

Engineering Materials

A) Speciality polymers :-

Introduction:-

- i) Variety of polymers are used for engineering & medical applications.
- ii) The demand for polymers with specific properties (for specific use) has increased. This leads to the development of new polymeric materials called speciality polymers.
- iii) Speciality polymers exhibit remarkable role in certain critical applications such as, surgical implants, sutures, fire retardant i.e. in textile fabric preparations which are used for fire fighters. Used for making membrane for gas liquid separations etc.

1) Engineering Thermoplastics :-

Engineering thermoplastics are group of materials obtained from (high polymer resins) which provide one or more remarkable properties when compared with common thermoplastics such as polystyrene, polyethylene etc.

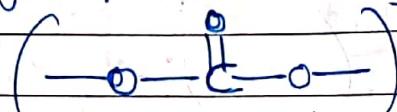
Advantages:-

- i) High thermal stability.
- ii) High tensile strength.
- iii) High flexibility.
- iv) Light weight.
- v) Readily mouldable into complicated shapes.
- vi) Excellent chemical resistance.

⇒ Engineering Thermoplastic—Polycarbonate:

Polycarbonate :- (Lexan or Mardon) (PC)

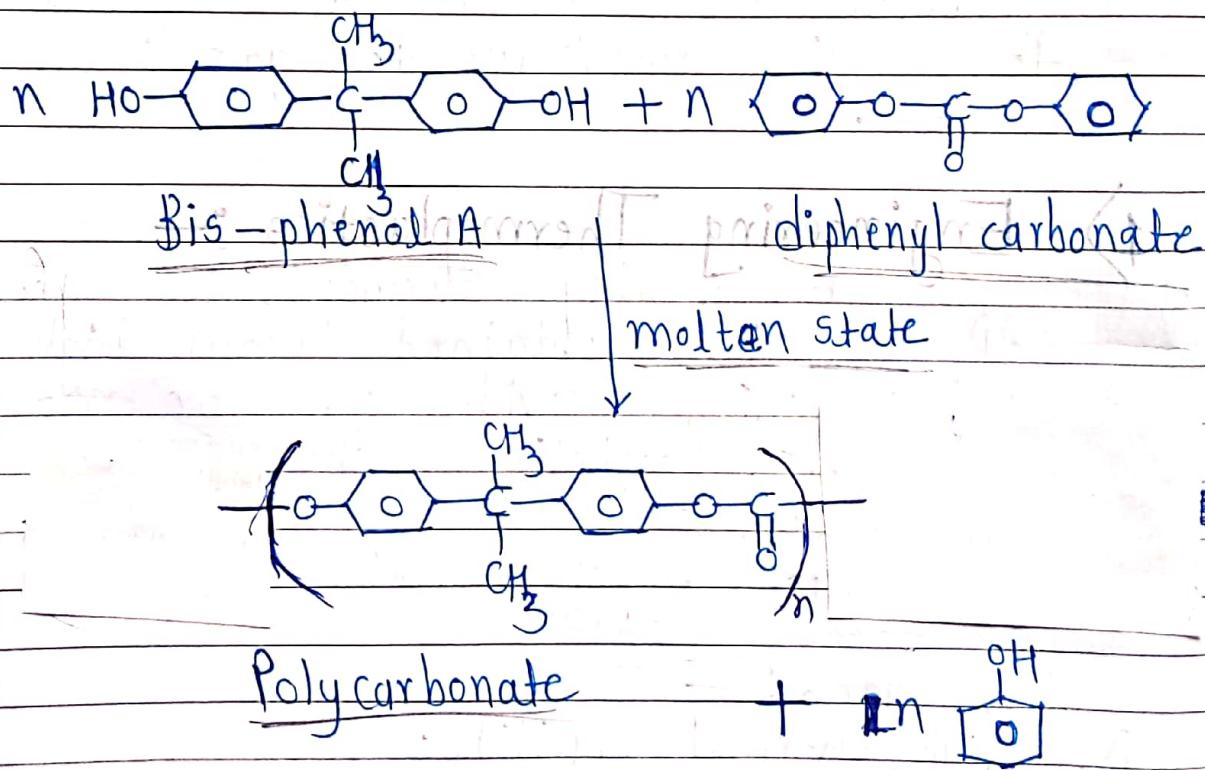
i) Polycarbonates are thermoplastic polymers having functional group linked together by carbonate groups, in long molecular chain.



ii) They are commercially known as Texan or Merlon.

iii) The most common type of polycarbonate is obtained by interacting Bisphenol A with diphenyl carbonate.

Preparation :-



This redⁿ is carried out in molten state (i.e. no use of solvent) & the product is crystallised after separation of biproduct phenol.

