

# Bansilal Ramnath Agarwal Charitable Trust's

# VISHWAKARMA INSTITUTE OF INFORMATION TECHNOLOGY

Department of Engineering & Applied Sciences

### F.Y.B.Tech

Course Material ( A brief reference version for students)

**Course: Engineering Chemistry (AY20-21)** 

Unit 2: Chemistry of Engineering Materials (2020course)

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### **Unit 2 – Chemistry of Engineering Materials**

**Objective:** To understand chemistry of various engineering materials and relate it to properties and applications

**Course outcome:** Explain chemistry of Portland cement, polymers used in construction, electronic and mechanical industry, nano materials, modern batteries and relate it to the properties and applications

### **Contents**

### **Unit II – Chemistry of Engineering Materials**

**Portland Cement**: Composition of Portland cement, Setting and hardening of cement, ISI specifications of Portland cement

### **Polymers:**

Specialty polymers: Conducting polymers, Liquid Crystal polymers, Electroluminescent polymers, Fiber reinforced polymers (FRP)

Applications of polymers in construction industry, electronic industry and mechanical industry. Polymer recycling

**Nano materials:** Introduction to Nanotechnology, Types of nano materials, Nano materials and their applications

**Modern Batteries**: Concept and applications of Lithium batteries

### 2.1 Portland Cement:

#### 2.1.1 Introduction

- 1)Cement is a material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks etc.
- 2) Main constituents of cement are compounds of Ca (Calcarious) and Al+Si (Argillaceous). The cements have property of setting and hardening under water by virtue of certain chemical reactions with it and are therefore called 'hydraulic cements'.

#### 2.1.2 Portland Cement

It is also called as 'magic powder'. It is made by calcining (at about 1500°C) an intimate and properly proportioned mixture of clay and lime containing raw materials. After calcinations, retarder like gypsum is added.

#### 2.1.3 Manufacture of Portland

Raw materials i) Calcareous materials CaO (lime-stone, chalk etc ii) Argillaceous materials  $Al_2O_3$  and  $SiO_2$  (such as clay, shale, slate) iii) Powdered coal or fuel oil iv) Gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) v) Iron oxide

Portland cement can be made by following two different processes – a dry process and a wet process

Raw materials are combined in the correct amounts and fed into the kiln system. In the dry process, the materials are grounded, mixed, and introduced into the kiln system in a dry state. In the wet process, the raw materials follow all of the steps with water added and are introduced into the kiln system in a slurry state. After burning, further steps are grinding, storage and packaging.

### 2.1.4 Functions of ingredients of cement

a) CaO (Lime): Principal constituent of cement

Its proportion should be regulated as, excess amount reduces the strength making it to expand and disintegrate while lesser amount reduces the strength making it quick-setting.

- b) Silica: It imparts strength to cement.
- c) Alumina: It makes the cement quick-setting. Excess of alumina however weakens the cement.

- d) Calcium sulphate: It helps to retard the setting action of cement. It actually enhances the initial setting time of cement.
- e) Iron oxide: It provides colour, strength and hardness to the cement.
- f) Sulphur trioxide: It (only in small amounts) imparts soundness to cement.
- (Soundness expresses expansivity of cement set in 24 hours between 25° C and 100° C)
- g) Alkalis: It is present in excess cause the cement efflorescent. It imparts colour to cement
- h) Fuel oil or powdered coal: For burning

After mixing and burning, these ingredients undergo compound formation.

Composition of Portland cement							
	Constituent	Chemical formula	Abbreviation	%	Setting time in days		
1	Tricalcium silicate	3CaO.SiO <sub>2</sub>	$C_3S$	45	7		
2	Dicalcium silicate	2CaO.SiO <sub>2</sub>	$C_2S$	25	28		
3	Tricalcium aluminate	3CaO.Al <sub>2</sub> O <sub>3</sub>	C <sub>3</sub> A	1	1		
4	Tetracalcium aluminoferrate	4CaO. Al <sub>2</sub> O <sub>3.</sub> Fe <sub>2</sub> O <sub>3.</sub>	C <sub>4</sub> AF	9	1		
5	Calcium sulphate	CaSO <sub>4</sub>		-	5		
6	Calcium oxide (free)	CaO		-	2		
7	Magnesium oxide	MgO		-	4		

#### 2.1.5 Characteristics of constituents

i) **Tricalcium silicates** (C<sub>3</sub>S): It has medium rate of hydration. It develops high ultimate strength rapidly. Its heat of hydration is 500 kJ/kg. It is largely responsible for early strength as it hardens rapidly as shown

The tobermnite gel thus formed is responsible for the binding action between the aggregates.

ii) **Dicalcium silicate** ( $C_2S$ ): It has quite low early strength but develops ultimate strength of slightly less than that of  $C_3S$ . It hydrates slowly. It is also responsible for ultimate strength. It possesses the heat of 250 kJ/kg. It has slower rate of hydration.

$$2[2CaO.SiO_2] + 4H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 + heat (250 kJ/kg)$$
  
tobermorite gel Crystals

iii) **Tricalcium aluminate** (C<sub>3</sub>**A**): It hydrates quickly. It is the first compound to hydrate and it contributes to strength development in the first few days. Its heat of hydration is about 880 kJ/kg. The behaviour of cement can be altered by modifying the relative percentages of these compounds.

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O +880 \text{ kJ/kg}$$

Hydrated calcium aluminate

This is highly exothermic reaction. Cements with low  $C_3A$  contents usually generate less heat, develop higher strengths and show greater resistance to sulphate attacks.  $C_3A$  is the least desirable component because a) its high heat generation b) its reactiveness with soil and water containing moderate to high sulphate concentrations.

iv) **Gypsum:** The presence of gypsum in the cement helps to retard the speed of the initial set due to the formation of calcium sulphoaluminate by the reaction between gypsum and C<sub>3</sub>A which does not show any tendency to rapid hydration. This reaction prevents high concentrations of alumina in the cement solution, thereby retarding the early initial-set of the cement.

$$3CaO.Al_2O_3 + xCaSO_4.2H_2O \longrightarrow 3CaO.Al_2O_3.xCaSO_4.2H_2O$$

$$C_3A \qquad Gypsum \qquad Tricalcium sulphoaluminate (x=32)$$

v) **Tetracalcium aluminoferrite** (C<sub>4</sub>AF): This compound assists in the manufacture of Portland cement by allowing lower clinkering temperature. Even though, it hydrates very rapidly it contributes very little to the strength of concrete.

$$4\text{CaO.Al}_2\text{O}_3.\text{Fe}_2\text{O}_3 + 7\text{H}_2\text{O} \longrightarrow 3\text{CaO.Al}_2\text{O}_3.6\text{H}_2\text{O} + \text{CaO.Fe}_2\text{O}_3.\text{H}_2\text{O}$$

# 2.1.6 Setting and hardening of Portland cement

When cement is mixed with water it forms a plastic mass called cement paste then hydration reaction begins resulting in the formation of gel and crystalline products. The interlocking of crystal bind sand, crushed stones very strongly.

The process of solidification consists of i) setting ii) hardening.

Setting is defined as stiffening of the original plastic mass due to initial gel formation. It can be divided into (i) Initial setting (ii) Final setting

Initial setting is when paste begins to stiffen

Final setting is when paste begins to harden and able to sustain some load

Hardening is development of strength due to crystallization.

After setting, gradual progress of crystallization in the interior leads to hardening. The strength developed by cement depends upon the amount of gel formed and the extent of crystallization.

I)Initial setting(Day1): Initial setting of cement paste is mainly due to the hydration of tricalcium aluminate  $(C_3A)$ . It takes place within a day. When dry cement is mixed with water, it forms a plastic mass. This mass loses plasticity gradually as the time passes. In about half an hour initial set of cement paste starts and the mass becomes jellified. The paste becomes rigid which is known as initial setting or flash setting .Cement paste should be worked and put in proper mould before initial setting is complete.

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O + 880 \text{ kJ/kg}$$
  
 $C_3A + 6H_2O \longrightarrow C_3A. 6H_2O + 880 \text{ kJ/kg}$ 

C<sub>4</sub>AF (tetracalcium aluminoferrite) undergoes hydration slowly to form gel.

$$4\text{CaO.Al}_2\text{O}_3.\text{Fe}_2\text{O}_3 + 7\text{H}_2\text{O} \longrightarrow 3\text{CaO.Al}_2\text{O}_3.6\text{H}_2\text{O} + \text{CaO.Fe}_2\text{O}_3.\text{H}_2\text{O} + 420 \text{ kJ/kg}$$

Tetracalcium aluminoferrite

$$C_4AF + 7H_2O \longrightarrow C_3A. 6H_2O + CF. H_2O + 420 kJ/kg$$

II)**Final setting (Day 2 to7)(initial strength)**: After initial setting, C<sub>3</sub>S begins to hydrate to give tobermorite gel and crystalline Ca(OH)<sub>2</sub> which is responsible for initial strength of cement.

Hydration of C<sub>3</sub>S gets completed within 7 days. Once cement paste is finally set, it loses its plasticity and then it can neighther be moulded into shape nor it can be remixed.

Tobermorite gel possess a very high surface area and very high adhesive property. (1g cement has surface area of above 10<sup>3</sup> cm<sup>3</sup> whereas 1g tobermorite has has a surface area of 10<sup>6</sup>cm<sup>3</sup>)

III) **Hardening(Day 7 to 28)(Final strength):** Dicalcium silicate (C2S) reacts with water very slowly. Reaction is completed in 7 to 28 days. It is also assisted by hydration of C3S. The hydration of C2S and C3S gives gel (tobermorite gel) which contains distorted crystalline layer structure of calcium silicates.

2[2CaO.SiO<sub>2</sub>] + 4H<sub>2</sub>O 
$$\longrightarrow$$
 3CaO.2SiO<sub>2</sub>.3H<sub>2</sub>O + Ca(OH)<sub>2</sub> + heat (250 KJ/kg)  
Tobermorite gel Crystals

$$2C_2S + 4 H_2O \longrightarrow C_3S_2.3H_2O + Ca(OH)_2 + 250 KJ/kg$$

Increase in strength is due to formation of tobermorite gel and crystals of Ca(OH)<sub>2</sub>

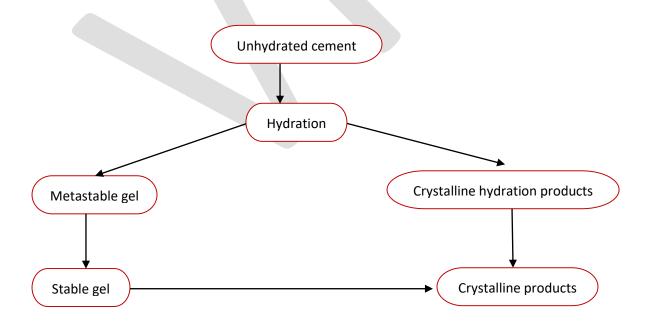
Hardening takes place through crystallisation.

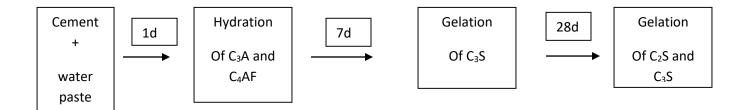
**Function of Gypsum:** Tricalcium aluminate combines with water very rapidly with evolution of large amount of heat.

$$C_3A + 6H_2O \longrightarrow C_3A$$
.  $6H_2O + heat$ 

After initial set, paste becomes stiff. Addition of gypsum retards the dissolution of C3A by forming insoluble calcium sulfo aluminate

When cement is hydrated, gypsum reacts with C<sub>3</sub>A quickly to generate calcium sulfoaluminate hydrate which deposits and forms a protection film on the cement particles to hinder the hydration of C<sub>3</sub>A and delay the setting time of cement.





