MODULE -3

ENGINEERING MATERIALS

Polymers

Polymers are high molecular weight compounds or macromolecules formed by the repeated union of several simple molecules called *monomers*. The monomers are linked through strong covalent bonds. They are called the building blocks of polymer chain. E.g., Polythene, Polystyrene, Teflon, PVC, etc.

Classification of polymers

Polymers are classified into two types as follows:

1) Natural Polymers: These polymers are obtained naturally by plants and animals.
   E.g., Silk, wool, natural rubber, protein, starch, cellulose.
2) Synthetic Polymers: These polymers are artificially prepared also known as manmade.
   E.g., PVC, Polythene, Phenol Formaldehyde resins.

Term Used

Monomer: These are simple molecules which combine to form polymers. These are building blocks of polymer.

Polymerization: The process of linking of monomers to form polymers with or without the elimination of by-products is called as polymerization.

Degree of Polymerization(n): The total number of monomers present in a single chain of polymer is called as degree of polymerization.

POLYURETHANES

They are characterized by the presence of urethane (-NH-CO-O-) linkage. These are prepared by the poly addition of a diisocyanate and a diol .

$$n\ O{=}C{=}N{-}R{-}N{=}C{=}O + n\ OH{-}R^{1}{-}OH \longrightarrow$$

$$\left[-\underset{\displaystyle \overset{\|}{O}}{C}-NH-R-NH-\underset{\displaystyle \overset{\|}{O}}{C}-O-R^{1}-O- \right]_n$$

Polyurethanes

Properties:

- ➢ High abrasion and impact resistance.
- ➢ The foams are available in both rigid & flexible.
- ➢ These are resistant to water, oil, grease & corrosive chemicals.
- ➢ They exhibit good electrical insulating properties.

Uses:

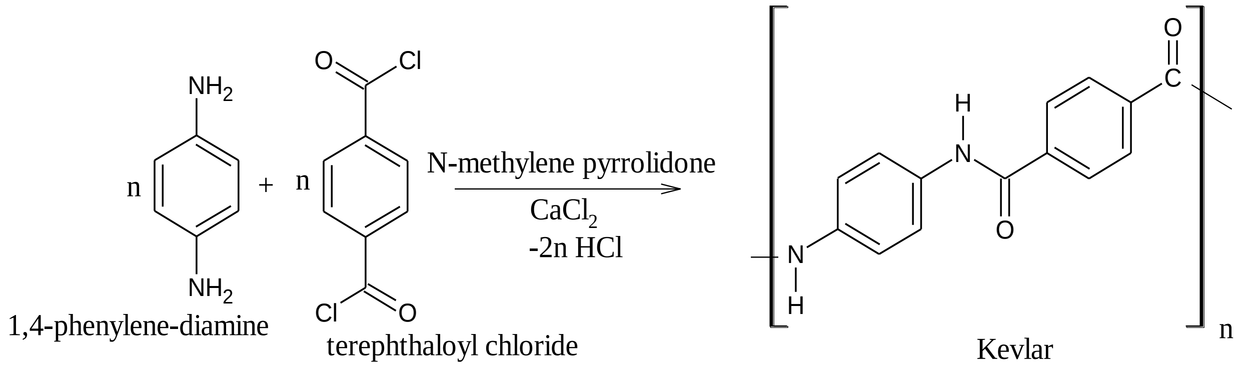
- ✓ They are used in tyre treads & industrial wheels.
- ✓ Used in light weight garments and swimsuits
- ✓ These are used to coat gymnasium floor & dance floor
- ✓ Used as cushions for furniture & automobiles.

Polymer Composites

Composite material is a combination of two or more distinct components to form a new class of material. A polymer composite is produced by bonding a fiber material with a polymer resin matrix and curing the same under heat & pressure. The matrix includes epoxy resins or a polyamides. The fibers used are carbon fiber or Kevlar, combining Fiber and Matrix materials gives the composites of low density, high strength, abrasion and corrosion resistance, etc., which the individual materials do not possess. These composites are generally used in aircraft, space industry, automotive and railway applications. Example FRP.

KEVLAR

Kevlar is a strong synthetic aramid fiber prepared by the condensation reaction of 1,4-phenylene-diamine and terephthaloyl chloride in a solution of N-methyl-pyrrolidone and calcium chloride with the liberation of HCl as byproduct.



Properties:

- High tensile strength
- Chemically stable at high temperatures
- Flame retardant
- Low electrical conductivity
- High resistance to abrasion & impact.
- Light weight
- Difficult to drill and cut.

