UNIT-III

CHEMISTRY OF ADVANCED MATERIALS

NANO METERIALS

Introduction

- The materials like metals, non-metals, and ceramics, polymeric or composite which are made up of nano sized particles i.e. particles in the range of 1 nm to 100 nm are called nanomaterials.

Or

- Nanomaterials are those which have structure components with atleast one dimension less than 100 nm.

Examples:

Size of hydrogen atom	-	0.1 nm
Size of water molecule	-	<1 nm
Size of RBC	-	500 nm
Size of human hair	-	50000 nm
Diameter of carbon nanotube	-	1.3 nm

- The properties of materials like melting point, conductivity, colour, reactivity, reaction rate, catalytic activity are different for different sizes i.e. bulk and nano.

Examples:

- Bulk gold looks yellow but 12 nm nano sized gold particles look red.
- Bulk silver is inert but nano scale silver shows anti bacterial activity.
- Graphite possesses less mechanical strength, carbon nanotubes posses' high mechanical strength.
- The catalytic activity of materials at nano scale is much higher than large size.

- Nanomaterials can be effectively used for many specific applications which cause revolutionary changes in the field of electronics, medicine, energy, agriculture, space, security, defence, construction etc.
- Nano means 10^{-9}. A nanometer is one thousand millionth of a meter. Atoms are extremely small and the diameter of a single atom can vary from 0.1 to 0.5 nm depending on the type of the element. For example, one carbon atom is approximately 0.15 nm in diameter.

Nanomaterials: The materials in which the atoms are in the order of 1 to 100 nm and these atoms will not move away from each other, called as nanomaterials.

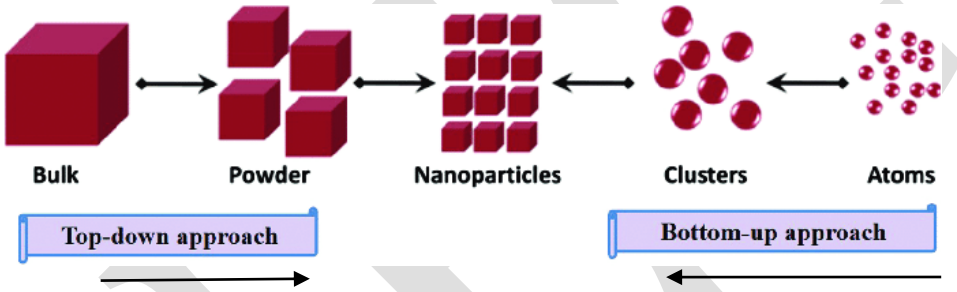
Ex: C, ZnO, Cu–Fe alloys, Ni, Pd, Pt etc.

1. Materials that are nanoscale in one dimension called as nano layers [Thin films, surface coatings].
2. Two dimensional nanomaterials are called as nano tubes and nanowires.
3. Three dimensional nanomaterials are called as nanoparticles. **Ex:** Precipitates, Colloids & Quantum dots, tiny particles of semi-conductor materials.

General methods of preparation:

There are basically two major types of approach for the preparation of nano materials.

1. **Top-down approach:** Top down approach refers to successive cutting of a bulk material to get nano sized particle. Attrition or milling is a typical top down method in making nano particles.



2. **Bottom-up approach:** Bottom up approach refers to the buildup of a material from the bottom *viz* atom by atom, molecule by molecule or cluster by cluster. Colloidal dispersion is a good example of bottom up approach in the synthesis of nano particles.

Sol-Gel method: It is a wet chemical process, widely used for the fabrication of nano structured ceramic materials and thin films. Sol-gel process involves the conversion of precursor solution (usually metal salts or metal alkoxides) into nano structured inorganic solid through inorganic polymerization reactions catalyzed by water. In general, metal alkoxides (M-OR) are widely used as precursors, because they are readily react with water. The reactions involved in sol gel process are

1. **Hydrolysis:**

   $M\text{-}OR + H_2O \longrightarrow M\text{-}OH + R\text{-}OH$

   (Metal Alkoxide) (Metal hydroxide)

2. **Condensation:**

   $M\text{-}OR + M\text{-}OH \longrightarrow M\text{-}O\text{-}M + R\text{-}OH$

The M-O-M undergoes poly condensation reaction, results to form polymer network in all directions.