## 2.1.7 I.S.I. specifications of portland cement as per Indian standard 269-1975

i) Lime saturation factor 
$$\frac{CaO - 0.7SO_3}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3} = 0.66 \ to \ 1.02$$

- ii) The ratio  $\frac{Al_2O_3}{Fe_2O_3}$  shall not be less than 0.66
- iii) Insoluble residue should not exceed 2%.
- iv) The weight of magnesia (MgO) should not exceed 6%
- v) Total sulphur contents calculated as sulphuric anhydride (SO<sub>3</sub>) shall not be more than 2.75%.
- vi) Loss on ignition shall not exceed 4%.
- vii) Fineness not to exceed 10% after sieving the residue (by weight) on B.S. 170-mesh test sieve.
- viii) Setting times: Initial= 30 minutes

ix) Heat of hydration

After 7 days ≤65 cal/g

After 28 days  $\leq 75$  cal/g

### 2.2 Polymers

### 2.2.1 Polymers Introduction

The technological development of the society largely depends on the materials. The search of new material led to the preparation of synthetic polymers. These polymers offered range of properties which are not achieved by materials such as wood, metals and ceramics.

Typical examples of synthetic polymers include polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polymethyl methacrylate (PMMA), nylons, polyesters etc.

Polymer exist in nature also. Typical natural polymers are starch, cellulose from plants, proteins, rubber, silk, wool etc.

Advantages of polymer to be used as materials are-

- Polymers can be resistant to chemicals.
- Can be used as thermal and electrical insulators.
- Light in weight with varying degrees of strength.
- Can be processed in various ways depending on applications.
- Simple changes in the chemical structure of given polymer can change mechanical properties. It can be soft to be used as wrapping material or can be hard to make water tanks. Polymer can be insulator or can be modified as a conductor.

### 2.2.2 Polymers and Monomers

The term polymer is derived from Greek words, poly – many and meros – units.

Polymer is a large molecule, formed by repeated linking of small molecules called 'monomers'

Polymers are made by sequentially adding monomers to form long chain.

If 'X' is a monomer, then polymer can be represented as,

$$nX \rightarrow -X - X - X - X - \equiv (-X - X -)_n$$

For example, polythene (polyethylene) is a polymer formed by linking togather, large number of ethylene molecules.

Thus, monomers can be defined as small molecules which combine with each other to form polymer molecules.

#### 2.2.3 Specialty Polymers

They are made for special applications

Some examples of the specialty plastics are polytetra fluoroethylene (PTFE), thermoplastic polyurethanes (TPU), polysulphones (PSO), Polyacetylene, Kevlar, etc.

They are used as building materials, packaging, transportation, electronics, mechanical applications etc.

# 2.2.3–(1) Conducting Polymers

Most of the polymers are used for electrical insulation, as they are bad conductor of electricity. Since these polymers do not possess large number of free electrons, they do not conduct electricity.

Conducting polymers have been synthesised within past several years, which possesses conductivity comparable with that of metals.

Conductivity in polymers is observed because of different reasons. Accordingly they can be categorized into different types.

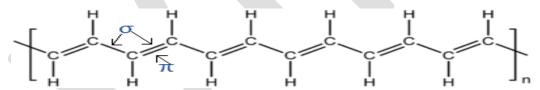
### A] Intrinsically conducting polymer (ICP):

Some polymers can conduct electricity of their own because of their structural features. Such polymers are known as intrinsically conducting polymers. For e.g. trans-polyacetylene

### **Structural requirement of ICP:**

A polymer shows appreciable conductivity if,

• The polymer chain shows conjugation i.e alternate  $\sigma$  and  $\pi$  bonds throughout its chain as shown in fig. so that there resonating or mobile electron for conduction.



- Such polymers are **highly crystalline** and there is **high planarity** in structure.
- Presence of **aromatic rings** in the chain **with continuous resonance** enhances conductivity.
- Conductivity is also observed in heteroatomic system due to delocalised electron pair

Trans – polyacetylene

# Polyaniline

# Polyphenylene

Polypyrrole

### **Doped conducting polymers:**

Intrinsically conducting polymer possesses low conductivity (They are semiconductors). Their conductivity can be improved by **doping.** 

Conductivity of Intrinsically conducting polymer can be improved by creating positive or negative charges on polymer chain by oxidation or reduction. This technique is called doping.

i) **P-doping:** It includes doping of intrinsically conducting polymer with Lewis acids like I<sub>2</sub>, Br<sub>2</sub>, PF<sub>6</sub>. Oxidation (removal of electrons) takes place and positive charge is developed on polymer chain increasing conductivity.

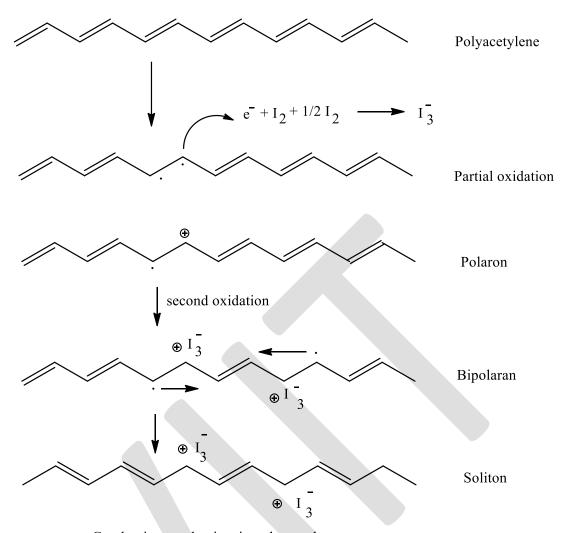
$$\begin{array}{c} 2(C_2H_2)_n + 3I_2 \xrightarrow{Oxidation} \ 2[(C_2H_2)_n^+ \ I_3^-] \end{array}$$
 Polyacetylene

**ii) N-doping:** It includes doping of intrinsically conducting polymer with Lewis base like lithium, sodium metals. Reduction (addition of electrons) takes place and negative charge is developed on polymer chain, increasing conductivity.

$$\begin{array}{c} 2(C_2H_2)_n + \text{Na} \xrightarrow{\text{Reduction}} \\ \text{Polyacetylene} & \xrightarrow{} 2[(C_2H_2)_n^- \text{Na}^+] \end{array}$$

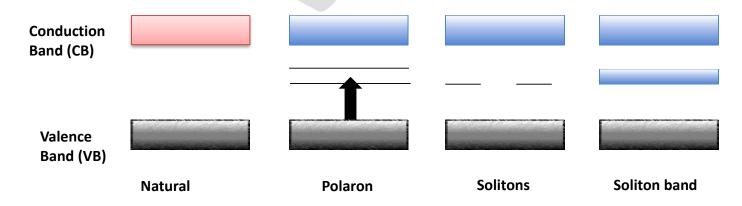
# Doping of polyacetylene (Conduction mechanism in polyacetylene after doping):

- An electrically conductive polymer is able to conduct electricity because of the conjugated  $\pi$  bond system.
- The conjugated double bonds permit easy electron mobility throughout the molecule because the electrons are delocalized.
- When the oxidative dopants such as  $I_2$  is added, it takes away an electron from the  $\pi$  back bone of the polyacetylene chain and creates a positive charge (hole) on one of the carbons. The other  $\pi$  electron resides on the other carbon making a radical cation known as **polaron**.
- A **bipolaron** is formed on further oxidation. As the 2 electrons are removed, the chain will have 2 positive charges (holes). When a potential is applied, they migrate from on carbon to another and account for conductivity.
- If polyacetylene chain is heavily oxidized, polarons condense pairwise into **solitons** (alternating pattern of double-single bonds is reversed.)



Conduction mechanism in polyacetylene

Conjugated polymers have extended delocalised bonds ( $\pi$  conjugated system) that create a band structure similar to silicon, but with localised states. When dopants are added, conductivity increases due to additional band in between valence and conduction band decreasing band gap.



### **B**] Extrinsically conducting polymers:

These are conducting polymers whose conductivity is achieved because of externally added ingredient in them.

It can be achieved by two ways:

**Conductive element filled polymer:** Obtained by mixing metallic fibers, metal oxides or carbon black in the polymer during moulding. Conducting plastics containing carbon black find uses in wires and cables, video discs, audio records etc.

**Blended conducting polymer:** It is obtained by blending conducting polymer with conventional polymer, physically and chemically.

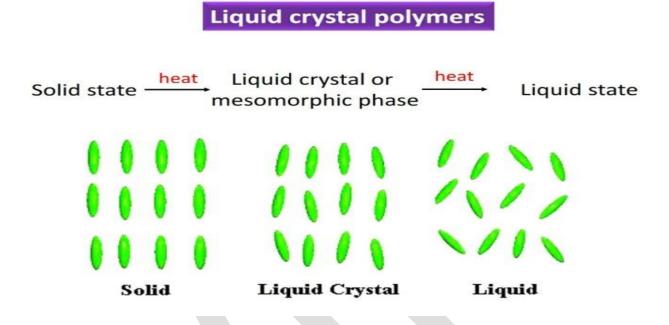
# **Applications of conducting polymers:**

- 1) Rechargeable batteries.
- 2) An antistatic material.
- 3) Optical filters.
- 4) Sensors.
- 5) In electronics.
- 6) Photovoltaic cells.
- 7) In telecommunication system.
- 8) In molecular wires and switches
- 9) In electromagnetic screening materials.
- 10) Light Emitting Diodes (LEDs)
- 11) Lasers used in flat televisions

# 2.2.3 -(2)Liquid Crystal Polymers (LCP)

A polymer that under suitable conditions of temperature, pressure and concentration, exist as liquid crystal is known as liquid crystal polymer.

Polymers that form liquid crystal stage contains long, rigid units or disc shaped molecular structure called as mesogens.



Liquid crystal polymers are a unique class of partially crystalline polyesters/polyamides that provide previously unavailable high performance properties

Liquid crystal polymers have tendency to align the polymer chains over long distance before crystallization from their melts or solution.

### **Types of Liquid crystal polymers:**

There are two types of liquid crystal polymers –

### 1) Thermotropic liquid crystal polymers:

The polymers which have tendency to align their polymer chains (mesogens) over a large distance before their crystallization from the melt, is called as thermotropic liquid crystal polymers. For e.g.: Vectra, Victex, Xyder etc.

### 2) Lyotropic liquid crystal polymers:

The polymer which have tendency to align their polymer chains (mesogens) over a long distance before their crystallization from the solution is called as lyotropic liquid crystal polymers. For e.g. Kevlar

There are three states or structural forms of liquid crystal structure. Based on that, they are further classified as,

### i) Smectic liquid crystal polymers:

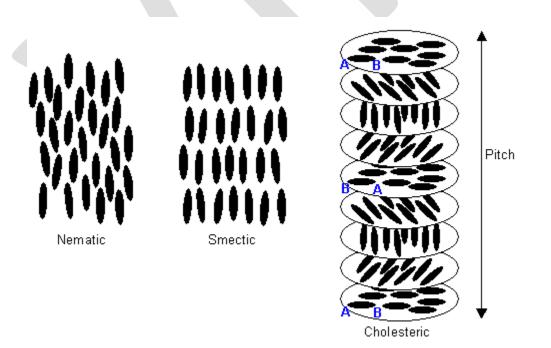
Polymer chains (mesogens) maintain orientational order, but also tend to align themselves in layers i.e. mesogens are arranged in parallel and lateral order.

