers are not having side groups have low T_g value. Examples: Poly (α -methyl styrene) has higher T_g value (170°C), where as polystyrene has lower T_g value (100°C).

A small amount of branching will tend to lower T_g . Increase in chain ends in branched chain polymers increase the free volume thus decreasing the T_g . These branches are more flexible than the main polymer backbone



iv). **Molecular weight:** The T_g of all polymers, in general, increases with molecular weight up to 20,000 and beyond which the effect is negligible. Under high molecular mass, long polymeric chains coil and entangle with one another. This restrict the free mobility of chains and thus increasing T_g .

iv). **Stereo regularity:** Polymers with stereo-regular structure are crystalline and hence more is T_g . Polymers with irregular backbone or randomly placed side groups are amorphous and possess less T_g .

Isotactic polymer and syndiotactic polymers are more symmetric than atactic configured polymer.

Significance of Tg:

1. Tg valve gives an idea about the thermal expansion,
2. Tg valve gives an idea about heat capacity,
3. Tg valve gives an idea about electrical and mechanical properties
4. Tg valve gives measure of flexibility of polymer.
5. Tg valve gives an idea for choosing right temperature for fabrication operations.

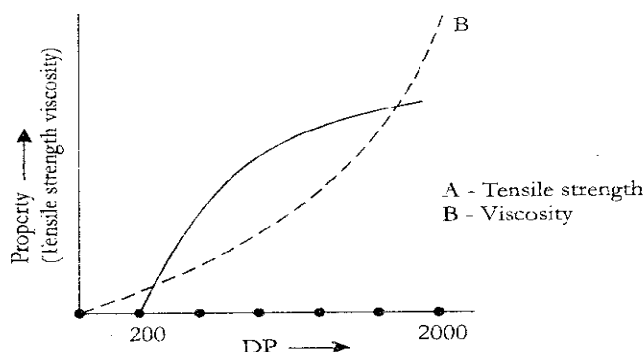
Structure-property relationship:

The structure of a polymer has profound influence on some of the properties of polymers. The properties such as crystallinity, tensile strength, elastic nature and chemical resistance are largely dependent on the structure of the polymer.

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

Examples HDPE, isotactic and syndiotactic polypropylene, PVC, etc.

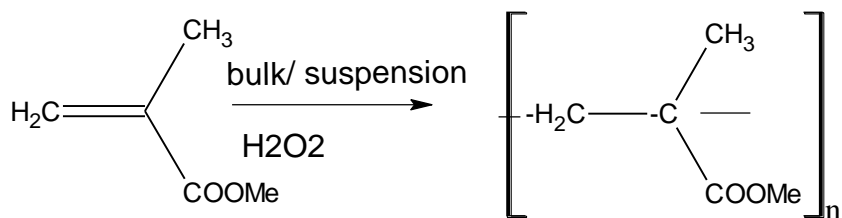
2. **Tensile strength:** Density, melt viscosity and tensile strength are a few important mechanical properties of a polymer. These are highly influenced by molecular weight of polymers. Tensile strength is increases with molecular mass of the polymer up to 20000. Beyond that the increase is negligible. The melt viscosity of the polymer initially shows a gradual increase with the molecular mass and steep increase at higher molecular masses. For polymer to be commercially useful it should have low melt viscosity, high tensile and impact strength



3. **Elasticity:** The property by which the polymer undergoes elongation several times under the applied force and regains their original size when the force is released fully is called elasticity. The elastic property of elastomers is mainly because of their linear and coiled polymer chains. For a polymer to show elasticity the individual chains should not break on prolonged stretching. Breaking takes place when the chains slip past each other and get separated.
4. **Chemical resistance:** The chemical resistance of a polymer depends on the composition of the polymer and also on the nature of attacking reagents. The hydrocarbon polymers having no polar groups are generally swell or dissolved in hydrocarbon solvents like gasoline, benzene etc. but chemically resistance towards polar solvents. The polymer containing polar groups are attacked by polar solvents, but chemically resistance towards non-polar solvents. Polymers containing residual unsaturation undergo oxidative degradation when exposed to air and light. Natural and synthetic rubbers which contain residual unsaturation are susceptible for oxidative degradation in service. The higher degree of Crystallinity, greater will be the chemical resistance. Higher the degree of cross linking in the polymer, higher its chemical resistance. For a given polymer chemical resistivity increase with increase in molar mass. Linear polymers have lower resistivity than branched chain and cross- linked polymers
5. **Plastic deformation of polymer:** Some polymers on application of heat and pressure initially become flexible and soft. On further heating above melting point, they melt and flow. Such a property is called plastic deformation. On cooling they return their original state. Thermoplastics exhibit plastic deformation as they are linear, closely packed and polymeric chains are held by Vander Waal forces, polar interaction and dipole-dipole interactions. Stress on the polymer material and finding the deformation caused. When these polymers are heated, the chains acquire sufficient energy and overcome these inter-chain attractive forces. They attain molecular mobility and flow like viscous fluid. On the other hand thermosetting polymers do not exhibit plastic deformation because they undergo cross linking on heating to form three dimensional structure. All monomer units are held together through strong primary covalent bond throughout the structure. Primary covalent bonds are not easily broken by heat. On strong heating, charring occurs instead of deformation.