Process:

Step-1: Sol formation by Hydrolysis: Preparation of homogeneous solution either by dissolution metal salt in water or metal alkoxide in inorganic solvent (usually alcohol) i.e. miscible in water. It involves the conversion of homogeneous solution in to a sol due to hydrolysis reaction.

Step-2: Gel formation by Condensation: The colloidal solution is kept for few hours. During this condensation reaction between to metal hydroxyl and alkoxy species leads to M-O-M bonds with elimination of water. This condensation process continuous and finally results in gel an inter connected a rigid and porous network covered completely with liquid phase. This transformation is called Sol-Gel transition.

Step-3: Drying of Gel: It involves removal of liquid phase from gel network. There are different ways of drying gel.

- If the gel medium is dried by removing the liquid solvent without destroying the gel network, aerogel is produced.
- If the solvent is dehydrated by under ambient conditions (removal of R-OH groups) xerogels are produced.
- If the gel network is heated at high temperature (800^{o}C), densification, decomposition of gel results in complete collapse of gel network in to powder.

Chemical reduction method of preparation:

This method is also belongs to bottom up approach. Metal nano particularly silver nanoparticles are prepared by this method.

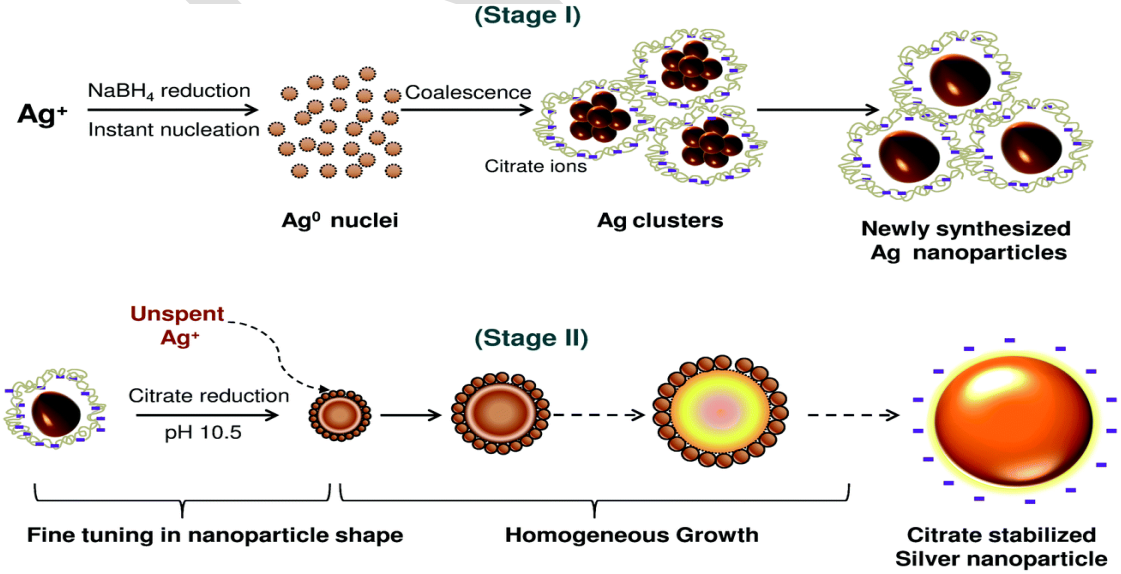
Synthesis of silver nanoparticles:

General preparation is carried out by mixing the metal salts with phase transfer agents and reducing reagents. Different phase transfer reagents are used for the preparation of different metal nanoparticles.

Metal salt solution + Metal salt precursor + Stabilizer + Reducing agent → Stand for some time → Nanoparticles separate → Purification → Centrifugation → Freeze drying → Metal nanoparticles.

Example:

- For the preparation of silver nano particles $AgNO_3$ solution (from 1 ppm to 6 ppm) and 8% w/w sodium dodecyl sulphate (SDS) are used as metal salt precursor and metal stabilizing agent respectively.
- Hydrizine hydrate (2-12ppm) and citrate solution (1ppm) are used as reducing agents.
- The transparent colorless solution will be converted to pale yellow and pale red colour which indicates the formation of silver nanoparticles.
- To remove the excess silver ions the solution is washed with deionizer water under nitrogen stream for three times.
- The nano particles are characterized by UV and X-ray crystallography.