### ii) Nematic liquid crystal polymers:

The polymer chains (mesogens) are arranged in parallel order but not in lateral order.

### iii) Cholesteric liquid crystal polymers:

This is a modified nematic phase. In this, mesogens are oriented parallel to one another (just like nematic phase) but the directions vary from one layer to another. The distance between two identical layer is called as pitch which is sensitive to the environment.



### Properties of liquid crystals:

Properties of a part, moulded from liquid crystal polymer depend on the morphology of the part, which is determined by conditions of processing.

In general, due to its crystalline structure, liquid crystal polymers have,

- i) Good thermal stability
- ii) High dimensional stability
- iii) Are easily moulded
- iv)Good electrical properties at high temperature
- v) Very low coefficients of thermal expansion
- vi)High chemical and solvent resistance

### **Applications:**

Liquid crystal polymers find uses

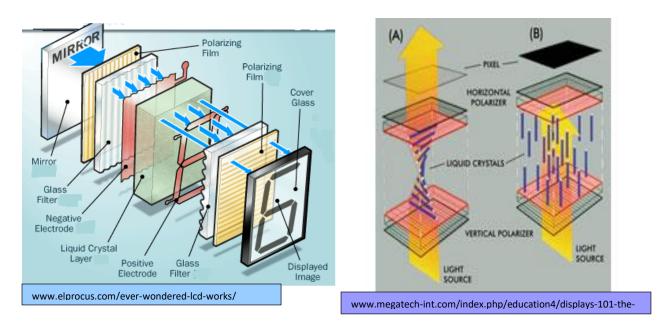
- 1) In electronic and electrical equipments like flat panel displays, switches, computer memory modules etc.
- 2) In optoelectronics components such as Fiber optic cables.
- 3) In data storage discs.
- 4) In chemical appliances.
- 5) In encapsulation of IC devices.
- 6) In housing for light wave conductors.
- 7) In variety of aerospace applications.
- 8) As filler for composite material.
- 9) In military communications.

## Liquid crystal display



**Liquid crystal display (LCD)**, electronic display device that operates by applying a varying electric voltage to a layer of liquid crystal, thereby inducing changes in its optical properties. LCDs are commonly used for portable electronic games, as viewfinders for digital cameras and camcorders, in video projection systems, for electronic billboards, as monitors for computers, and in flat-panel televisions.

Liquid crystal display screen works on the principle of blocking light rather than emitting light. LCDs require a backlight as they do not emit light by them.



The optics of liquid crystal display are shown in the figure. The cell with nematic liquid crystal is placed between two crossed polarisers. Polarised light entering the cell follows the twist of nematic liquid crystal, is rotated through 90°, and as such can allow passage of light through second polarizer. Application of electric fields changes the molecular alignment in the liquid crystal such that polarisation is not altered in the cell and no light is transmitted. If a mirror is used behind the second polarizer, the display will appear black when the voltage is applied. If

electrodes are shaped in 7 segment pattern of digits then numeric display will appear on application of voltage.

The nematic phase of liquid crystals is the one most often used in LCD displays. The molecules are rod-shaped and can move with respect to each other. Changes in this alignment of the nematic phase are seen when an external electric field is applied. Twisted versions of these nematic phases are used in the formation of pixels. A twisted nematic liquid crystal is trapped between two parallel glass sheets with polarizers at 90° to each other placed on either side of this sandwich. The nature of the liquid crystal is such that the orientation of a beam of polarized light will be turned through 90° allowing it to pass, unchanged, through the pixel as it will now be at the correct angle to pass through the second polariser. This causes the device to be in an on state and glowing. On application of an external electric field, the liquid crystal molecule will realign so that polarized light is not transmitted by the molecule and as such does not pass through the second polarizer (Figure 2) turning that pixel off. A series of transistors is used to turn on and off pixels in order to make up an image.

### 2.2.3 – (3)Electroluminescent polymers

Electroluminescent polymers are the polymers which emit light in response to the passage of electric current or strong electric field.

Conjugated polymers derive their semiconducting properties from having delocalised  $\pi$  electrons along the polymer chain. Electroluminescence from conjugated polymers was first reported using poly (phenylene vinylene) i.e. PPV as a single semiconducting layer between metallic electrodes.

One of the major applications of electroluminescent polymers is polymer light emitting diode (PLED) for display devices.

In 1990 Friend et al. reported an OLED based on a single layer of a conjugated polymer (poly(p-phenylenevinylene), PPV

Electroluminescence of conjugated polymers arises from their electronic structure which resembles that of inorganic semiconductors. In fact, conjugated polymers are considered organic semiconductors

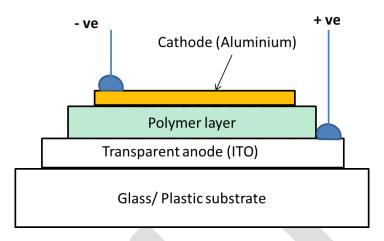
In the simplest setup of an PLED, a thin layer of the electroluminescent polymer is sandwiched between two electrodes (the anode and the cathode), one of which, at least, must be transparent .

A variety of materials can be used as electrodes: generally, the cathode consists of a metal layer such as aluminum or calcium, whereas indium tin oxide (ITO) is commonly used as the transparent anode supported on a glass or plastic substrate.

Upon the application of a relatively low voltage (2–10 V), electrons and holes are injected into the polymer layer from the cathode and anode, respectively. The injected charge carriers migrate to the opposite electrode driven by the applied electric field, hopping from polymer chain to

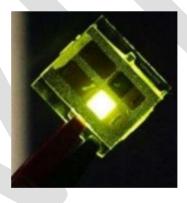
polymer chain, and when they recombine, the emission of a photon (light) can result from the generated excited state (exciton).

The band gap (energy difference between valence band and conduction band) determine the wavelength and colour of emitted light.



### **Applications of Electroluminescent polymers:**

Electroluminescent polymers have potential applications in light emitting diode (LED) devices such as Flat panel displays for computer monitors, television screens, mobile phone displays and colour pixels in ink jet printing



2.2.3. -(4)Fiber reinforced plastic (FRP)

### **Polymer Composites:**

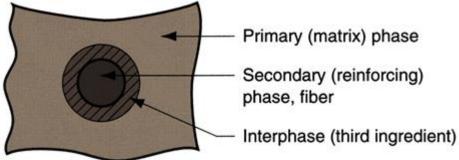
Modern technology demands the structural material which should have unusual combination of properties such as low density, high abrasion and corrosion resistance for number of applications such as high temperature reactors, aircrafts, missiles, gas turbines etc. Any single metal, alloy, ceramic or polymeric material cannot offer the combination of above properties. In order to meet these demands, a new class of materials called "composites" have been developed.

Composites are formed by the combination of two or more different materials with the properties of resultant material superior to that of individual materials. The components of composite do not dissolve or merge completely into each other but act together retaining their individual identities. Polymer composite is one of them.



Polymer composite is the material which is made up of polymer matrix and reinforcing materials being put together with a defined interface.

The boundaries between the matrix and reinforcement is called interface. Strength of interfacial bonds affects the properties of polymer composites.



### Fiber reinforced plastic (FRP):

Fiber reinforced plastic is a composite material made of a polymer matrix reinforced with fibers.

Sometimes fillers or modifiers are added to ease processing, impart special properties and reduce cost.

The characteristics properties of fiber reinforced composites depend on

- i) Nature, orientation and distribution of fibers
- ii) Nature of polymer matrix
- iii) Strength of interfacial bonds between fiber phase and polymer matrix phase.

### General properties of FRP -

They possess

- i) High tensile strength
- ii) High elastic modulus
- iii) High stiffness
- iv)Lower density

**Commonly used reinforcement fibers are** – glass, carbon, aramid, aluminium, asbestos, paper, wood fibers etc.

**Commonly used polymer matrix** are – thermoplastic such as nylon, polyethylene, polypropylene, ABS plastic etc. and thermosetting resins such as polyesters, epoxy and phenolic resins.

Some important types of fiber reinforced composites are –

# A] Glass fiber reinforced polymer composite -

They use glass fibers reinforced in polymer matrix containing nylons, polyesters etc. Glass fibers are obtained by forcing glass melt through spinnerate (Having small holes) and rapidly pulling and cooling to get fibers.

### Advantages:

They show improved properties as,

- i) High tensile strength and impact resistance
- ii) Lower densities
- iii) Excellent resistance to corrosion and chemicals.

#### **Limitations:**

- i) Since polymer matrix deteriorates or flows at high temperature, they show applications in limited temperature range.
- ii) Since the material do not possess desired stiffness and rightly, they can not be employed as structural components.

## **Applications:**

They are used on automobile parts, storage tanks, industrial flooring, plastic pipes etc. They are extensively used in automobile to reduce vehicle weight and boost fuel efficiency.

### B] Carbon fiber reinforced polymer composites –

They use carbon fiber reinforced in polymer matrix like epoxy or polyester resins. Carbon fibers are obtained by pyrolysis of cellulose/acrylonitrile in an inert atmosphere. Carbon fibers have much higher elastic modulus than glass fibers and show better resistance to temperature and corrosive chemicals. However, they are short fibers and are more expensive.

#### **Advantages:**

They show improved properties as,

- i) Excellent resistance to corrosion
- ii) High elastic modulus
- iii) Low density
- iv)High temperature resistance

### **Applications:**

They are used as structural components (like wings, body, stabilizer) of aircrafts and helicopters. They are used in making sports goods (rockets, archery, racing bicycles), laptops, fishing rods, musical instruments (violin bows, guiter pickguards)

### C] Aramid fiber reinforced polymer composites-

They use aramid fibers reinforced in polymer matix like polyesters and epoxy resins. Aramid fibers are obtained by spinning liquid crystal aramid (Kevlar)

# **Advantages:**

1) High tensile strength

- 2) High impact resistance
- 3) High thermal stability
- 4) High abrasion resistance
- 5) High compression strength

#### **Limitations:**

Fibers are susceptible to degradation by acids and strong base.

Aramid fiber composites are classified into two types:

- **Short fiber reinforced composites**: Short fibers have high surface area, toughness, i) strength, heat stability, wear resistance
  - Applications: Used in automobile brakes and clutches
- **Long fiber reinforced composites** Aramid fibers are capable of absorbing energy so ii) they show high compressive strength and ductility Applications: Used as structural and advanced engineering material for aircrafts and helicopter parts

# 2.3 Applications of polymers in construction industry, electronic industry and mechanical industry

#### 2.3.1 **Polymers for Construction industry**

The use of polymer in the civil engineering has increased significantly over the last 100 years. Polymer and polymer composites are widely used in structural components in civil engineering fields (buildings construction, bridges, highways & express ways construction, airstrips, helipads, railway, unpaved road etc.).

The building and construction industry uses a variety of classic building materials like metals, glass, wood and stones, but plastic materials are becoming increasingly important due to their outstanding performance and excellent desirable properties like high strength, low density and less weight. Construction applications of plastics include pipes and guttering, window and door profiles, roofing, sealants and adhesives, cement, insulation, flooring and building panels.

### **2.3.1.** – (1) <u>Piping and Conduit</u>

Piping and Conduit are the largest users of polymers in construction and consume 35% of production producing cabling, rainwater goods, large diameter pipes for sewage, drainage and potable water made from PVC and Polyethylene.

### I)Polyvinyl Chloride (PVC):





Polyvinyl chloride is prepared by polymerization of Vinyl chloride.