Synthesis, properties and applications of polymers:

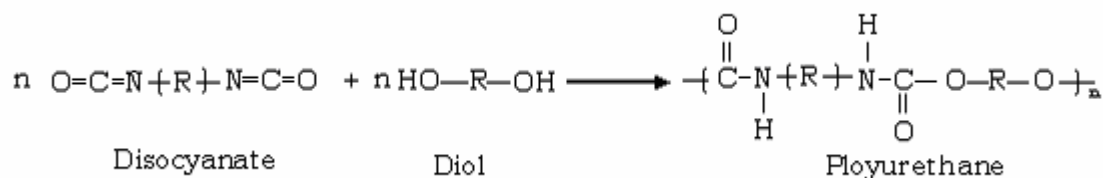
Polymethylmethacrylate (Plexiglass): Polymethylmethacrylate is also known as plexiglass. It is synthesized by subjecting methylmethacrylate to emulsion polymerization at 60-70°C in presence of H₂O₂ as initiator.



Properties: a). It is highly transparent, thermoplastic polymer. b). It has optical clarity. c). It has good mechanical properties, but it has poor scratching resistance.

Applications: 1. it is used in making light fixture, aircraft windows, plastics, sign boards. etc. 2. It is used in making acrylic emulsion paints. 3. It is used in making transparent bottles, tubes, etc.

Polyurethanes: It is prepared by the reaction of diisocyanate with glycol.



Di-isocyanate Diol polyurethane Hexamethylene di-isocyanate Tetra methylene diol
Perol - U polyurethane

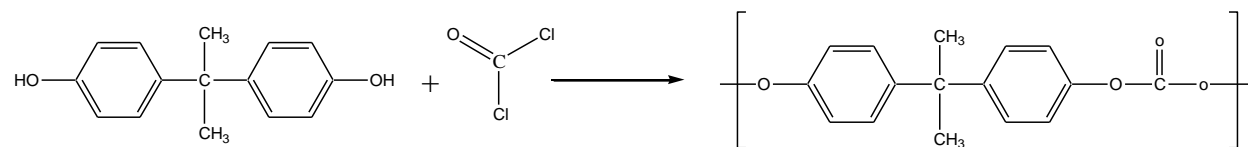
Properties: a). It is a spongy transparent, liner, thermoplastic. b). It has high degree of flexibility). Resistant to oil, water and corrosive chemical.

Applications:

1. they are used for tyres treads and industrial wheels, because of their resistance to oil, water and chemical resistance.
2. Fibers of this polymer are used in light weight garments (swim suits).
3. Polyurethane foams are used as cushion for furniture and automobiles.

Polycarbonates: are polymeric materials, which have repeat carbonate interunit linkages (-o-coo-). Linear polycarbonates are formed by the condensation of Bisphenol-A with diphenyl carbonate.

The condensation of Bisphenol-A with Phosgene at 200⁰c under reduced pressure gives polycarbonate



- Properties:
1. High melting point
 2. Tensile strength and impact resistance.
 3. It has excellent mechanical properties.