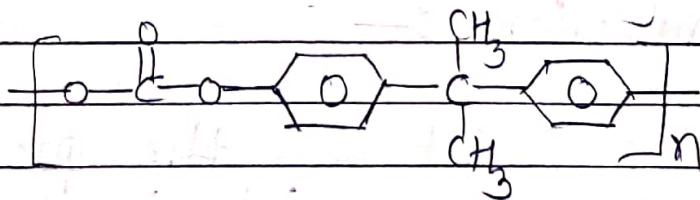
Properties :-

- i) Polycarbonate has very high impact strength & tensile strength.
- ii) It has transparent refractive index 1.58
- iii) It dissolves in organic solvents & alkali
- iv) It is not resistant to UV.
- v) It has a good heat resistance.
- vi) It is resistant to water & many organic compounds.

Applications :-

- i) Polycarbonate is used as bullet proof material for windows of vehicles & houses.
- ii) It is used for making moulded domestic ware, helmets, covers of vehicle lights.
- iii) It is used as insulators in electronics.
- iv) It is used for making CD & DVD
- v) Polycarbonate is used for making handles of screw driver & many more.
- vi) Also used for making housing apparatus.

e.g. → Polystyrene; Polyvinyl chloride (PVC)



Polycarbonate structure

2) Biodegradable Polymers :

~~Poly~~ Impact of synthetic (polymer) plastics on environment :

- i) The increasing use of synthetic polymers for consumer, engineering, medical etc applications resulted in producing solid waste. This discarded plastic solid waste has bad effect on environment.
- ii) eg. The solid waste affects aquatic life, burning of such solid liberates poisonous gases, makes road sides, sea shores, residential areas dirty, block the drainage systems.

Need of Biodegradable polymers :

- i) To reduce nonbiodegradable synthetic plastic solid waste which affects environment badly.
- ii) To reduce dependence of man on synthetic polymers.
- iii) Biodegradable polymers if used, they will reduce the solid waste disposal problem & pollution. These are ecofriendly.

Biodegradation :-

- i) Definition : It is the process of converting polymer material into harmless simple gaseous products, by the action of enzymes of micro-organism & water.
- ii) The enzymes act on polymer chain to convert the polymer into small fragments which then consumed by microorganism.
- iii) Bacteria get food from such fragments, finally fragments are converted to gases

like N_2 , CO_2 , CH_4 etc. However the overall process of biodegradation is slow.

Organic biodegradable polymer molecules $\xrightarrow{\text{enzymes from bacteria, slow}}$ Harmless gases

Components involved in Biodegradation :-

Following three components are important, in biodegradation of organic polymers ;

(or) Factors responsible for biodegradation of polymer.

- (a) Organisms
- (b) Environment
- (c) Nature of polymer

(a) Organisms or Microorganisms —

- i) There is large variety of micro-organisms like protozoa, azetobacter, various fungi present on our planet are responsible for biodegradation .
- ii) They carry out some specific or non-specific action on polymers by aerobic or anaerobic way , during the biodegradation.

(b) Environment —

The favourable environment for survival, multiplication & action by microorganisms include suitable temperature, moist condition, presence of salts, suitable pH, oxygen for aerobic bacteria etc .

(c) Nature of polymer —

- i) The polymer chain should contain bonds which can be easily hydrolyzed or oxidized by the enzymes action.

ii) There should be N, O, S like atoms in the chain of polymer.

iii) The highly aromatic chains are most tough for degradation.

~~Factors that accelerates degradation are:~~

- i) Hydrophilic chain with atoms like O, N, S in polymer chain.
- ii) More amorphous nature of polymer.
- iii) Small size of polymer material or ~~not~~ high porosity.

Limitation of biodegradable polymers:

- i) They can not be manufactured on large scale.
- ii) They are very costly.
- iii) They do not possess high mechanical strengths.

Features of Biodegradable polymers :