# **Properties:**

- 1) The most important properties of PVC are superior fire retardancy, high ignition temperature (455 °C) and relatively low heat release in burning It has high softening temperature (148 °C), greater stiffness and rigidity as compared to polyethylene but is brittle.
  - 2) it presents strong resistance to oxidation, good chemical resistance to acid and alkali chemicals.

# II) High density polyethylene (HDPE)



HDPE or High-Density Polyethylene, also known as polyethylene high density (PEHD) is a thermoplastic. When used for pipes, it is also sometimes called 'alkathene' or 'polythene'. It has several advantages such as low cost, quick fabrication, corrosion resistant etc. Some of the favourite uses of HDPE included low-pressure natural gas services, water distribution and used a lining material in carbon steel pipe.

HDPE is prepared by polymerization of ethylene. ) The pipes made from HDPE are manufactured using the extrusion process.

n 
$$CH_2$$
  $\longrightarrow$   $CH_2$   $\longrightarrow$   $CH_2$ 

### **Properties:**

- 1) High-density polyethylene is highly resistant to chemicals and corrosion.
- 2) It has better tensile strength and higher softening point.
- 3) Density 0.925 to 0.94 g/cm<sup>3</sup>
- 4) High impact resistant
- 5) Abrasion resistant
- 6)Easy to process (fabricate, weld, machine)
- 7) Moisture resistant

2.3.1 
$$-(2)$$
 Cladding and Profiles

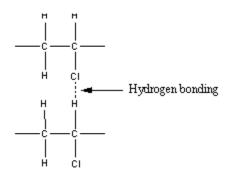
Cladding and profiles for windows, doors, coving, and skirting made from PVC-U, or UPVC

### I) PVC –U (Unplasticised PVC):





### Unplaticised PVC is very hard and stiff due to hydrogen bonding



### **Properties:**

- 1. UPVC is highly chemical resistant and is used popularly for both residential as well as commercial purposes. UPVC has excellent chemical resistance, which eliminates the formation of limescale and provides good flow characteristics.
- 2. UPVC is odorless and tasteless, it is suitable for transport of processed water, wastewater, as well as for a large number of chemicals.
- 3. UPVC is a tough, transparent and hard-wearing material
- 4. UPVC is suitable for use at temperatures ranging from 0°C to 65°C at a wide range of operating pressures, depending on the selected system
- 5. It is resistant to UV rays but also resistant to rain and water.
- 6. UPVC is recyclable and energy efficient and thus regarded as an environment-friendly option.
- 7. UPVC doors and windows are weatherproof and provide a high level of insulation. The doors and windows made with UPVC are sound-proof. They cut out all the unnecessary noise and sound thus keeping the stress levels to all-time low.
- 8. The UPVC doors and windows are easy to install as well as uninstall.

[Plasticised PVC is obtained by addition of platicizers during moulding process that weakens intermolecular forces making PVC soft]

$$2.3.1 - (3)$$
Insulation

Insulation is generally produced from Polystyrene rigid foam (expanded polystyrene foam- EPS) which is incorporated into panels or sandwiched into construction of walls and roofs. The insulation combines lightness and strength and is simple to install. It is applied in foundations, walls and roofs.

### **Polystyrene (PS):**

It is prepared by polymerisation of styrene

### **Expanded polystyrene foam (EPS):**



It involves heating of polystyrene either with steam (the most common method) or hot air (for high density foam, such as that used for a coffee cup)

**EPS foam** is the most common in everyday life: this white foam can be seen in cups for hot beverages, refrigerators, insulation, packaging, etc. The foam plastic consists of 96 - 98% air and 2-4% polystyrene. Granules are heated with steam in such a way that they are rapidly expanding (foaming) and forming a low-density block (in a special form)

**Insulation foam** – **EPS is** used for a variety of applications because of its excellent set of properties including good thermal insulation, good damping properties and being extremely light weight. From being used as building materials to white foam packaging, expanded polystyrene

has a wide range of end use applications.

Expanded Polystyrene insulation is a light weight, rigid, closed cell insulation. This closed-cell structure provides minimal water absorption and low vapor permanence.

Properties of EPS:

- 1) It shows thermal resistance and insulation
- 2) It shows chemical inertness
- 3) It shows bacterial resistance
- 4) It shows excellent impact strength and dimensional stability

# 2.3.2 Polymers for electronic industry

Two major applications of polymers are considered here -1) Polymers for optical fibers (POF) and 2) Polymer Light Emitting Diode (PLED)

$$2.3.2 - (1)$$
Polymers for optical fibers

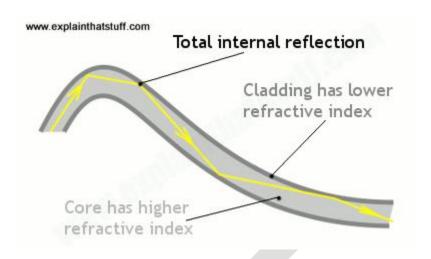
### **Introduction:**

In case of electronic communication, the information was carried over in the form of microwaves and radio waves, through copper wires and coaxial cables. But information carrying capacity of these wires is restricted due to limited bandwidth.

If the light waves are used instead of radio waves and microwaves, the number of signals transmitted can be increased enormously. Communication using light waves cannot be done directly. It requires some guiding medium (optical fibers) in which the information carrying light waves could be transmitted.

### **Optical Fiber:**

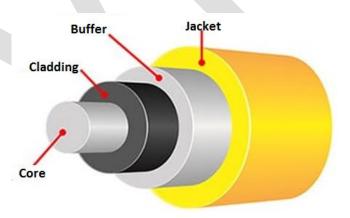
Optical fiber is flexible, transparent fiber made of silica (glass) or plastic which is slightly thicker than a human hair. It is a form of guided non conducting medium .Its working is based on Total Internal Reflection. It permits transmission over longer distance and at higher bandwidth than other forms of communications.



### **Optical Fiber construction**:

Optical fiber, in general, consist of following regions:

- *Core-* Inner most region, which is light guiding region with a higher refractive index than cladding. It is made up of glass or plastic
- *Cladding-* It is made up of glass or platic. It is having lower refractive index than core
- *Buffer-* It protects core and cladding from moisture, abration and give mechanical strength to the fiber
- *iv)* **Jacket** It holds one or more fibers in a cable



### **Polymer optical fibers (POF):**

Polymer optical fiber that is made up of polymer that transmit light (for illumination or for data transfer) through polymer core.

POFs are made of low cost plastic materials such as poly methyl methacrylate (PMMA), polystyrene, polycarbonates etc. with their transmission windows in the visible range (500–800 nm).

POFs are much safer and easier to handle and with greater resilience to bending, shock, and vibration, as compared with silica optical fibers which must be handled carefully and safely.

For long distance links where the attenuation and dispersion effects are of prime importance, glass fibers are superior. However, POF is advantageous for short distance networks which are less concerned with attenuation and more concerned with flexibility, hazard-free handling, and low-cost installation.

For short distance applications, multimode optical fiber with large core size is preferred over single mode fiber. Conventional multimode silica glass fiber cannot have a very large core size, because large fiber becomes very brittle and inflexible.

## **Advantages of POF:**

- The materials which POF is made up of are low-cost polymers
- Installation of POF with associated assemblies is not expensive.
- It is flexible and solid, able to bend without breakage.
- The network using polymer optical fiber can be installed by untrained personnel.
- Polymer optical fibers are safe when installed in a house without risk to children in case of breakage.
- Shows compatibility with organic and biomedical materials

#### **Disadvantages of POF:**

- The signal attenuation and dispersion of POF are typically very high, hence it is limited to short distances (generally up to 100 meters).
- POF cannot withstand the extreme temperature.
- It does not show long term stability

### **Applications of Polymer Optical Fiber (POF):**

1) Lighting: for decoration purpose

- 2) Inspection of mechanical welds in pipes and engines (airoplane, rockets, automobiles
- 3) Medical applications- endoscope, bronchoscope, laproscope
- 4) Communication- used for shortdistance network cables
- 5) Sensors- optical measurement of flow, biosensor (measures fluorescence produced by biological activity is collected and transmitted by POF. Moisture sensor
- 6) Automobile-number of electronic devices are connected by POF

# Difference between Polymer optical fiber (POF) and Glass optical fiber (GOF)

Sr.	Polymer Optical Fiber (POF)	Glass Optical Fiber (GOF)
No.		
1	It consists of polymer core	It consist of glass core
2	Wider core diameter	Narrow core diameter
3	Greater flexibility, light in weight	Less resistant to flexibility and accidental
		breakage
4	Less expensive	More expensive
5	Can not sustain extreme temperature	Can sustain higher temperature
6	Better signal strength	Poor signal strength
7	Used in low speed short distance	Used in longer distance transmission with
	applications	higher speed
8	Used in car network, home network,	Used in underground data transmission system
	industrial network	

# **Materials used:**

Material to be used for POF should have following characteristics

- a) it should be a clear plastic with a good optical transmission quality for efficient optical transmission
- b) it must be flexible and must be able to be drawn into long fibers
- c) cladding and the core materials should have slightly different refractive indices to satisfy total internal reflection.

Optical polymers are clear plastics that provide excellent light transmission. The key transparent polymers for optical and photonic applications include acrylic, usually polymethylmethacrylate (PMMA) or a modification of this material, polycarbonate (PC), polystyrene (PS), allyl diglycol carbonate (ADC) and cyclic olefin copolymer (COC).

The polymers mentioned here have light transmittance values exceeding 88 percent within the wavelength range 380 to 1000 nm. PMMA and COC typically have 92 percent transmittance over this range, while others fall somewhat lower.

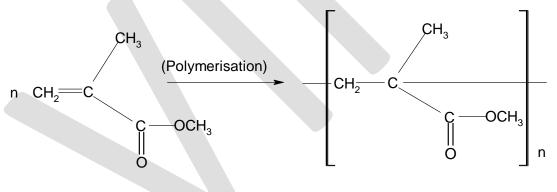
# I) Poly Methyl Methacrylate (PMMA):

The material most frequently used for the fabrication of POF is the thermoplastics PMMA (Poly methyl methacrylate), better known as Plexiglas/acrylic glass/Acrylite. PMMA has many technical advantages over other transparent polymer (PC, polystyrene etc.), as follows:

- High resistance to UV light and weathering,
- Excellent light transmission

### **Preparation of PMMA:**

• It is prepared by polymerization of Methyl methacrylate (MMA) PMMA produced by radical polymerization (all commercial PMMA) is atactic and completely amorphous.



Methyl methacrylate (MMA)

Poly Methyl methacrylate (PMMA)

### **Characteristics of PMMA POF**

- PMMA is used as the core, with refractive indices of 1.49.
- Generally, fiber cladding is made of silicone resin (refractive index ~1.46).
- High refractive index difference is maintained between core and cladding.
- Have high mechanical flexibility and low cost.
- Bandwidth is high (~5 MHz-km @ 650 nm)

[Bandwidth refers to the amount of data you can transfer in a unit of time, as well as the range of frequencies used to transmit the data]

## II) Polystyrene (PS):

Polystyrene is a thermoplastic homo polymer made up of styrene.

#### **Characteristics of PS POF:**

- PS is used as the core, with refractive indices of 1.59
- Generally, fiber cladding is made of silicone resin (refractive index ~1.46) or PMMA (refractive index ~1.49).
- Since PS is transparent, inexpensive and available in large quantity, a use for POF seems profitable.
- Although PS fibers have advantages like a decreased water uptake, a higher RI 1.59 and a
  theoretical lower attenuation limit between 600 and 700 nm wavelength compared to
  PMMA-POFs, their commercial success was limited. The mechanical characteristics and
  superior chemical resistances of PMMA might be responsible for this. However, for special
  applications such as fluorescent fibers or sensing (pH-sensors, scintillators, etc.) PS-POFs
  are commonly used.