Characterization of nanomaterials:

Brunauer–Emmett–Teller (BET) method:

- **Brunauer–Emmett–Teller** (**BET**) **theory** aims to explain the physical adsorption of gas molecules on a nano material surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of nano materials.
- The BET method applies to systems of multilayer adsorption and usually utilizes probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface area.
- Nitrogen is the most commonly employed gaseous adsorbate used for surface probing by BET methods. For this reason, standard BET analysis is most often conducted at the boiling temperature of N_2 (77 K).
- Further probing adsorbates are also utilized, albeit with lower frequency, allowing the measurement of surface area at different temperatures and measurement scales. These have included argon, carbon dioxide, and water.
- Specific surface area is a scale-dependent property, with no single true value of specific surface area definable, and thus quantities of specific surface area determined through BET theory may depend on the adsorbate molecule utilized and its adsorption cross section.

TEM (Transmission Electron Microscopy) method:

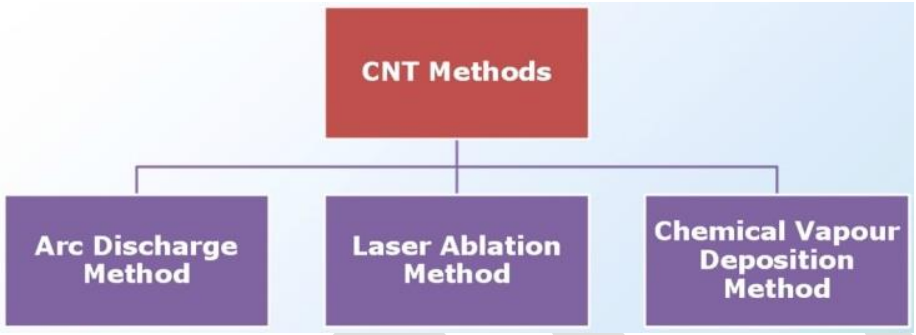
- **Transmission electron microscopy** is a microscopy technique in which a beam of electrons is transmitted through a nanomaterial to form an image. The nanomaterial is most often an ultrathin section less than 100 nm thick or a suspension on a grid.
- An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the nanomaterial. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a scintillator attached to a charge-coupled device.
- Transmission electron microscopy is a major analytical method in the physical, chemical and biological sciences. TEMs find application in cancer research, virology, and materials science as well as pollution, nanotechnology and semiconductor research, but also in other fields such as paleontology and palynology.

Carbon Nano Tubes

CNT are sheets of graphite about 0.4 nm in diameter rolled up to make a tube of few nano meters in diameter. These are cyllendrical fullerenes and are also known as bucky tubes.

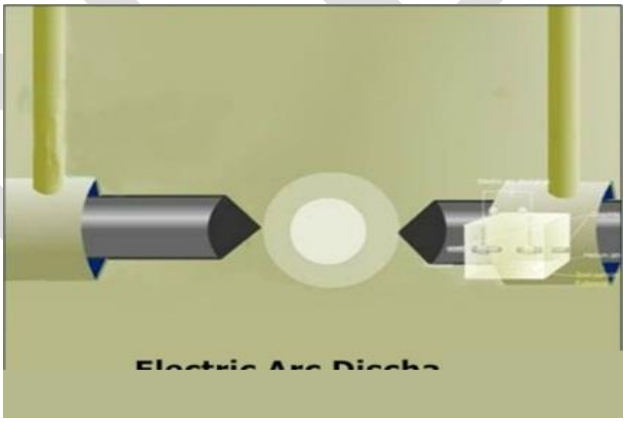
Preparation:

CNTs are prepared by three methods such as:



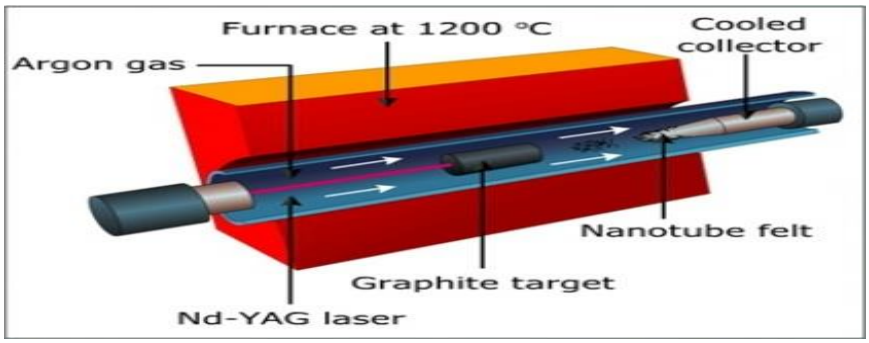
Arc Discharge Method:

- In this method CNT's are produced by the arc discharge of graphite electrodes in the presence of ionized gas at high temperature by using a current of 100 amperes.
- The carbon contained in the negative electrode sublimates during the process.
- In this method the yield is 30% and both the single and multiwall nanotubes are produced.