Applications:

The polymer is used in the manufacture of safety goggles, telephone parts, automobile taillight lenses and unbreakable glazing appliances

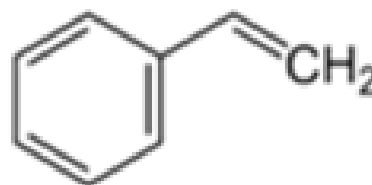
Acrylonitrile butadiene styrene (ABS)



Acrylonitrile



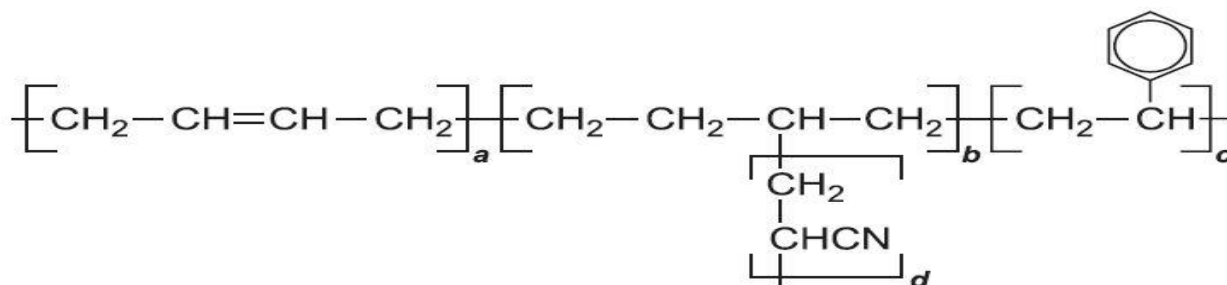
Butadiene



Styrene

Acrylonitrile butadiene styrene (ABS) (chemical formula $(C_8H_8)_x \cdot (C_4H_6)_y \cdot (C_3H_3N)_z$) is a common thermoplastic polymer. Its glass transition temperature is approximately 105 °C. ABS is a terpolymer (copolymer consisting of three distinct monomers) made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene.

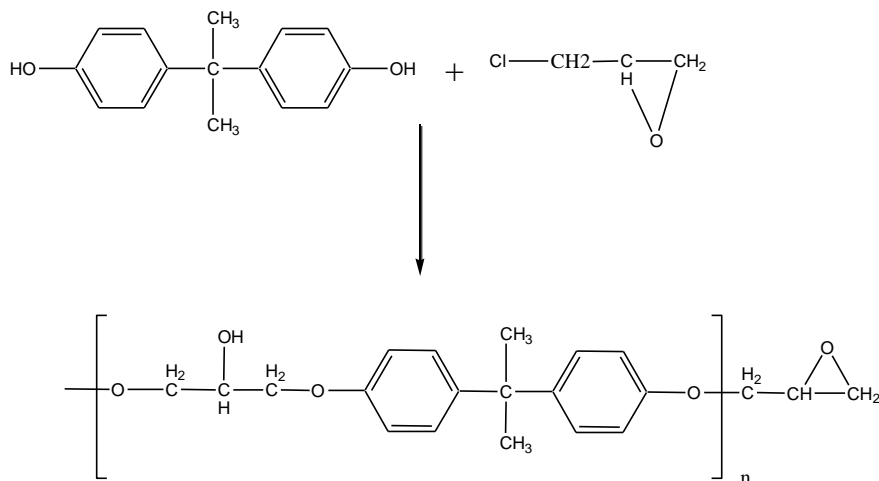
The result is a long chain of polybutadiene criss-crossed with shorter chains of poly(styrene-co-acrylonitrile)



- ✓ The nitrile groups from neighboring chains, being polar, attract each other and bind the chains together, making ABS stronger than pure polystyrene.
- ✓ The styrene gives the plasticity, mouldability a shiny, impervious surface
- ✓ The polybutadiene, a rubbery substance, provides impact resistance and toughness even at low temperatures.
- ✓ Acrylonitrile gives Ageing resistance , chemical resistance and heat resistance

Adhesives: An adhesive is defined as a “nonmetallic compounds which can hold firmly two materials together by surface attachment” OR An adhesive is defined as a “polymeric substance used to bind together two or more similar or dissimilar materials so that the resulting material can act or be used as single piece” Classification of adhesives:

Preparation and applications of epoxy resin: It is prepared by the condensation of excess of epichlorohydrine with bis phenol-A catalyzed by an alkali.