Electroluminescence from conjugated polymers was first reported using poly (phenylene vinylene) i.e. PPV as a single semiconducting layer between metallic electrodes.

Polyphenylene vinylene (PPV) is a conducting polymer with conjugated  $\pi$  system.

#### **Properties of PPV:**

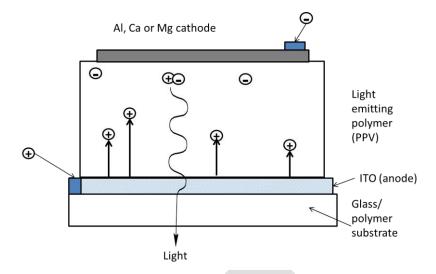
1)PPV has very low intrinsic electrical conductivity (10-13 S/cm)

- 2)The electrical conductivity increases upon doping with iodine, ferric chloride, alkali metals etc.
- 3)PPV is water insoluble, but its precursors can be manipulated in aqueous solution
- 4)It gives bright yellow-green fluorescence on application of electric field
- 5) As a material, PPV has several advantages over classical inorganic light emitting semiconductors-
  - > The ease of processing PPV permits it to spread onto large areas and curved surfaces
  - ➤ PPV shows tensile strength and elastic modulus as high as aramid fibers. This helps the polymer to service under harsh conditions prevailing during device operation.

# A basic polymer LED (PLED) based on PPV:

A typical polymer LED is composed of a layer of electroluminescent polymer (like PPV) situated between two electrodes, the transparent anode (ITO) and cathode (Al, Ca, Mg), all deposited on polymer and glass substrate. An applied electric field leads to injection of holes (positive charge, majority charge carrier) and electrons (negative charge, minority charge carrier) into light emitting polymer film from two electrode contacts. Recombination of electron – hole pair within the polymer may result in the emission of photons (light). Since holes migrate much easily through PPV than the electrons, electron –hole recombination takes place in the vicinity of cathode.

Due to stability, processibility, electrical and optical properties, PPV is used in organic light emitting diode (OLED). Devices based on PPV as emissive layer, emit bright yellow green fluorescent light. For different colours, derivatives of PPV can be used.



# 2.3.3 Polymers for Mechanical industry

2 major applications are considered here1) Polymers for automobile and 2) Polymers for 3 D printing

# 2.3.3 – (1)Polymers for automobile

### 1) PC (Polycarbonate)

It is prepared by reaction of Bisphenol A with diphenyl carbonate

$$n \ HO \longrightarrow CH_3 \longrightarrow CH_3$$

Amorphous polycarbonate polymer offers a rare combination of stiffness, hardness and toughness. It shows excellent weathering, creep, impact, optical, electrical, thermal properties and UV resistance, with transparency levels almost good as acrylic.

Applications: Bumpers, headlamp lenses, security screens, aircraft panels

### 2) Acrylonitrile/butadiene/styrene (ABS)

It is tricopolymer of acrylonitrile, butadiene and styrene.

Acrylonitrile Butadiene Styrene is a durable thermoplastic. It is a copolymer built by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The styrene gives the plastic a shiny, impervious surface. The butadiene, a rubbery substance, provides resilience even at low temperatures. A variety of modifications can be made to improve impact resistance, toughness, heat resistance, weather and some chemicals resistance.

*Applications:* Automotive body parts, dashboards, wheel covers manufacture of housings, Covers and linings.

### 3) Polyamide (Nylon 6/6, Nylon 6)

$$\begin{array}{c|c} \begin{pmatrix} \mathbf{H} & \mathbf{H} & \mathbf{O} & \mathbf{O} \\ \mathbf{I} & \mathbf{I} & \mathbf{II} \\ \mathbf{N} - (\mathbf{C}\mathbf{H}_2)_6 - \mathbf{N} - \mathbf{C} - (\mathbf{C}\mathbf{H}_2)_4 - \mathbf{C} \end{pmatrix}_n \\ \mathbf{Nylon 66} \end{array}$$

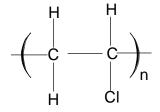
$$\frac{\begin{pmatrix} \mathbf{H} & \mathbf{O} \\ \mathbf{I} & \mathbf{II} \\ \mathbf{N} - (\mathbf{CH}_2)_5 - \mathbf{C} \end{pmatrix}_n$$

### Nylon 6

Common polyamides are nylon 6.6 or nylon 6. It is a general purpose nylon that can be both molded and extruded. Nylon 6/6 has good mechanical properties and wear resistance. They are frequently used when a low cost, high mechanical strength, rigid and stable material is required. They also absorb water easily and components in wet or humid conditions will expand. The main application of polyamide is the manufacture of parts which are under the engine hood, mainly using the types of polyamide (PA) reinforced by fiberglass.

Applications: Gears, bushes, cams, bearings, weather proof coatings.

### 4) PVC (Polyvinyl chloride)



This is a material used in automotive industry for the manufacture of the protection for the bottom floor in the car, for internal lining and coating of electric cables in the vehicle. Polyvinyl chloride can be moulded in various ways such as injection moulding, compression moulding, blow moulding to form a huge variety of products, either rigid or flexible depending on the amount and type of plasticizers used [Plasticizers are the compounds which are added during moulding process to make PVC soft].

PVC attributes to automobile applications because-

- It has good resistance to chemical and solvent attack.
- Its vinyl content gives it good tensile strength.
- PVC has good flexibility, is flame retardant, and has good thermal stability, a high gloss.
- It has controlled oxygen and water vapour transmission
- It provides soft and scratch resistant skin for dashboards
- It is resistant to cold temperature and has UV stability
- It is lighter in weight
- It is affordable

Applications: automobile instruments panels, sheathing of electrical cables, door parts 5) PUR (Polyurethane)

#### **Polyurethane**

Polyurethanes are a large family of polymers with wide range of properties and uses all based on the reaction product of an organic isocyanate with compounds containing a hydroxyl group. Polyurethanes may be thermosetting or thermoplastic, rigid and hard or flexible and soft, solid or cellular with great property variances. Principal applications are in coatings, elastomers and foams. Polyurethane has excellent abrasion resistance but high hysteresis. Rigid polyurethane foams have become widely used as insulation materials because of their combination of low heat transfer and good cost effectiveness

*Applications:* Flexible foam seating, foam insulation panels, elastomeric wheels and tires, automotive suspension bushings, cushions, hard plastic parts.

### 6) PMMA (Acrylic)

Methyl methacrylate (MMA)

Poly Methyl methacrylate (PMMA)

PMMA (Acrylic) is a transparent thermoplastic; it is often used as a lightweight or shatter-resistant alternative to glass and good UV and weather resistance, high optical quality and surface finish with a huge colour range. It's cheaper than PC but is also more prone to scratching and shattering.

Applications: windows, displays, screens.

# 2.3.3 - (2) Polymers for 3D printing

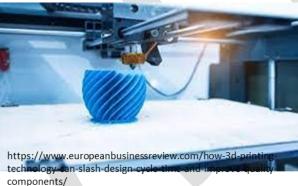
3 D printing technology is an emerging Additive manufacturing (AM) technology that enables the design and rapid manufacturing of materials with complex microstructures. Developments in 3D printing have allowed manufacturing companies to expand from design and 3D printing of prototypes to the rapid manufacturing of end products. Additive manufacturing enables the manufacturing of components in a layer-by-layer fashion, opposite to common manufacturing methods that rely on machining, molding (subtractive methods) to obtain the final product. It uses computer-aided design software that allows for the design of virtual objects. Considering mechanical and chemical properties, polymers are the most utilized materials for 3 D printing. Polymers used for 3 D printing involves thermoplastics, thermosets, elastomers, polymers with incorporated fillers and other additives. The specific design and choice of polymers can lead to materials with enhanced functionalities, mechanical properties, porosity, and stability.



https://www.amazon.in/idea-Imagine-Create-Print-Pro/dp/B07H21QPTT/ref

# **Process of 3D printing:**

Since the 1980s, 3D printing has become very popular as a result of the rapid manufacturing of components with architectures designed to meet specific applications. 3D printing allows for the manufacturing of a variety of shapes in a layer-by-layer fashion, often without the need of post-processing such as machining. The computer controls the stage and dispenser of the 3D printer allowing prototypes to be manufactured.



### Polymers in 3D printing industry:

Polylactic acid (PLA), Polycarbonate (PC), acrylonitrile butadiene styrene (ABS), poly ether ester ketone (PEEK) and Nylon are common polymers or plastics that are processed by heating to a semi-liquid state and close to the melting point. Particularly, polymers in the pure state lack mechanical strength for load-bearing applications. The addition of fillers, such as silica and carbon fibers is often used to generate materials with high mechanical strength.

#### I) Acrylonitrile/butadiene/styrene (ABS)

This thermoplastic polymer is what is called a 'terpolymer' and obtained most often by polymerization of acrylonitrile and styrene in the presence of polybutadiene – generally 20% acrylonitrile, 25% butadiene and 55% styrene. Manipulating these proportions can therefore modify the properties of ABS; styrene, for example, is the element that gives ABS its rigidity and brilliance, while butadiene gives it its impact resistance and low temperature properties.

#### Properties:

- 1) ABS material has good rigidity, high impact resistance and great lightness, while remaining very affordable in terms of price
- 2) ABS is used in 3D printing when heated between 230°C and 260°C.
- 3) Although it is more difficult to print than PLA, ABS remains a very popular material for 3D printing professionals due to its resistance to impact and high temperature (between -20°C and 80°C).
- 4) It is opaque, offers smooth and shiny surfaces and can be welded by chemical processes using acetone
- 5) The use of a heating plate (between 80 and 130°C) is mandatory. ABS plastic shrinks on contact with air, causing the part to shrink (or warp) and thus detaching itself from the plate.
- 6) 3D printer with a closed enclosure is preferable because ABS plastic emits particles that can be dangerous for the user.
- 7) ABS loaded with carbon fibers or aramid fibers (Kevlar) reduce the warping phenomenon of ABS and provide greater precision.

### II) Polylactic acid (PLA):

PLA, also known as polylactic acid or polylactide, is a thermoplastic made from renewable resources such as corn starch, tapioca roots or sugar cane by fermentation, unlike other industrial materials made primarily from petroleum. In this case, the natural product is ground to separate the starch from the corn, mixing it with acid or lactic monomers. With this mixture the starch is broken into dextrose (D-glucose) or corn sugar. Finally, glucose fermentation produces L-lactic acid, the basic component of PLA. It is often the preferred choice for beginners in 3D printing as it is a very easy material to work with.

#### Properties:

- 1) PLA is considered as a semi-crystalline polymer, has a melting temperature of 180°C, lower than ABS filament, which starts melting between 200°C and 260°C. This means that when printing with PLA, the use of a heated printing bed is not necessary, and the closed chamber is not a necessity either.
- 2) The only drawback is that the PLA filament has a higher viscosity which can clog the print head if you are not careful.
- 3) This filament does not have the mechanical properties as the ABS filament. It shows lesser resistance and flexibility than ABS. However, PLA has greater resistance to heat, so it is often used in the food industry.
- 4) PLA has the benefit of being biodegradable, unlike ABS.It is manufactured using renewable raw materials such as corn starch.
- 5) PLA is one of the easiest materials to print, though it does have a tendency to shrink slightly after 3D printing therefore do not require a heated platform when printing in PLA, unlike with ABS.
- 6) PLA also prints at a lower temperature than ABS, between 190°C to 230°C.
- 7) PLA is a more difficult material to manipulate due to its high cooling and solidification speed. It is also important to mention that models can deteriorate when in contact with water. However, the material is consistent, simple to use, and comes in a wide variety of colors, making it suitable for 3D printing.