Uses:

- ✓ In high performance race cars
- ✓ Bullet proof vests
- ✓ Aerospace industries
- ✓ Combat helmets
- ✓ Industrial Gaskets

Conducting Polymers:

An organic polymer with highly delocalized pi-electron system, having electrical conductance of the order of a conductor is called a conducting polymer. An organic polymer can be converted into a conducting polymer if it has a linear structure and carbon backbone consisting of alternate double bond & singlebonds. Conducting polymers are obtained by doping an oxidizing or reducing agent into organic polymers. The doping results in delocalization of electrons which is responsible for conduction. E.g., Polyaniline, Polypyrrole, Polythiopene and Polyacetylene.

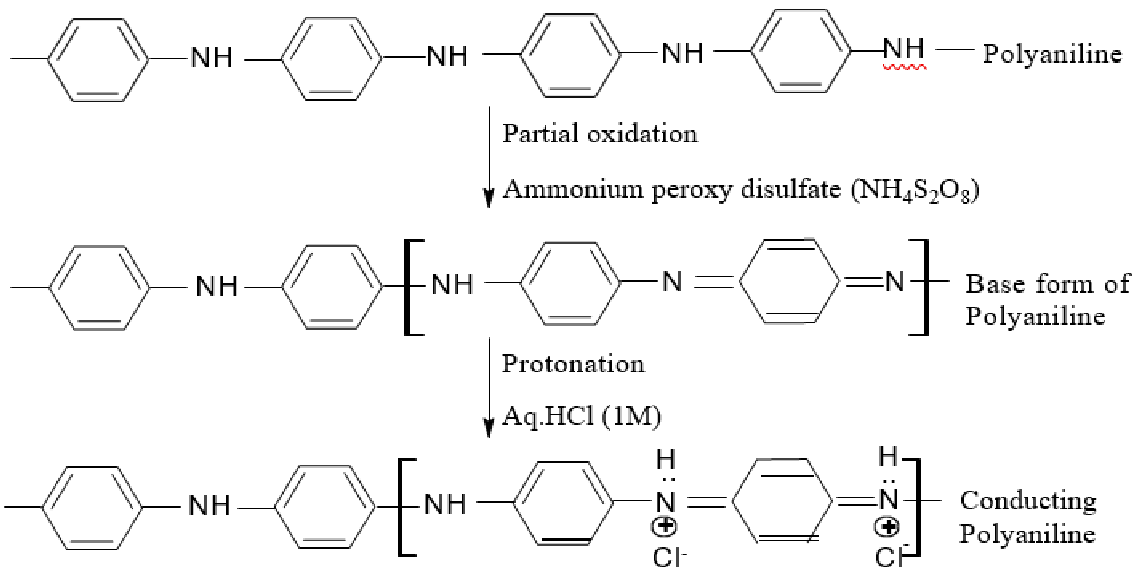
Polyaniline (PANI):

Polyaniline (PANI) is a conducting polymer which is prepared by oxidative polymerization of aniline when a solution of ammonium persulphate is added to a solution of aniline in 1M HCl at low temperature (0-5 ^{o}C).

$$\mathbf{n\ C_6H_5NH_2 + [O] \rightarrow [C_6H_4NH]_n + H_2O}$$

The conducting polymers are synthesized by doping the PANI in which charged species are introduced in organic polymers having pi-back bone. These are generally prepared by protonic acid doping (p-doping).

Mechanism of conduction in Polyaniline:



In protonic acid doping technique, current carrying charged species (-ve / +ve) are created by the protonation of imine nitrogen. Polyaniline is partially oxidized first, using a suitable oxidizing agent, into a base form of aniline which contains alternate reduced and oxidized forms of aniline polymer backbone. This base form of aniline when treated with aqueous HCl (1M), undergoes protonation of imine nitrogen, creating current carrying charged sites (+ve) in the polymer back bone. These charges are compensated by the anions (Cl-) of the doping agent, giving the corresponding salt. This type of protonic acid doping of polyaniline results in an increase of conductivity by approximately 9-10 orders of magnitude.

Applications:

- Corrosion protection
- As conductive tracks on printed circuit boards.
- As sensors – humidity sensor & gas sensor
- Electrochromic display windows

Factors influencing the conductivity of organic polymer

- Effect of Dopant: It has been observed that conductivity increases by doping till a saturation point is reached.
- Effect of Temperature: It has been observed that conductivity increases by temperature. Sometimes becomes constant after a particular temperature.
- Effect of Band Gap: The conductivity increases with decreasing band gap.