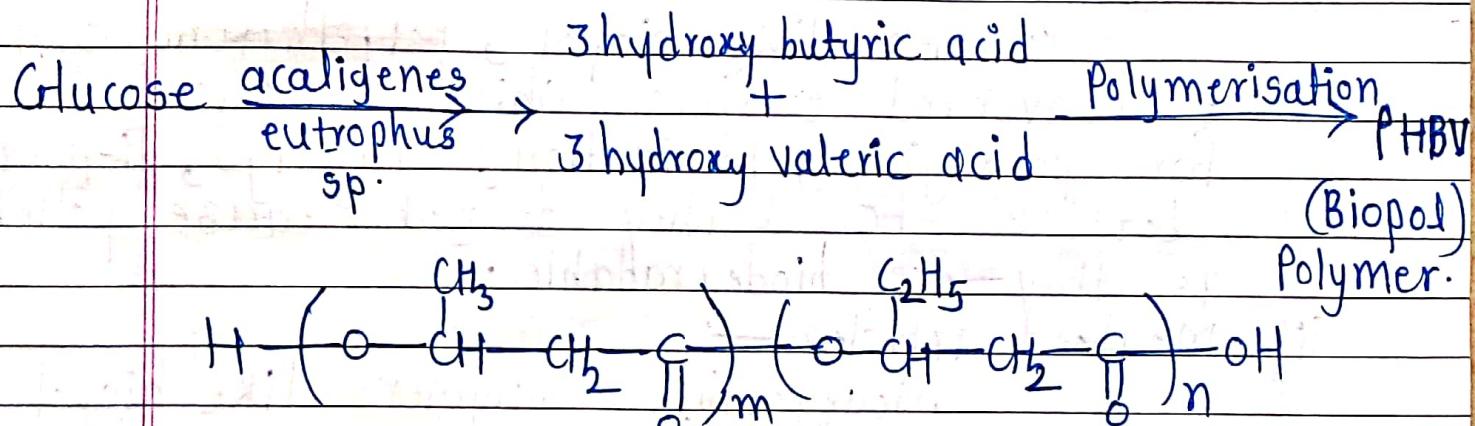
- i) Naturally occurring polymers are biodegradable eg wood
- ii) If polymer chain contains atoms other than carbon, it may biodegrade depending on functional groups.
- iii) Synthetic polycondensation polymers are generally biodegradable to different extent depending on functional groups involved (ester > ether > amide)
- iv) Hydrophilic polymers degrade faster than hydrophobic eg Biodegradable polymer - Poly (hydroxybutyrate-hydroxyvalerate)
- v) Amorphous polymers are more susceptible for biodegradation compared to crystalline polymers.

Poly(hydroxybutyrate-hydroxyvalerate):—

Biopol Biopol (PHBV)

Preparation:-

- i) It is the copolymer of 3 hydroxy butyric acid & 3-hydroxy valeric acid & it is produced by fermentation of glucose by *acaligenes eutrophus* species.
- ii) The polymer formed is a block co-polymer or random copolymer depending upon the culture conditions.



Biopol

Properties:-

- i) It is biodegradable, soft, flexible, easily mouldable & can be converted to films.
- ii) The resistance of PHBV (biopol) to oil is very good.
- iii) This polymer is moisture resistant.
- iv) The physical properties of Biopol co-polymer vary with hydroxyvalerate content of polymer. As the HV content increases in the range of 0.21% the polymer flexibility, toughness increases.

Uses:

- i) PHBV (Biopol) is useful for moulded articles, films for packaging & lamination.
- ii) It is used for sustained release of fertilizers, medicines, growth hormones for plants.

Applications :- of Biodegradable polymers:

i) Packaging -

Polymers like biopol can be converted to films which are useful for packaging, lamination, carrybags, disposable bottles etc & they do not cause pollution as they are biodegradable.

ii) Moulded articles -

Biodegradable polymers like biopol can be used for ^{making} moulding articles of common consumer applications.

iii) Medical field -

Polymers like polylactic acid, polyglycolic acid are important in biomedical applications like surgical sutures, orthopaedic treatment, slow release drugs.

iv) Agriculture -

Biodegradable polymers are used to control release of fertilizer, pesticides etc.

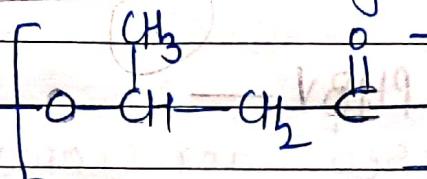
* Biodegradation of PHBV

It shows complete biodegradation in both aerobic & anaerobic conditions. The final product of biodegradation is CO_2 & water in aerobic condⁿ & methane with CO_2 in anaerobic condⁿ. Its rate of degradation depends on moisture, temp., pH, nutrient

2) Biodegradable polymer

Polyhydroxybutyrate — (PHB)

- i) PHB is produced by the fermentation of glucose by the bacterium Alcaligenes eutrophus. These

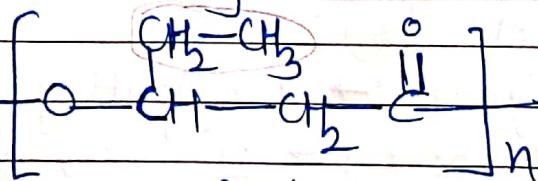


Polyhydroxybutyrate (PHB)

- ii) PHB is brittle, highly crystalline, water soluble, non toxic polymer which is relatively resistant to hydrolytic degradation.
- iii) It shows good O_2 permeability & is rapidly biodegradable.

Polyhydroxyvalerate (PHV)

PHV can be produced by A. eutrophus as well as another bacterium P. oleovorans depending up on the type of carbon structure available during fermentation.