# **Applications of 3D printing:**

# 1) Biomedical engineering applications -

3D printing is used to fabricate hard tissues (bones, teeth, cartilage) and soft tissues (organs, skin, and others. 3D printing allows for the rapid manufacturing of customized prosthetics and implants with controlled architectures. ABS and PLA are the most suitable polymers used for the manufacturing of scaffolds.

# 2) In the aerospace industry

Aerospace applications typically require light weight and high strength materials. The aerospace industry has replaced the conventional manufacturing methods of molding and machining with 3D printing technology for small scale production. The main use for 3D printing has been focused on prototyping, modeling and producing jigs, fixtures and tools. Recently, NASA designed a rover, named Desert RATS, that can support humans in a pressurized cabin in space . The rover is intended to transport humans to Mars. It contains 70, 3D printed parts that include flame-retardant vents and housings, camera mounts, large pod doors, front bumpers, complex electronics, and others.

### 3) 3D printed electronics

Electronic devices require suitable mechanical, geometrical, and optical functionalities to allow for miniaturization, low energy consumption, and smart capabilities The conventional method for manufacturing electronic devices is using subtractive methods that involve masking and etching of materials.

3D printing is being used to substitute steps for mounting and assembling electronic devices. The additive process of 3D printing deposits material in a controlled layer-by-layer process allowing the manufacturing of complex geometries and dimensions. Along with miniaturization, 3D

printing allows the manufacturing of small parts that would otherwise be difficult to obtain. 3D printing has found application for thin films, inductors, solar cells and others. The most common 3D printing techniques for electronics are inkjet and direct writing of conductive inks.

# 2.4 Polymer Recycling

Recycling of plastic is the process of recovering waste plastic and reprocessing the material into useful product.

- e.g. Waste soft drink plastic bottles can be melted and casted into plastic chairs and tables.
- (i) Thermoplastics can be remoulded.
- (ii) Thermosetting plastic once moulded it cannot be remoulded.

# 2.4.1 Difficulties in recycling plastic

- (i) Some plastics which are thermosetting cannot be recycled
- (ii) There are a lot of grades of thermoplastic materials which cannot be mixed and remelted together. If different types of plastics are melted together, they tend to separate into different phases. The phase boundaries cause structural weakness in resulting material limiting its application.

# 2.4.2 General recycling process

- **Step 1:** Plastic wastes are collected together.
- **Step 2:** They are sorted and separated depending upon types of plastics and their codes.
- **Step 3:** They are reprocessed. It includes melting of polymer (except thermosetting plastics)
- **Step 4:** It involves manufacturing new product from the melted plastic.

### **Sorting of plastics**

Thermoplastics are sorted by Plastic Identification Code (PIC) introduced by Society of Plastic Industry (SPI). It provides uniform system for identification of different polymer types and sort accordingly.

Plastic identification code	PETE	L23 HDPE	4	LDPE	253 PP	A PS	OTHER
Type of plastic	Polyethylene	High density	Polyvinyl	Low density	Polypropylene	Polystyrene	Other plastics
	terephthalate	polyethylene	chloride	polyethylene	PP	PS	usually layer
	PET/	HDPE	PVC	LDPE			or mixed
	PETE						plastics
							includes
							polycarbonate, ABS plastic

Type 1 and 2 are commonly recycled. Type 4 is less commonly recycled. Rest of the types have less potential for recycling.

- After cycling, polymers are chopped, ground into flakes
- The flakes are washed with water to remove dirt, labels and sinkable impurities (heavy metals)
- The flakes are then dried in hot air
- Colour pigments and other additives are added to these flakes. Then they are reheated and pelletized by passing it through pelletizer.
- Pellet are then used for manufacturing different goods

# 2.4.3 Types of recycling processes

Depending upon type of material, different recycling processes are used.

- i. **Primary recycling** It includes regrinding, remelting and reforming. Product contain similar feature of original plastic. The most popular process is represented by the primary recycling due to their simplicity and low cost. This process refers to the reuse of products in their original structure. The disadvantage of this process is represented by the existence of a limit on the number of cycles for each material
- ii. Secondary recycling (Physical recycling)— It refers to the process of physical and thermal reprocessing into secondary product. Products have different characteristics from those of original. This process is represented by a physical method, in which the plastic wastes will be formed by cutting, shredding or washing into granulates, flakes or pellets of appropriate quality for manufacturing, and then melted to make the new product by extrusion. Also, the reprocessed material can be blended with virgin material to obtain superior results. After the plastic is sorted, cleaned, dried and then directly processed into end products, the quantity of the waste plastic will be dramatically reduced. The disadvantages of this method refer to the heterogeneity of the solid waste and the deterioration of product's properties in each cycle which occurs due to the low molecular weight of the recycled resin
- iii. **Tertiary recycling (Chemical recycling)** The process involves chemical or thermal treatment to transform waste plastic into their monomers and fuels

Polyesters, nylons, polyurethenes can be depolymerized by chemical processes like glycolysis, methanolysis and hydrolysis to give momomers. These monomers can be again used for polymerization.

e. g. PET can be subjected to methanolysis to give its monomers, ethylene glycol and dimethyl terephthalate (DMT).

Assorted polymers or thermoset materials such as vulcanized rubber can be subjected to thermal depolymerization to give fuels

iv. **Quaternary recycling** – It uses energy from plastic by burning or incineration. This method is a good solution because it generates considerable energy from polymers, but it's not ecologically acceptable because of the health risk from airborne toxic substances

### 2.4.4 Recycling of thermosets –

Thermoset polymers cannot be remoulded however they can be incinerated or mechanically recycled i. e. polymer can be ground to fine particles and can be used as filler for new plastic. The material so obtained is slightly of lower quality.

# Recycling of tyres -

Scraped tyres can be ground into crumb for use in pads, mats, carpet backing, moisture barriers, rubber modified asphalt etc.

Scrap tyres can also be depolymerized to generate electricity and produce synthesis gas (H<sub>2</sub> and CO).

# 2.4.5 Limitations of plastic recycling –

- 1. Glass, paper etc. can be recycled again and again. Plastics are usually recycled once. Plastic recycling requires more energy, more resources and more cost
- 2. For recycling, plastics must be sorted out properly. Sorting is normally done by hand which is expensive and time consuming.
- 3. Recycled plastic is of low quality. This gives less market potential and price for the products.
- 4. Use of dyes, fillers and other additives in plastic may cause problem in recycling. They cannot be removed by cheaper way.
- 5. Incineration of plastic may involve emission of toxic substances.

# 2.4.6 Options Available

- 1) Use of biodegradable polymer.
- 2) **Solid state shear pulverization (S<sup>3</sup>P):** It is a new technology for plastic recycling. It is continuous one step process in which unsorted plastic waste is subjected to high shear and pressure. Frictional heat is removed by cooling and melting of plastic is prevented.

The process converts multicoloured, unsorted plastic waste into uniform, light coloured, partially reactive powder. The plastic size of the powder can be controlled. The powder can be used in variety of consumer products and special products like automotives, appliances, furniture etc.

#### 2.5 Nano materials

# **2.5.1 Introduction to Nanotechnology**:

Nanotechnology is a field of applied science focused on the design, synthesis, characterisation and application of materials and devices on the nanoscale.

The first acknowledgement of importance of nanoscale range attributes to the Nobel Laureate physicist Richard Feynman in his famous lecture "There is Plenty of Room at the Bottom" in which he proposed the properties of materials and devices at nanometer scale

 $(1 \text{ nano meter} = 10^{-9} \text{ meters})$ 

Bulk materials always exhibit macroscopic physical properties. The same material at the nano scale can have properties (e.g. optical, mechanical, electrical etc) which are very different from the properties at bulk scale.

The material properties of nanostructures are different from the bulk due to the high surface area over volume ratio and possible appearance of quantum effects at the nanoscale. The study of size and shape effects on material properties has attracted enormous attention due to their scientific and industrial importance.

# 2.5.2 Scope of Nanotechnology:

#### **Nanotechnology in Electronics:**

- Nanomaterials with less than 100 nm size are used in microprocessors in electronic industry.smaller size allows faster processing, more processing power in given area.
- Improved quality of screen, less power consumption due to decrease in weight and thickness
- Density of memory chips can be increased by using nanomaterials. Integrated nanosensors are used for collecting, processing and communicating massive amount of data with minimum size, weight and power consumption
- The transistors used in ICs can be reduced to smaller size

# Nanotechnology in Health and Medicine:

Nanotechnology can be used as nanomedicine (medical use of nanomaterials) to nanoelectronic biosensors. Nanomedicine has a potential to enable early detection, prevention and treatment. Some nanomaterial based biosensors can be used for detection of cancer.

### **Nanotechnology in Transportation:**

- Nanomaterials will allow cars and planes to become safer and cheaper. The light nanomaterials will replace the weight of heavy structural materials in transport industry which will help in achieving greater milage
- Improved nanocatalyst could reduce or eliminate the emission of pollutants from engine
- Nanocoating on the metallic surface achieve super hardening, low friction and enhanced corrosion protection.
- Nanoparticles of inorganic clays and polymers will replace carbon black tyres and therefore will have eco-friendly, wear resistant tyres.

### **Nanotechnology for Energy and Environment:**

- Using nanotechnology more clean and less expensive energy production is possible. Nanotechnology has a great contribution on renewable energies from solar energy to nanocatalysis, fuel cells and hydrogen technology.
- Nanotechnology can help in developing new environmental safe and green technologies that can minimise the formation of undesirable by products or effluents.

# **Nanotechnology for Space exploration:**

• Rocket scientists are actively researching new forms of space propulsion systems because today's rocket energies rely on chemical propulsion. Electric propulsion (EP) is heavily researched area. A new EP concept proposes to utilise electrostatically charged and accelerated nanoparticles as propellant.

#### 2.5.3 Nanomaterials:

Nanomaterials can be metals, ceramic, polymeric or composite materials. They are characterised by a small size ranging from 1-100 nm. The structural features of nanomaterials are inbetween those of atoms and bulk materials. The properties of nanomaterials are significantly different than those of atoms and bulk materials because of following features:

Larger fraction of surface atoms

High surface energy

Spacial confinement

Reduced imperfections, which do not exist in corresponding bulk materials

### 2.5.4 Types of Nanomaterials:

Nanomaterials are classified as zero-dimensional, one-dimensional, two-dimensional, three-dimensional nanostructures.

#### 1)Zero-dimensional nanomaterials:

Materials wherein all the dimensions are measured within the nanoscale (no dimensions)

The best example of zero-dimensional nanomaterials are 'nanoparticles'.

### 2)One –dimensional nanomaterials:

Nanomaterials exist in one-dimensional structure. This leads to needle like nanomaterials.

One –dimensional materials include nanotubes, nanorods and nanowires.

### 3)Two-dimensional nanomaterials:

Two-dimensional nanomaterials exhibit plate shapes.

Two-dimensional nanomaterials include 'nanofilms, nanolayers and nanocoatings'

### 4) Three-dimensional nanomaterials:

'Bulk nanomaterials' are materials that are not confined to the nanoscale in any dimension. These materials possess nanocrystalline structures or involve the presence of features at nanoscale.

In a nanoscale, three-deminsional nanomaterials can contain dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multinanolayers.