Applications: 1. They are widely used as structural adhesives 2. They are used as laminating materials. 3. They are used for moulding and laminating process. 4. They are used as surface coating in industry because they have excellent chemical resistant

Conducting polymers: “An organic polymer with highly delocalized pi-electron system having electrical conductance of the order of a conductor is called conducting polymer” Conducting polymers are generally produced by doping an oxidizing or a reducing agent into an organic polymer with conjugated back bone consisting of pi-electron system. Examples: Conjugated polymers such as polypyrrole, polythiophene, polyaniline, etc.

An organic polymer can be converted into a conducting polymer if it has

1. Linear structure
2. Extensive conjugation in polymeric back bone (Pi-back bone)

The conducting polymers are synthesized by doping, in which charged species are introduced in organic polymers having pi-back bone. The important doping reactions are;

1. Oxidative doping (p-doping)
2. Reductive doping (n-doping)
3. Protonic acid doping (p-doping) Mechanism of conduction:

The removal of an electron from the polymer pi-back bone using a suitable oxidizing agents leads to the formation of delocalized radical ion called polaron. A second oxidation of a chain

containing polaron followed by radical recombination yields two charge carriers on each chain. The positive charges sites on the polymer chains are compensated by anions I_3^- - formed by the oxidizing agent during doping. The delocalized positive charges on the polymer chain are mobile, not the dopant anions. Thus, these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction. On doping polyacetylene using iodine in CCl_4 , for partial oxidation, the conductivity increases from $10^{-5} \text{ S.cm}^{-1}$ to $10^3 - 10^5 \text{ S.cm}^{-1}$. 3. Reductive doping (n-doping): in n-doping, pi-back bone of a polymer is partially reduced by a suitable reducing agent. This creates negatively charged sites on polymer backbone. These negatively charged sites are responsible for the conduction. The most commonly used reducing agent for partial reduction of polymer back bone is solution of sodium naphthalide in tetra hydro furan. Mechanism of conduction: The addition of an electron to the polymer back bone by using a reducing agent generates a radical ion polaron. A second reduction of chain containing polaron, followed by the recombination of radicals yields two charged (-ve) carriers on each chain. These charge sites on the polymer chains are compensated by cations (Na^+ ions) formed by the reducing agent.

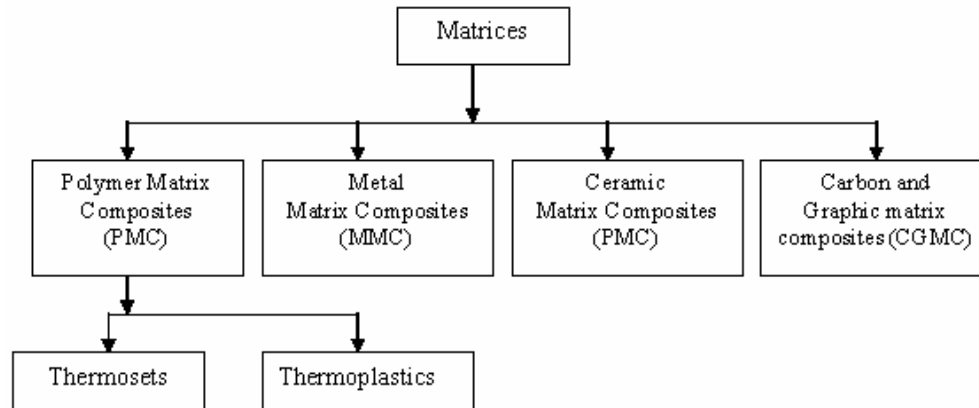
Applications: 1. As electrode material for commercial rechargeable batteries. 2. As conductive tracks on printed circuit board. 3. As bio-sensors, humidity sensor, gas sensor, radiation sensors. 4. In electro chromic display windows. 5. An information storage device. 6. As film membrane for gas separation. 7. In fuel cells as the electro catalytic materials.