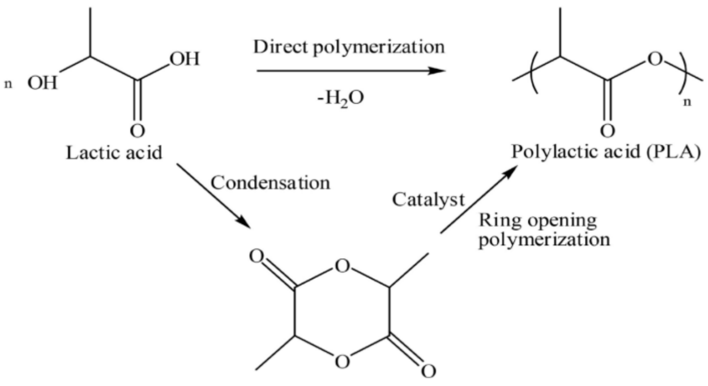
Biodegradable Polymers:

Biodegradable polymer are a special class of polymer that breaks down safely and quickly into raw materials of nature after its intended purpose by bacterial decomposition process to result in natural byproducts such as gases(CO_2, N_2), water, biomass, and inorganic salts. The products formed are nontoxic biproducts in this process. These polymers are found both naturallyand synthetically made, and largely consist of ester, amide, and ether functional groups. Natural biodegradable polymer includes silk, cotton, cellulose and natural rubber. Synthetic polymer examples are polylactic acid and polyglycolide etc. The basic requirements to conduct biodegradation are substrate (Biodegradable polymer), microorganism, temperature, pressure, moisture, oxygen etc.

Polylactic acid (PLA)

PLA is a thermoplastic polyester obtained from condensation of lactic acid with loss of water. The monomer Lactic acid can be prepared by fermentation of corn or sugarcane juice. The direct condensation of lactic acid monomers can also be used to produce PLA. This processneeds to be carried out at less than 200 °C. It can also be prepared from ring opening polymerization of lactide, the cyclic dimer of basic repeating unit. It is a bio degradable polymer.

The cyclic lactide monomer in presence of metal alkoxide catalyst undergoes ring opening to give required polymer.



Properties:

- ✓ Amorphous PLA are soluble in various organic solvents, including acetone, acetonitrile, and methylene chloride, whereas crystalline PLA can only be dissolved in dichloromethane or benzene at high temperatures.
- ✓ It is very good Heat-resistant and can withstand temperatures of 110 °C.
- ✓ Poor ductility, low impact strength and brittle.
- ✓ Nontoxic & Biodegradable

Uses:

- ➢ Drug delivery
- ➢ Medical implants (Fixation of fractured bones in form of plates, pin, screws and wires)
- ➢ Plastic films / bottle
- ➢ 3D printing
- ➢ Food packing
- ➢ Biomedical application in sutures (commonly called stiches).

QUESTION BANK

1.*Write a note on Polyurethanes.*

2. Explain the synthesis, properties and uses of Kevlar.

3.What are conducting polymers. Explain the mechanism of conduction in polyaniline.

4.Explain the mechanism of conduction in Polyaniline & factors effecting conductivity in Organic polymer.

5.Explain the synthesis, properties and uses of Polylactic acid.

6. write a note on biodegradable polymer.

NANO MATERIALS:

The word *Nano* is derived from Greek word meaning dwarf or something very small (10^{-9}) of a unit. *Nano particles are materials having sizes in the range of 1-100 nanometers*. Materials of nanoscale often have unique optical, electronic or mechanical properties. Nano particles can be naturally occurring or synthetically derived. Naturally occurring includes volcanic ash, soot from forest fires etc. Nanoparticles exist in nature in form of biological origin materials or byproduct of human activities. The typical examples are wax crystals covering a lotus, butterfly wings, milk, blood and bone matrix. Synthetic nanoparticles include fullerenes, carbon nanotubes, metal or metal oxide nanoparticles.

Nanomaterials are used in

- Medicine for diagnostics, drug delivery, cancer therapy, synthetic bones, tissue engineering;
- In nano cosmetics for keeping the skin soft and wrinkle free.
- In Information & Communication technology
- In nano sensors such as biosensors, chemical sensors, mechanical sensors, etc.
- In water purification.

Properties of Nano materials (Size dependent)

Controlling the structures of nanoparticles at Nano scale dimensions, properties of Nano structures can be tailored in a very predictable manner to meet the needs of variety of applications.