# 2.5.5 Nanomaterials and their applications:

### 1) Carbon black:

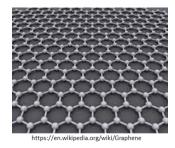


A pure elemental carbon in the form of colloidal particles is carbon black.

**Preparation:** An incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbon under controlled conditions produces carbon black. The average particle size of carbon black is few nanometers.

**Applications:** The primary use of carbon black is rubber products (@ 90%), mainly for tyres and automobile parts such as hoses, gaskets and rubber tubes. About 9% is used as pigments in tonners and inks and remaining 1% in diverse applications. Smaller amount of carbon black is used in manufacturing of dry cells.

# 2) Graphene:



A layer of one atom thick planar sheet of carbon atoms, densely packed together into honeycomb shaped crystal lattice is graphene.

Graphene is a basic structural unit of several allotropes of carbon including graphite, carbon nanotubes and fullerene. An isolated plane of graphite gives graphene. The carbon-carbon bond length in graphene is about 0.142 nm. Graphene is a material of importance due to its high electron mobility and its possible applications in electronics.

Graphene is a flat monolayer of carbon atoms tightly packed in 2 dimensional honeycomb lattice. It is a basic building block for graphitic materials in all dimensions. It can be wrapped into zero dimensional fullerene, rolled into one dimensional carbon nanotubes and stacked into three dimensional graphite .It shows excellent heat and electrical conductivity.

**Preparation:** In the process of obtaining graphene, an adhesive tape is used to repeatedly tear off graphite crystals into thin sheets. The optically transparent thin sheets obtained by the above process which is attached to the tape, It is dissolved in acetone. After few steps flakes including monolayers are sedimented on a silicon wafer. Individual atomic plane of graphene then viewed in optical microscope and separated. Graphene is also obtained by heating silicon carbide (SiC) to higher temperature (>1100°C) under low pressure ( $\sim 10^{-6}$  Torr).

#### **Applications:**

- 1) As a sensor for gas detection
- 2) In making transparent conducting electrodes
- 3) In solar cells
- 4) In conducting plates of ultracapacitors
- 5) For gas storage by physical adsorption

# 3) Fullerenes:



Fullerene is zero dimensional allotropes of carbon.

Fullerene is sphere of carbon atoms formed by interconnecting six membered rings and five membered rings. C60 fullerene (Buckminister fullerene) contains 20 hexagonal faces and 12 pentagonal faces. All 60 carbon atoms are SP<sup>2</sup> hybridised and contain single and double bonds. In the fullerene structure, all Carbon sites are equivalent and the bond length for double bond is 0.14nm and for single bond is 0.146nm.

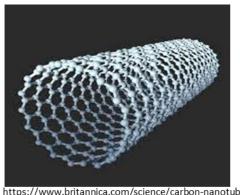
#### **Preparation:**

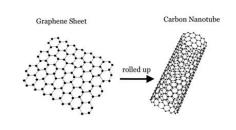
A common method used to produce fullerene is to send a large current between two nearby graphite electrodes in an inert atmosphere. The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated.

#### **Applications:**

- 1. Electrical conductivity of fullerene is very low. It is increased several times by doing with alkali metals and can be used as a superconductor. It has been reported that K3C60 composite possess high super conductivity at critical temperature
- 2. Fullerene is tough and has high impact resistance. It is spherical in nature, therefore, it can be used as a lubricant (molecular bearings)
- 3. C60 incorporated with alkali metals can act as a catalyst for chemical reactions.
- 4. It can act as a medium for hydrogen storage by physical adsorption of hydrogen gas. One unique characteristic of fullerenes which makes them ideal storage molecules for hydrogen is the hydrogenation of their C-C bonds to form C-H bonds which actually possess lower bond energies therefore heating breaks the C-H and reverts the molecule back to its original distinctive fullerene structure. Thus-fullerenes are able to retain a maximum of 6.1% of hydrogen due to their chemistry and cage molecular structure
- 5. The properties of fullerene may be tuned to suit applications via addition of elements and molecular species into fullerene lattice within the cage or coating the surface of fullerene with transition metals. These properties can be used for drug delivery, facial cream, moisturisers, lubrications, electronic circuits. Fullerenes can be made to be potential drug carriers for cellular delivery because of their good biocompatibility, selective targeted delivery and controlled release of carried drugs. By attaching hydrophilic species on them, fullerenes become water soluble, as such they become exceptional in drugs and gene cellular delivery
- 6. It is used in organic solar cell as acceptor material. Fullerene have found profound usefulness in photovoltaic devices, organic electronics and photo catalysis because they combine with suitable electron donor components to form donor-acceptor (D-A) dyads that can generate long-lived charge separated states.

#### 4) Carbon Nanotubes:





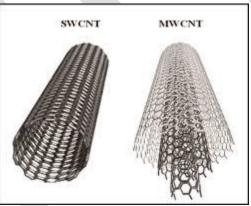
https://ysjournal.com/carbon-nanotubes-the-future-of-the-planets-freshwater/

https://www.britannica.com/science/carbon-nanotube

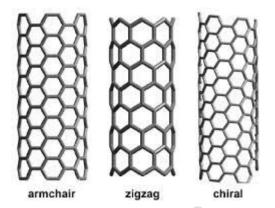
Carbon Nanotubes is a tubular form of carbon with a diameter as small as 1 nm and length of few nanometers to a micron. CNT is configurationally equivalent to a grapheme sheet rolled into a tube. Nanotubes are the strongest fiber known. A single perfect nanotube is about 10 to 100 times stronger than steel per unit weight. They are very stable at high temperature and resistant to acids

# **Types of carbon nanotubes:**

Carbon nanotubes are two main types- Single Walled Nanotubes (SWNT) and Multi Walled Nanotubes (MWNT).



**Single Walled Nanotubes (SWNT):** Structure of SWNT can be wrapping a single atom thick layer of graphite (graphene) into a cylinder. Depending on the direction of rolled up grapheme hexagons, carbon nanotubes can be classified as zigzag, armchair and chiral. Armchair type shows metallic conductivity whereas other two are semiconductors. Multi Walled Nanotubes (MWNT): It contains multiple graphene layers telescoped about one another. The length, diameter and hence the properties of MWNTs differ from **SWNTs** 



### **Preparation:**

Carbon nanotubes can be prepared by different methods:

- 1. **Pyrolysis of hydrocarbons**: Pyrolysis of hydrocarbons such as an acetylene at about 700°C in the presence of catalysts like Fe-graphite, Co-graphite under inert conditions yield CNTs
- 2. **Arc vaporisation of graphite**: It is carried out by striking a direct current arc between the graphite electrodes separated by about 1 mm in inert atmosphere. The method gives MWNTs.

SWNTs are prepared by DC arc vaporisation of graphite in the presence of metal catalyst like iron, cobalt, nickel in helium atmosphere.

- 3. **Laser ablation or evaporation**: In this process, a laser vapourise a graphite target containing small amount of Cobalt and Nickel at a high temperature (~1200°C) quartz tube reactor in inert atmosphere. The method gives high amount of SWNTs.
- 4. Chemical Vapour Deposition (CVD): It involves decomposing a hydrocarbon gas such as methane, acetylene, ethylene etc. at high temperature of about 1100°C in the presence of metal nanoparticles catalysts like Ni, Co, Fe supported on MgO or Al<sub>2</sub>O<sub>3</sub>. Carbon atoms are produced after decomposition of hydrocarbon which condense on cooler surface containing metal catalyst to form CNT.

#### **Applications:**

- 1. **Hydrogen storage**: CNTs can be used as hydrogen storage material in fuel cells. It has been estimated that a CNT can hold 7.7% hydrogen by weight by physical adsorption.
- 2. **Batteries:** CNTs can be used in lithium batteries. Lithium can be intercalated for battery applications.
- 3. **Field Emitting Transistors (FET):** CNT field emitting transistors are used as switching components in computers. Field emission (emission of electrons from the surface of conductor under the influence of a strong electrostatic field) is exhibited by semiconducting nanotubes connecting two metal electrodes, when a small electric

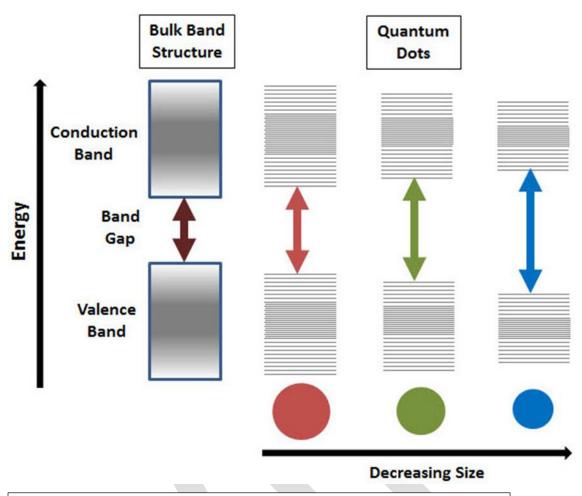
- field is applied between the electrodes parallel to the tube axis. A combination of p-FET and n-FET can be used as a logic gate.
- 4. **Sensors:** CNTs may be used as miniaturised chemical sensors. On exposure to the gases such as NO<sub>2</sub>, NH<sub>3</sub>, or O<sub>2</sub>, the electrical resistance changes.
- 5. **Probe in microscopy**: CNTs attached to scanning probe microscope tips have been used to image biological or industrial specimens.
- 6. **Composite material**: Because of high stiffness, CNTs can be used as reinforcement with high strength and low weight. Tennis rackets, bulletproof jackets are some applications
- 7. **Drug delivery vessel**: CNTs can be used for drug delivery within the body by placing the drugs within tubes or by attaching the drugs tom the side walls of the tubes.

### 5) Quantum dots:

Quantum dots (QDs) are man-made nanoscale crystals that that can transport electrons. A quantum dot gets its name because it's a tiny speck of matter so small that it's effectively concentrated into a single point (in other words, it's **zero-dimensional**). As a result, the particles inside it that carry electricity (electrons and holes) are trapped ("constrained") and have well-defined energy levels according to the laws of quantum theory

Quantum dots are extremely small semiconductor structures ranging from 2 to 10 nm in diameter. Quantum dots semiconductor are the most widely used materials. Each quantum dot is actually a tiny semiconductor. When UV light hits these semiconducting nanoparticles, they can emit light of various colors.

Quantum dots have quantized energy levels. Dots made from the same material (say, silicon) will give out *different* colors of light depending on their size and shape. The biggest quantum dots produce the longest wavelengths (and lowest frequencies), while the smallest dots make shorter wavelengths (and higher frequencies); in practice, that means big dots make red light and small dots make blue, with intermediate-sized dots producing green light. The explanation for this is simple. A small dot has a bigger band gap, so it takes more energy to excite it; because the frequency of emitted light is proportional to the energy, smaller dots with higher energy produce higher frequencies (and shorter wavelengths). Larger dots have more (and more closely) spaced energy levels, so they give out lower frequencies (and longer wavelengths). Thus, the energy band gap of quantum dots depends on the particle size of the material. By changing the particle size, the band gap will change and so the colour of light emitted. This occurs because the specific wavelength of light emitted is a function of the energy band gap. Cadmium sulphide (CdS), zinc selenide (ZnSe), cadmium selenide (CdSe), Indium phosphor (InP) and Indium arsenic (InAs) are examples of quantum dots.



httns://www.sigmaaldrich.com/technical-documents/articles/materials-science/nanomaterials/guantum-

# **Fabrication methods of quantum dots:**

Generally, quantum dots have a core/shell structure.