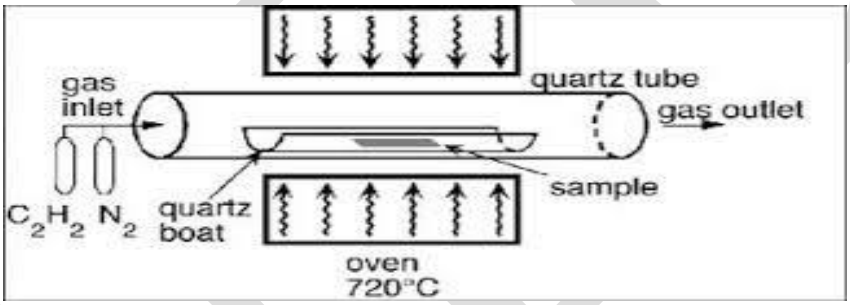
Laser Ablation Method:

- This method was developed by Dr. Richard Smalley. A pulsed laser vaporizes a graphite sheet in a high temperature reactor, through which an inert gas is sent. A mixture of cobalt and nickel is used as a catalyst.
- CNTs are obtained on the cooler surface of the reactor.
- In this process the yield is 70%. This is an expensive method.



Chemical Vapour Deposition method:

- It is a low cost method.
- In this method, a substance is prepared with a layer of catalyst nickel or cobalt nanoparticles.
- The substance is heated to 700^0C and a mixture of nitrogen and carbon containing acetylene or ethylene or methane is passed over it. The CNTs are produced on the surface of catalyst particles.



Properties:

- CNTs are posses high tensile strength upto 100 giga pascals (GPa)
- These are very hard and can withstand a pressure upto 25 Gpa without deformation.
- Multiwalled CNTs exhibit striking telescopic properties.
- CNT is semiconducting and involves quantum effects.
- CNTs show optical properties due to the absorption of photoluminescence.
- CNTs are very good thermal conductors and posses a thermal conductivity of 3500 $WM^{-1}K^{-1}$.
- CNTs are toxic and can induce harmful effects and can cause cell death.

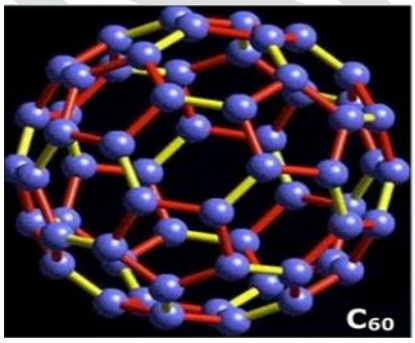
Applications:

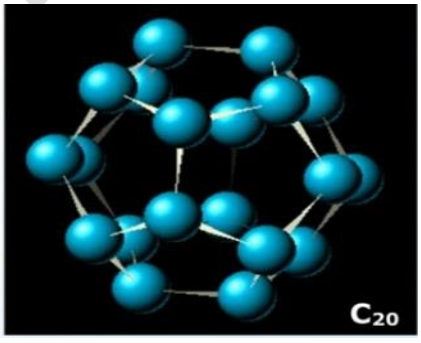
- CNTs are used to make space elevators, stab-proof, bullet-proof clothing.

- Semi conducting nanotubes are used for the preparation of CNT field effect transistor.
- These are also used in the making of nano-tube polymers used in the manufacturing of electrical cables and wires.
- CNTs are used in the preparation of paper batteries which can be used for stable power output.
- A mixture of CNT and fullerenes is used in solar panels.
- CNTs are used for the storage of hydrogen gas.
- Single walled CNT is used to cure cancer.
- CNTs are also used in textiles for the manufacture of fabrics which are antibacterial and electrically conductive.

Fullerenes

- Previously it is assumed that carbon is present in two crystal structures, such as diamond, graphite and in amorphous form.
- In 1985, Richard Smalley *et al.* at Rich University discovered new group of molecules, entirely made up of carbon atoms called fullerenes.
- A fullerene is any molecule composed entirely of carbon in the form of a hallow sphere, ellipsoid or tube.
- Speherical fullerene, are also called buckyballs as they resembles the balls used in football.