COMPOSITE POLYMERS

A composite material is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. If one of the constituent is polymer then it is called polymer composite

TYPES OF COMPOSITES

Based on the type of matrix phase, classified into four types



Polymer Matrix: Polymers make ideal materials as they can be processed easily, possess lightweight, and desirable mechanical properties. Polymer matrix imparts light weight coupled with high stiffness and high strength. Two kinds of polymers are used

Thermosets: Epoxy resins, PF, UF, MF

Thermoplastics: Polystyrene, Polyethylene, polyamide, Nylon, polypropylene

Metal Matrix:

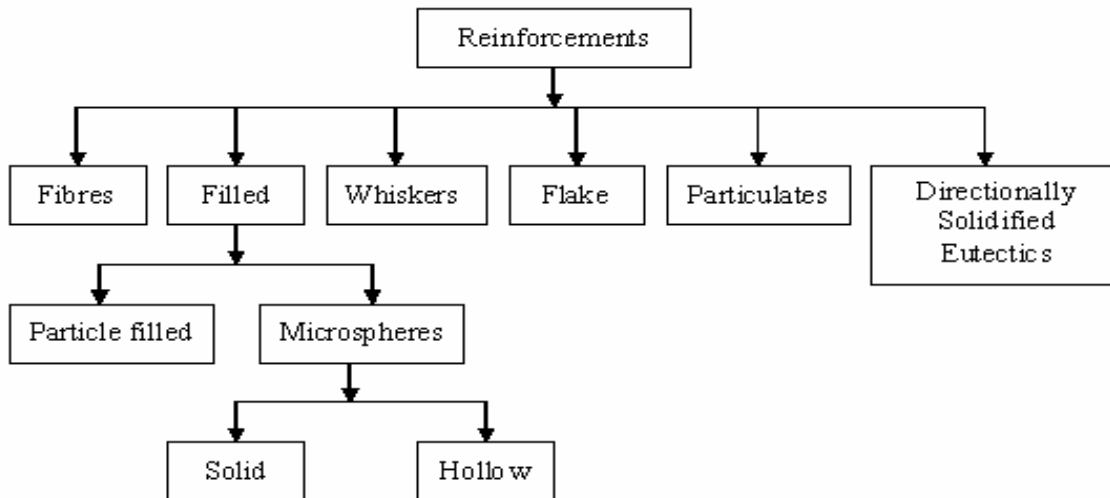
High **strength**, **fracture toughness** and **stiffness** are offered by metal matrices than those offered by their polymer counterparts. They can withstand elevated temperature in corrosive environment than polymer composites. Most metals and alloys could be used as matrices and they require reinforcement materials which need to be stable over a range of temperature and non-reactive too. Example: Titanium, Aluminium and magnesium are the popular matrix metals

Ceramic Matrix:

High melting points, good corrosion resistance, stability at elevated temperatures and high compressive strength, render ceramic-based matrix materials a favorite for applications requiring a structural material that doesn't give way at temperatures above 1500°C.

Example: Clay, Silicon carbide, porcelain

Carbon and Graphite matrix:



Types of Reinforcements: Based on the type of reinforcements, classified into six types

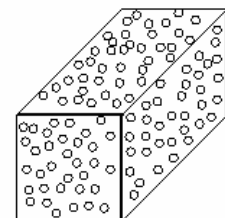
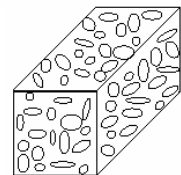
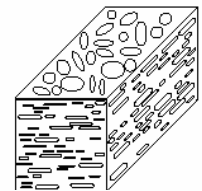
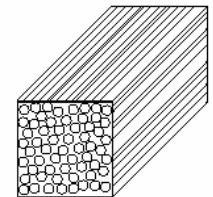
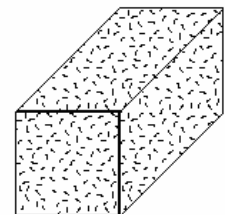
Fibers are the important class of reinforcements, as they satisfy the desired conditions and transfer strength to the matrix constituent influencing and enhancing their properties as desired.

Whiskers Single crystals grown with nearly zero defects are termed whiskers. They are usually discontinuous and short fibers of different cross sections made from several materials like graphite, silicon carbide, copper, iron etc. Typical lengths are in 3 to 55 N.M. ranges. Whiskers differ from particles in that, whiskers have a definite length to width ratio greater than one. Whiskers can have extraordinary strengths up to 7000 MPa.

Flakes are often used in place of fibers as can be densely packed. Metal flakes that are in close contact with each other in polymer matrices can conduct electricity or heat, while mica flakes and glass can resist both. Flakes are not expensive to produce and usually cost less than fibers.