Electrical properties

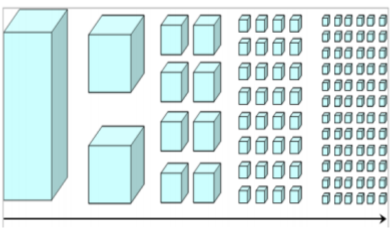
In case of bulk molecules, there is delocalization of electrons and electron move in any directions. There is overlapping of orbitals in bulk particle. But in Nano scale there is discrete band gap. Hence metals which are good conductors in bulk, become semiconductor and finally insulator when size is decreased to Nano level.

Optical properties

Band gap increases with the decrease in size of materials due to less overlappingof orbitals. The discrete electronic states of nanoparticles allow absorption and emission of light of specific wavelength. Hence nanoparticles exhibit unique colors different from bulk. The nanomaterial has higher optical band gap when compared to their bulk counterpart. This is due to interaction of conduction electron of nanomaterial with incident photons. Bulk gold is golden yellow colored but nano gold appears blue, red, green depending on various nano sizes. The particles are so small that electrons are not free to move about as in bulk gold. The restricted movement of particles makes particles behave differently with light.

Surface area

The total surface area (or) the number of surface atom increases with reducing size of the particles. The physicaland chemical properties property of nanomaterials is sizedependent, because in nano scale more surface area will be exposed compared to bulk materials.



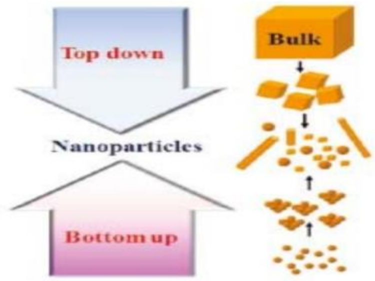
If the bulk materials are subdivided into nanomaterials, the collective surface area is greatly increased. Change in surface to area volume on breaking down the molecules affects the physical, chemical, mechanical and other properties invariably. If the surface size is larger so a greater amount of the material comes in to contact with surrounding materials and increases reactivity.

Catalytic properties

When the size of material is reduced to nanometer range, a large fraction of atoms is located at the surface of nanomaterial will modify its catalytic properties. Properties such as gas absorption and chemical reactivity increases as particle size decreases. Therefore, nanomaterial is more reactive than bulk scale or larger nanomaterial. E.g., TiO_2 Nano material doped with Ag, Au, Pt are good catalyst to absorb pollutants from atmosphere whereas bulk one is inactive.

<u>Synthesis of Nanomaterials:</u>

Bottom-up approach refers from small to big. In this method material is made from bottom; atom-by-atom, molecule-by-molecule, or cluster-by-cluster. These are simple, economical methods which involve *chemical technique* and have better control over chemical composition, size and products obtained are at high purity. E.g., CVD method.



Top-down involves where bigger particles are broken down into smaller nanosized particles by physical methods. E.g., Sol-gel method.

i) <u>Sol-Gel process</u> :

It is a process used to prepare mono sized Nano particle (metal oxide) at a low cost. A sol is colloidal suspension of solid particles dispersed in a liquid phase. A gel is colloidal solution made up of liquid particle dispersed in a solid phase. In general sol-gel consists of chemical transformation of sol to gel state and subsequent post treatment and transition to solid nanomaterials. Sol gel process can be explained by series of following steps.

a. <u>Preparation of sol:</u>

In this process metal alkoxide (MOR), R an alkyl group is used as precursor (starting material) to synthesize nanoparticles. First sol is prepared by dispersing precursors in solvent (alcohol), and then hydrolyzed with acidic or basic catalyst. Here alkoxide ligand is replaced by hydroxyl ligand

$$\mathbf{MOR + H_2O \rightarrow MOH}\ \textit{(Sol)}\ \mathbf{+ ROH\ (hydrolysis)}$$

b. <u>Conversion of a sol to gel:</u>

Sol is further converted to gel by polycondensation reaction between MOH and MOR resulting in formation of oxide or alcohol bridged network (gel). These are complex multistep process involving gel formation.

$$\mathbf{MOH + ROM \rightarrow M\text{-}O\text{-}M}\ \textit{(Gel)}\mathbf{+ ROH\ (condensation)}$$

c. <u>Aging of a gel (Syneresis):</u>

Polycondensation reaction continues until gel transforms into solid mass by contraction of gel network and expulsion of solvent from gel.

d. <u>Removal of Solvent</u>**:**

The gel formed by thermal evaporation at ambient temperature is called as xerogel. If the solvent is extracted under critical conditions, Aerogel is obtained.

e. <u>Heat Treatment:</u>

The gel is treated at high temperatures (400-800^{o}C) to collapse the pores in the gel network & to drive out remaining organic contaminants. Thus, nanosized metal oxide particles can be prepared.