- Fullerenes are similar in structure to graphite which is composed of stacked graphene sheets of linked hexagonal, pentagonal or heptagonal rings.
- The smallest fullerene is dodecahedral C_{20} and the most common fullerene is C_{60}.
- 60 carbon atoms combine to form hollow sphere like structure indicated by C_{60} and 70 carbon atoms from ellipsoidal structure indicated by C_{70}.
- When a metal is used as an inclusion compound it is called metallo fullerene.

Preparation

- Fullerenes are prepared by a large current between two nearby graphite electrodes in an inert atmosphere.
- The resulting carbon plasma between the electrodes cools into sooty residue from which fullerenes can be isolated.
- The fullerenes are extracted from soot using the multi-step procedure.

Properties:

- Fullerenes are stable with sp^2 hybridized carbon atoms.
- Fullerenes are sparingly soluble in many solvents. Common solvents for fullerenes are like toluene, CS_2.
- Fullerenes show a wave practical duality due to which several sculptures symbolizing wave particle duality are created.
- Some fullerenes are inherently chiral because they are D_2-symmetric and have been successfully resolved.
- Fullerenes undergo:

➢ **Hydrogenation:** C_{60} posses little aromatic character and undergo addition with hydrogen to form polyhydro fullerenes.

➢ **Halogenation:** Addition of F, Cl and Br occur for C_{60} under various conditions, produce a vast number of halogenated derivatives. **Ex:** $C_{60}Br_8$ and $C_{60}Br_{24}$.

Applications:

A fuel:

- Buckyballs are an efficient medium to make hydrogen fuel.

Medicine:

- Buckminster fullerenes inhibit the HIV virus.
- C_{60} inhibits a key enzyme in the human immunodeficiency virus known as HIV-1 protease which could inhibit the reproduction of HIV virus in immune cells.
- When impregnated with He, C_{60} buckyballs can be used as chemical traces in human body.

Solar cells:

- The optical absorption of C_{60} match the solar spectrum, hence find its application in solar cells.

LIQUID CRYSTALS

- Liquid crystals are matter in a state that has properties between liquid and solid.
- Many organic materials exhibit liquid crystals state over a restricted temperature range.
- The material becomes a crystalline solid at the lower end of the temperature range and becomes a clear liquid at the upper end.

- The liquid crystalline state is obtained by raising the temperature of solid and or by lowering the temperature of a liquid.

  Example: Cholesterol myristate is a crystalline solid below 71°C and above 71°C it becomes a cloudy liquid and at 86°C becomes a clear liquid. The intermediate state i.e. from 71°C to 86°C is said to be liquid crystal state.

Types of Liquid Crystals:

1. Thermotropic liquid crystals:

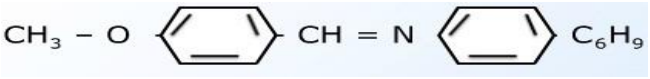
a) Nematic Crystals b) Cholestric Crystals c) Smectic Crystals

2. Lyotropic liquid crystals

Nematic Crystals:

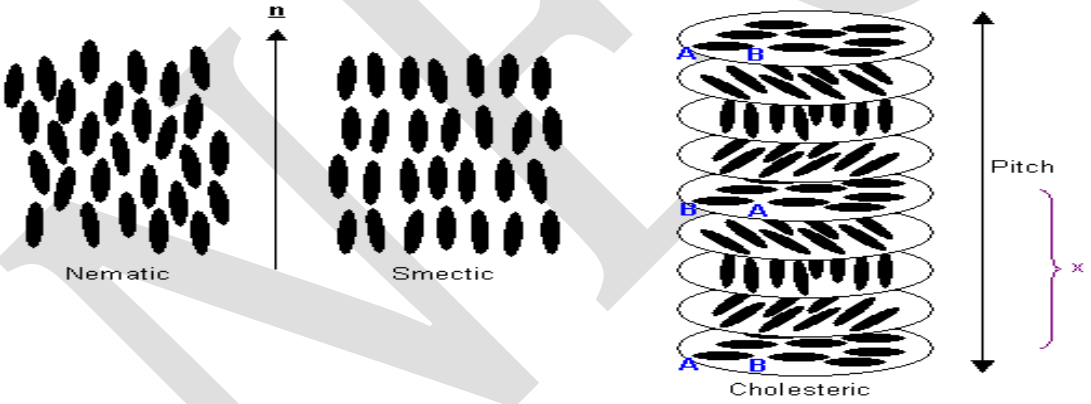
- In crystalline state, liquid crystal state and liquid state of an organic substance posses different arrangement of molecules.
- Solid state posses orderly arrangement and liquid state posses arrangement of molecules random in some directions and regular in others.
- The molecules exist in layers and within layers the molecules can slide around each other and layers can slide over one another. This molecular produces the fluidity characteristic of a liquid.
- Liquid crystals have the mobility of liquids and optical properties of solids.