Filled composites result from addition of filler materials to plastic matrices to replace a portion of the matrix, enhance or change the properties of the composites. The fillers also enhance strength and reduce weight. **Microspheres** are considered to be some of the most useful fillers. Their specific gravity, stable particle size, strength and controlled density to modify products without compromising on profitability or physical properties are it's their most-sought after assets

Particulates: *Microstructures of metal and ceramics composites, which show particles of one phase strewn in the other, are known as particle reinforced composites. Square, triangular and round shapes of reinforcement are known, but the dimensions of all their sides are observed to be more or less equal. The size and volume concentration of the **dispersoid** distinguishes it from dispersion hardened materials.*



Fiber Reinforced Polymer Composites

The fibre reinforced polymer composites constitute more than 90% (by weight) of the total composites used in various industries. The advantages of using polymer in structural composites are the ease of fabrication of complex structural shapes. It can be easily manufactured.

Preparation

- Fibre-reinforced plastics are produced by suitably bonding a fibre material with a resin matrix and curing them under heat and pressure.
- The main reinforcing agents used in FRP composites are, glass, graphite, alumina, carbon, boron, etc.
- The reinforcement material can be in different forms such as short fibres, continuous filaments or woven fabrics.
- The resin matrix commonly used in FRP is polyesters, epoxy, phenolic, silicone, and polyamide polymer resins.

Characteristics (or) Properties of FRP

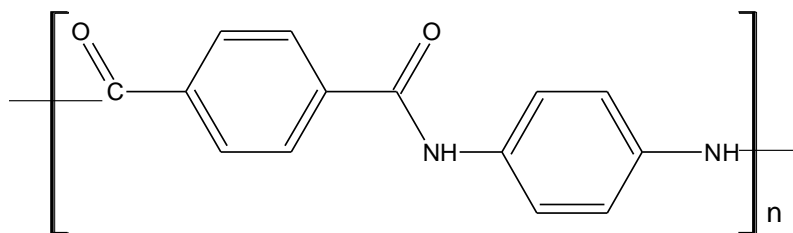
1. It possesses superior properties like higher, Yield strength, fracture strength and fatigue life.
2. Since fibre prevents slip and crack propagation, the mechanical properties of FRP gets increased.
3. It possesses high corrosion resistance and heat resistance property.

The properties of FRP mainly depends on nature of the resin matrix

- Polyester resin _____ provides very good strength & mechanical properties
- Epoxy resin _____ Imparts good mechanical strength
- Silicone resins _____ Impart excellent thermal & electrical properties
- Phenolic resins _____ withstand high temperatures

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

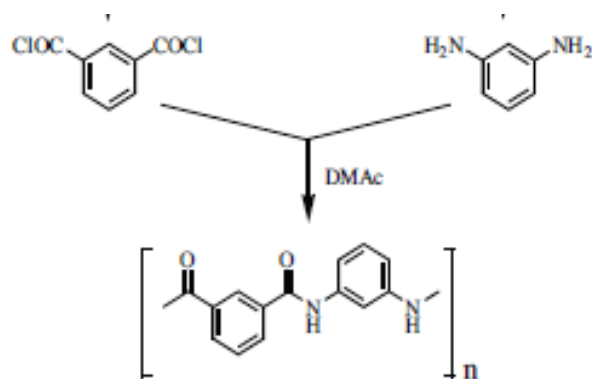
The linkage through para position s of the phenyl rings gives Kevlar a strong ability to stretch and hence its extra strength.



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

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

Synthesis properties and application of Nomex:



Properties:

- Are more rigid and more durable, Nomex is the premier example of a meta variant of the aramids (Kevlar is a para aramid).
- Unlike Kevlar, Nomex cannot align during filament formation and has poorer strength.
- However, it has excellent thermal, chemical, and radiation resistance for a polymer material.

Applications:

- Heat-resistance applications: Filter bags for hot gas filtration (e.g. from steel-making plants).
- Insulating paper for electric motors and transformers,
- Braided tubing for wire-insulation. Sewing thread for high-speed machine sewing

- Fire-resistance applications: Protective clothing for foundry workers, welders, pilots, racing drivers, and fire-fighters. Carpets, upholstery, and tents.
- Dimensional-stability applications: Conveyor belts, fire-hoses.
- Perm-selectivity applications: Hollow fibres of Nomex are excellent semi-permeable membranes, and are used commercially for desalination of seawater and brackish water.

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

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