Advantages:

- ✓ High purity compounds are obtained
- ✓ The sol-gel approach is a cheap and low-temperature technique that allows for the fine control on the product's chemical composition.

ii) Precipitation method:

In this method solid Nano particles are obtained by careful precipitation from their solution.

- Precursors used in this method are metal salt (metal nitrate or acetate) is dissolved in water and continuously stirred (Nucleation).
- These metallic salts are precipitated out as hydroxides using a suitable base NaOH (*Precipitation*) in suitable solvent under constant and continuous stirring.
- The obtained precipitate is dried and heated at high temperature in muffle furnace (*Calcination*) to obtain the metal oxide nanoparticles.
- The size of nanomaterial can be controlled by varying the stirringspeed, time and temperature of heating.

FULLERENES

A fullerene is an allotrope of carbon in the form of a hollow sphere, ellipsoid, tube & many other shapes. Fullerenes with different number of carbon atoms like C_{60}, C_{70}, C_{74} etc. have been prepared and investigated. C_{60} molecule has shape like a soccer ball and is called Buckminster fullerene.

Fullerenes are similar in structure to graphite, which is composed of stacked graphene's sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings.

Structure & Properties:

- It is containing 20 six membered ring (hexagon) and 12 five membered ring (pentagon) and contain 60 vertices. It has a cage-like fused-ring structure (truncated icosahedron) that resembles a soccer ball
- All carbon atoms are equal and are sp^2 hybridized. Each carbon atom forms three sigma bonds with other three carbon atoms. C-C bond length is 1.44 A^0.
- In spite of extensive conjugation fullerene behave chemically and physically as electron deficient alkenes rather than electron rich aromatic compounds.
- The fullerenes are found to be soluble in common solvents such as benzene, toluene or chloroform.
- The C_{60} molecule is extremely stable, being able to withstand high temperatures

Uses:

- ✓ Used as a lubricant.
- ✓ Absorbent for gases
- ✓ Drug delivery
- ✓ Production of Cosmetic products

CARBON NANO TUBES

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon called *graphene*. These sheets are rolled at specific and discrete "chiral" angles and the combination of the rolling angle and radius decides the nanotubes properties.

Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Individual nanotubes naturally align themselves into "ropes" held together by Vander Waals forces. Single walled nanotubes have a diameter of close to1 nm, with a tube length that can be many millions of times longer. The structure of a single walled nanotube can be single sheet of graphenes sheet wrapped together. Multi walled nanotubes consist of multi rolled sheets of graphene.

Properties:

- ✓ These are hundred times the tensile strength of steel.
- ✓ High electrical and thermal conductivity.
- ✓ Excellent Chemical & thermal stability.

- ✓ Highly flexible can be bent considerably without damage.

Uses:

- ✓ In manufacture of fibers and fabrics.
- ✓ Air and water purification units.
- ✓ Carbon nanotubes tipped with gold nanoparticles can be used to trap oil drops from polluting water.
- ✓ Biomedical applications in drug delivery.

GRAPHENES

- Graphene is a allotrope of carbon which exists in 2-dimensional planar sheet.
- Each atom has four bonds: one σ bond with each of its three neighbors and one π-bond that is oriented out of plane.
- The atoms are about 1.42 Å apart. All carbon atoms are sp^2 bonded to adjacent carbon atom & carbon atom is arranged in hexagonal lattice.
- These are held by weak Vander walls forces.
- Good conductor of heat, electrical conductivity and high melting point.
- Shows high tensile strength & optically transparent.

Uses:

- ✓ Graphene based Sensors.
- ✓ Touch panels.
- ✓ Water purification.
- ✓ Bullet proof jacket.
- ✓ Drug delivery.

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QUESTION BANK

1. *What is Nano material? Explain the synthesis of Nano material by sol gel method.*
2. *Write a note on fullerenes.*
3. *Explain the synthesis of Nano material by Precipitation method.*

4. *Write a note on carbon nano tubes.*
5. *Write a note on graphene's.*
6. *Write a note on any two properties of nanomaterial.*

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