- The most widely used ones twisted nematic liquid crystals which contain long axes of molecules which rotate by a small angle from one layer to the next.
- The nematic liquid crystal is made of MBBA molecule i.e. 4-methoxy-Benzylidine,4-butylaniline in which two benzene rings are linked in a single group.
- The molecular formula of MBBA molecule is



Cholestric Crystals

- In cholestric phase, the molecules are orderly arranged similar to nematic phase, but in planes. Here the only difference is the orientation will differ from one plane to another.
- The distance between the similar planes i.e., the planes in which the molecules has same direction is called 'pitch'.
- The cholestric liquid crystal has a special property that, if white light is allowed to pass through the crystal it appears coloured.



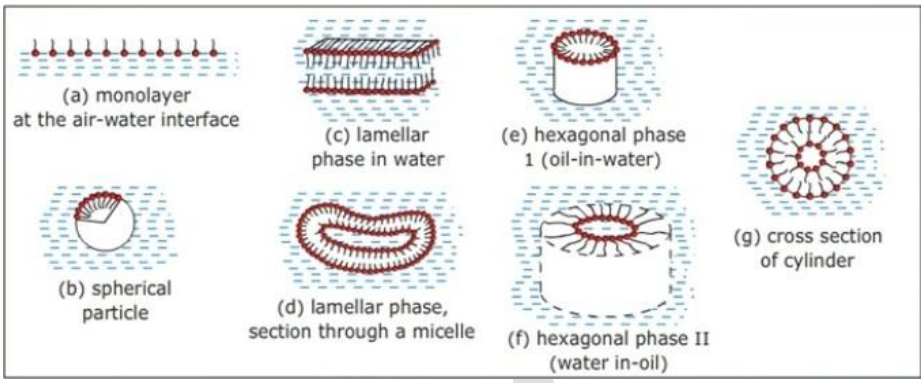
Smectic Crystals:

The word smectic is derived from the Greek word soap. In smectic state, the molecules posses a general orientation order like nematic but also tend to align themselves in layers or planes. The smectic state is more 'solid like structure' then nematic.

Lyotropic Crystals

- This crystal state occurs in concentrated solution of rod like molecules in isotropic solvents usually in water. This is shown in soaps, gels and colloids.

- Lyotropic liquid crystals transitions occure due to the influence of solvent. These are amphiphillic i.e., they consists of lyophilic (solvent attracting) and lyophobic (solvent repelling) parts and from micellar strctures.



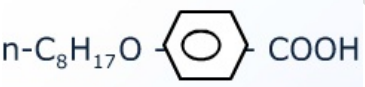
Examples of Liquid Crystalline Compounds

The liquid crystalline state is obtained by raising the temperature of a solid and or by lowering the temperature of a liquid.

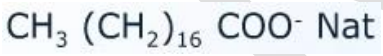
Liquid crystalline compounds

P-azonyanisole (PAA)

P-n-octyloxy Lengoic acid



Sodium stearete



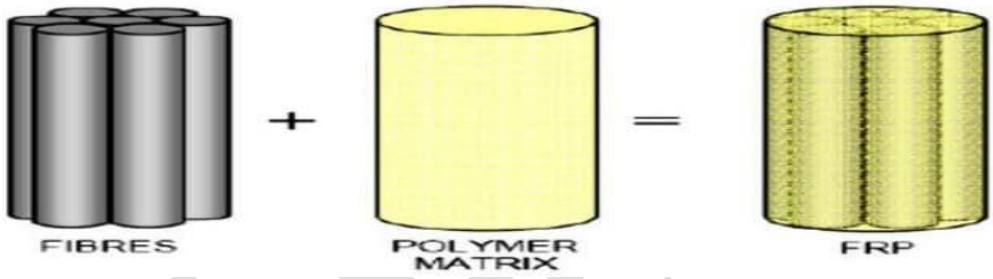
Applications of Liquid Crystals:

- Liquid crystals are used as display devices in TVs, watches, calculators and flat panel displays.
- Liquid crystals are used in gas liquid chromatography because their mechanical and electrical properties lie between solid and liquids.
- Cholesteric liquid crystals vary their colours depending in the temperature. They can be used to detect veins, arteries and tumors which are warmer than surrounding tissue.
- Liquid crystals are used as electro optical materials.
- Liquid crystals are used as radiation and pressure sensors.