There are several methods for fabrication of quantum dots

- 1) Molecular beam epitaxy (MBE)
- 2) Electron beam lithography and molecular beam epitaxy
- 3) Chemical vapour deposition (CVD)
- 4) Colloidal synthesis

# **Applications of quantum dots:**

- 1. **Life science**: Quantum dots preferentially stain the vascular and lymphatic systems, tumours etc. Cell staining, flow cytometry and cellular uptake are the examples of quantum dot applications
  - The small size of dots allow them to go anywhere in the body making them suitable for different bio-medical applications like medical imaging, biosensors, etc. At present, fluorescence based biosensors depend on organic dyes with a broad spectral width, which limits their effectiveness to a small number of colors and shorter lifetimes to tag the agents. On the other hand, quantum dots can emit the whole spectrum, are brighter and have little degradation over time thus proving them superior to traditional organic dyes used in biomedical applications.
- 2. **Display:** The applications of quantum dots are both in organic and inorganic light emitter devices such as electroluminescence (EL) devices. The quantum dot material is dispersed within or between phosphor layers and emits a specific colour of light. The emission of colours of nanophosphors based on quantum dots can be tuned by changing size of quantum dots.
  - Quantum dots are particularly significant for optical applications owing to their bright, pure colors along with their ability to emit rainbow of colors coupled with their high efficiencies, longer lifetimes and high extinction coefficient. Examples include LEDs and solid state lighting, displays and photovoltaics
- 3. **Photovoltaic devices:** It is possible to get multiple energy band gaps for quantum dots containing different size materials. Different layers of different band gaps can be used to reduce loss of incident light. Multiple band gaps can absorb photons from sever al different wavelengths according to their band gap energies. This allows increased photon to electron conversion efficiency in photovoltaic devices.
- 4. **Photonics and telecommunication:** The properties of quantum dots provide an opportunity to exploit and develop optical switches, modulators and other non linear optic devices. The optical switches and logic gates that work faster than 15 terabits per second can be achieved when quantum dots are being used.
  - Being zero dimensional, quantum dots have a sharper density of states than higher-dimensional structures. Their small size also means that electrons do not have to travel as far as with larger particles, thus electronic devices can operate faster. Examples of applications taking advantage of these unique electronic properties include transistors, solar cells, ultrafast all-optical switches and logic gates, and quantum computing, among many others.
- 5. **Security ink:** For security and anticounterfeiting applications, inks and paints incorporated with quantum dots can be applied to many types of surfaces, including papers, plastic and metals. The wide range of colour combinations of multiple quantum dots and other pigment creates a unique visible image that identifies any document when exposed to UV light.

#### 2.6 Modern Batteries

Many of the commercial batteries are not able to meet the performance requirements of many applications. Thus, a continual need exists for both conventional battery technology with improved performance and advance battery technologies with characteristics such as high energy level, long life, low cost, little or no maintenance and safety.

#### 2.6.1 Lithium batteries

Conventionally, cells having lithium anode are called as **Lithium cells** irrespective of the type of cathode used.

The group of batteries where lithium is used as anode is known as Lithium batteries

Lithium metal is attractive as a battery anode material because of its light weight, high voltage, high electrochemical equivalence, and good conductivity. Because of these outstanding features, the use of lithium has dominated the development of high-performance primary and secondary batteries during the last two decades.

# **Advantages of Lithium Cells**

Primary cells using lithium anodes have many advantages over conventional batteries. The advantageous features include the following:

- **1. High voltage:** Lithium batteries have voltages up to about 4 V, depending on the cathode material, compared with 1.5 V for most other primary battery systems. The higher voltage reduces the number of cells in a battery pack by a factor of at least 2.
- **2. High specific energy and energy density:** The energy output of a lithium battery (over 200 Wh/kg and 400 Wh/L) is 2 to 4 or more times better than that of conventional zinc anode batteries.
- **3. Operation over a wide temperature range:** Many of the lithium batteries will perform over a temperature range from about 70 to  $-40^{\circ}$ C
- **4. Good power density:** Some of the lithium batteries are designed with the capability to deliver their energy at high current and power levels.
- **5. Flat discharge characteristics**: A flat discharge curve (constant voltage and resistance through most of the discharge) is typical for many lithium batteries.

**6. Superior shelf life:** Lithium batteries can be stored for long periods, even at

elevated temperatures.

Lithium is a theoretically 'active material for negative electrode' of the electrochemical

cells owing to its least noble nature and low specific gravity.

2.6.2 Primary Lithium Batteries

Lithium batteries use non-aqueous solvents for the electrolyte because of the reactivity of

lithium in aqueous solutions.

Non-aqueous solvents such as acetonitrile, propylene carbonate (PC) and inorganic solvents

such as thionyl chloride are typical. A complete solute is added to provide the necessary

electrolyte conductivity.

Lithium-Manganese Dioxide [Li/MnO2] Cell

It is a primary lithium cell. It is available in many configurations (including coin, bobbin,

prismatic) in multi-cell batteries and designs for low, moderate and high drain applications.

It has high cell voltage [3.0 V], energy density, and good performance over a wide range of

temperatures, long shelf life and low cost.

**Construction:** 

**Anode:** Lithium

**Cathode:** heat treated MnO<sub>2</sub>

Electrolyte: lithium salts (LiCl, LiBr) in a mixed organic solvent (Propylene carbonate and

1,2 dimethoxy-ethane)

Voltage offered: 3.0 V

The Li/MnO<sub>2</sub>, battery uses lithium for anode

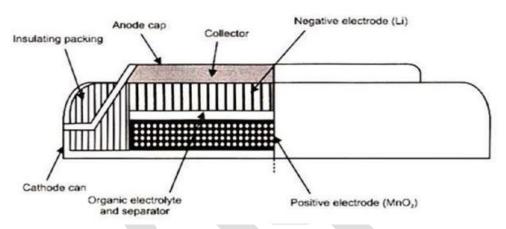
a specially prepared heat treated (>300°C to effectively remove water) form of manganese

dioxide for the active cathode material

57

- Both the electrode materials are separated by a non-woven polypropylene separator impregnated with an electrolyte.
- an electrolyte containing lithium salts like LiCl, LiBr in a mixed organic solvent (Propylene carbonate and 1,2 dimethoxy-ethane)

# Figure:



# Working:

- At anode, oxidation of lithium takes place producing Li<sup>+</sup> ions. Li<sup>+</sup> ions move into the electrolyte and electrons move into the external circuit to reach the cathode
- At cathode, MnO<sub>2</sub> is reduced from +4 oxidation state to +3 states to give LiMnO<sub>2</sub>

#### **Reactions:**

At Anode:

$$Li \rightarrow Li^+ + e^-$$

At Cathode:

Mn (IV) 
$$O_2 + Li^+ + e^- \rightarrow LiMn$$
 (III)  $O_2$ 

**Net reaction**: Li + Mn (**IV**) O<sub>2</sub>  $\rightarrow$  LiMn (**III**)O<sub>2</sub>

 $Mn^{4+}$  state is reduced to  $Mn^{3+}$  state by the interstitially occupied lithium ions in the  $MnO_2$  intercalation compound. LiMnO<sub>2</sub> signifies the interstitial Li<sup>+</sup> ion in the host

### MnO<sub>2</sub> lattice.

It exhibits both electronic and ionic conductivity. The voltage of the cell is 3.5 V.

#### **Characteristics/Advantages:**

- 1. High volumetric and gravimetric energy density
- 2. wide operating temperature range (— 20 to 55°C)
- 3. performance at high discharge rates
- 4. relatively low cost.
- 5.less pollution

### **Disadvantages:**

- 1. Not Rechargeable
- 2. Can Be Dangerous: Leaks within the appliances they are used in.Can also cause major problems such as the appliance getting overheated and igniting
- 3. When lithium batteries are found in large numbers, reactions can lead to potential explosions. For example, during collection, processing or disposal of large numbers of lithium batteries, the batteries could come into close contact with each other and cause friction. This can lead to rupture and eventually an explosion.

#### **Applications:**

The lithium-manganese cell is used in a wide variety of applications such as

- 1. long-term memory back-up,
- 2. safety and security devices,
- 3. cameras, lighting equipment and many consumer electronic devices.

# 2.6.3 Secondary (Rechargeable) Lithium Batteries

One of the basic concepts of investigation on rechargeable lithium battery is to develop batteries that have high energy density, power density, good cycle life and charge retention and to provide this high performance reliably and safely. In order to achieve the optimum balance for the construction of battery, it demands a compromise between the selection of the cell components and the design of the battery. The process is more complex for rechargeable batteries as the cell chemistry must be reversible and the reactions that occur during the charge affect all the characteristics and performance on subsequent cycling.

#### **Lithium Ion Batteries**

Today, a successfully developed battery system is the lithium ion battery (LIB) which has high volumetric and energy densities

- Lithium-ion battery uses a cathode (positive electrode), an anode (negative electrode) and electrolyte as conductor.
- The cathode is metal oxide and the anode consists of porous carbon.
- During discharge, lithium ions flow from the anode to the cathode through the electrolyte and separator; whereas charging reverses the direction and the ions flow from the cathode to the anode.

Thus, the cell reaction in LIB is merely the migration of lithium ions between +ve and -ve electrodes. No chemical changes are observed in the two electrodes or in the electrolytes.

The batteries in which lithium ions are used instead of lithium metal and movement of lithium ion through electrolyte takes place from one electrode to another electrode, such batteries are called lithium-ion batteries. Ex:- Lithium cobalt oxide [LiCoO2] battery.

# E.g. Lithium cobalt oxide [LiCoO2] battery:

#### Construction: -

- Anode is made up of Carbon electrode with thin copper foil as current collector.
- Cathode is made up of lithium cobalt oxide compound with thin aluminum foil as current collector.
- A porous polyethylene (or) polypropylene film is used as separator.
- A lithium salt in an organic solvent is used as electrolyte. This electrolyte effectively transport Li<sup>+</sup> ion to cathode during discharge of battery.

#### Working: -

- During discharging, Li-ions are dissociated from anode and migrate through electrolyte to cathode. (Deintercalation)
- During charging, lithium from cathodic material is ionized and move towards negative electrode. (Intercalation)

#### Reactions:-

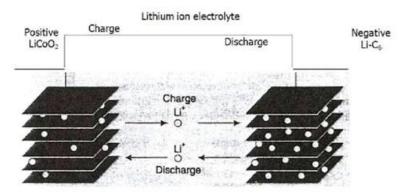
During discharging:

• At Anode:  $Li_xC_6 \rightarrow xLi^+ + xe^- + 6C$ 

• At Cathode:  $Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2$ 

• Net reaction:  $Li_{1-x}CoO_2 + Li_xC_6 \rightarrow 6C + LiCoO_2$ 

Reactions are reversed during charging



Typical structure of the lithium ion battery

### **Advantages**

- 1. They have high energy density than other rechargeable batteries
- 2. They are less weight
- 3. They produce high voltage out about 4 V as compared with other batteries.
- 4. They have improved safety, i.e. more resistance to overcharge.
- 5. No liquid electrolyte means they are immune from leaking.
- 6. Fast charge and discharge rate

### Disadvantage

- 1. They are expensive.
- 2. They are not available in standard cell types.

#### **Applications**

- 1. The Li-ion batteries are used in cameras, calculators.
- 2. They are used in cardiac pacemakers and other implantable device.
- 3. They are used in telecommunication equipment, instruments, portable radios and TVs, pagers.
- 4. They are used to operate laptop computers and mobile phones and aerospace application