COMPOSITES

- Composites, also known as Fibre-Reinforced Polymer (FRP) composites, are made from a polymer matrix that is reinforced with an engineered, man-made or natural fibre (like glass, carbon or aramid) or other reinforcing material.
- The matrix protects the fibres from environmental and external damage and transfers the load between the fibres. The fibres, in turn, provide strength and stiffness to reinforce the matrix-and help it resist cracks and fractures.

Fibre Reinforced Plastics (FRP): Fibre Reinforced Polymer (FRP) composite is defined as a polymer that is reinforced with fibre.



Types of Fibre Reinforced Polymer (FRP)

1. Glass Fibre Reinforced Polymer (GFRP)

In this type glass material is incorporated in plastic materials. Glass FRPs used because of durability, acid proof, water proof and fire proof nature of glass. Glass is drawn into threads in the form of fine cotton threads. Then these threads are woven in the form of mats. This mat is filled with plastic materials. The common plastics used are polyesters, polyamides and poly vinyl chlorides.

Properties:

- Good dimensional stability.
- High service temperature.
- Excellent chemical resistance.
- Excellent corrosion resistance.
- Good tensile strength.
- Posse's good thermal resistance.

Applications:

Fibre reinforced plastics are used in

- Auto motive parts
- Storage times
- Industrial flooring
- Plastic pipes
- Transportation industries to reduce vehicle weight.

2. Carbon Fibre Reinforced Polymer (CFRP)

Carbon Fibre Reinforced Polymer (CFRP) is a polymer matrix composite material reinforced by carbon fibres. The reinforcing dispersed phase may be in form of either continuous or discontinuous carbon fibres of diameter about 0.0004" commonly woven into a cloth. Carbon fibres are very expensive but they possess the highest specific (divided by weight).

Properties:

- Very high modulus of elasticity exceeding that of steel.
- High tensile strength, which may reach 1000 ksi (7 GPa).
- Low density: 114 lb/ft^3 (1800 kg/m^3).
- High chemical inertness.

Applications:

- It is widely used in aerospace and aircraft industries.
- It is used in sports industry (light weight badminton rockets and golf sticks).
- It is used in automobile industry (bonnet, bumper, car body parts and engine cover).

Cermets:

Composite materials composed of ceramic (cer) and metal (met). Cermet's deliver the benefits of both metal and ceramic in engineering material which can't be obtained from either one material. Ceremets are hot pressed or sintered materials, consisting of combination of ceramics and metals.

Properties:

- High refractoriness of ceramics
- High thermal conductivity of metals
- High thermal shock resistance of metals
- High shapability.

Applications:

- Used as cutting tool materials involving titanium carbide or titanium carbonitrides as the hard refractory phase.
- Cermets based on SiC & B_4C used in wear and corrosion resistance or antifriction applications and also in nuclear reactor applications.
- TiN & ZrN bonded with their respective metallic elements developed for special heat and corrosion resistant purposes.
- UO_2 or ThO_2 based cermets found application as a major fission component in nuclear reactor fuel elements.
- Combinations of Al_2O_3 with TiC are suitable for hot machining tools.
- Combination of ZrB_2 and SiC is resistant to erosion from the propulsion gases of chemical rockets.
- ZrB based cermets used in liq. Metal pumping system and also thermocouple sheathes.

UNIT-III

CHEMISTRY OF ADVANCED MATERIALS

IMPORTANT QUESTIONS

1. What are nano materials? Explain the preparation of nanomaterials by Sol-Gel and Chemical reduction method.
2. How to characterize nano materials by BET and TEM methods.
3. Explain preparation properties and applications of CNTs.
4. Explain preparation properties and applications of Fullerenes.
5. Discuss the types and applications of liquid crystals
6. What is FRP? Explain the properties and applications of FRP?
7. Write a short note on cermets.