Polyhydroxyvalerate

Addition of hydroxyvalerate (HV) to the polymer leads to several improvements in the properties as :-

- i) Drop in melting temperature
 - ii) Reduction in average crystallinity
 - iii) Increase flexibility & toughness
- This copolymer of hydroxybutyrate & hydroxyvalerate is produced by A. eutrophus

when grown in the presence of glucose either propionic acid or valeric acid.

Biopol is the trade name of PHB-HV or PHBV copolymer.

Applications of PHBV —

- i) PHBV are used for controlled drug delivery. This polymer slowly degrades to smaller fragments thus release drug in controlled manner.
- ii) PHBV are currently used for internal suture. It is non toxic, biodegradable, so it does not have to removed after recovery.
- iii) PHBV can be used as structural material for disposable personal hygiene.
- iv) PHBV can be used for packaging & as a coating on paper.

* Classification of Biodegradable polymers:-

Biodegradable polymers can be divided into 3 types (classes):

- 1) Natural Biopolymers → Originating from plant or animal resources. eg → cellulose, starch, protein etc.
- 2) Biosynthetic Biopolymers → Produced by fermentation process by micro-organisms. eg Polyhydroxy butyrate, Polyhydroxyvalerate.
- 3) Synthetic Biopolymers → These are produced synthetically eg → Polylactic acid, Polycaprolactone.

Q3) Conducting Polymers :-

Conductivity in polymers is observed because of different reasons, which includes high planarity & conjugation present in polymers. Accordingly they can be categorized in to different types as follows:

I) Intrinsically Conducting polymers (ICP) or Conjugated π electron conducting polymers:

Some polymers can conduct electricity of their own because of their structural features. Such polymers are known as Intrinsically conducting polymer.

Structural requirement —

Conducting polymers are linear, have high planarity in structure & possess conjugation in polymer chain.

When electric field is applied, conjugated π electrons of the polymer get excited & can be transported through the polymer through resonance. Increase in conjugation increases the conductivity to a larger extent.

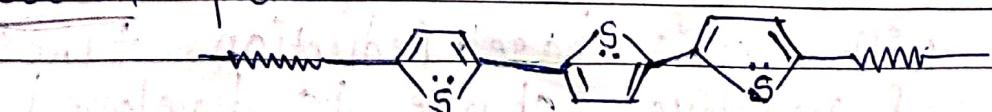
e.g.:-



Polyaniline

Conductivity can also be observed in aromatic heteroatomic system, due to delocalised electron pair.

e.g.



Polythiophene

Conjugated π electrons' conducting polymers

are used in polymer light emitting diodes (PLED), photodiodes & in solar cells.

II) Doped conducting polymer:-

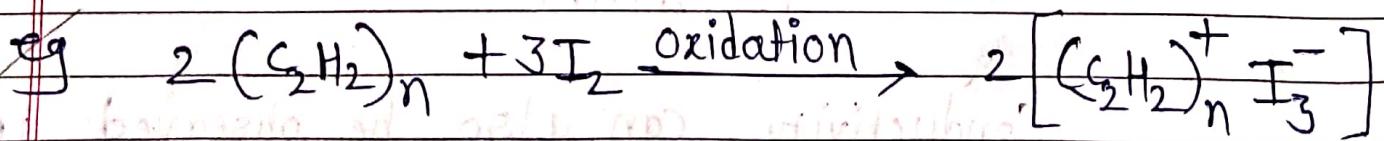
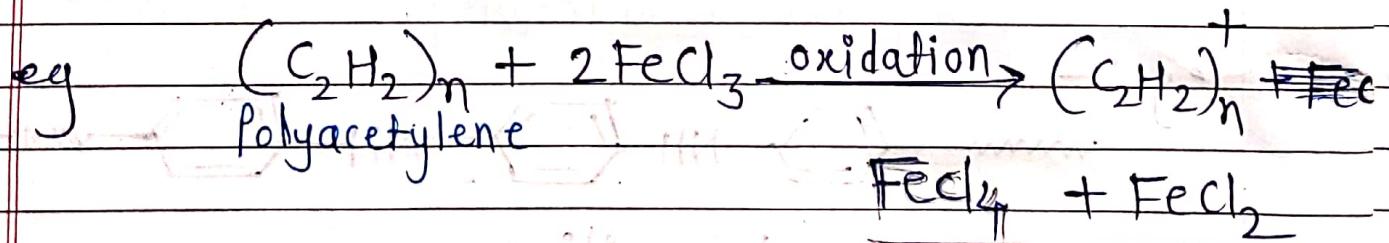
Intrinsically conducting polymers (TCP) possess low conductivity, but their conductivity can be improved by creating +ve or -ve charges on the polymer chain by oxidation or reduction. This technique is called as doping.

There are two types of doping techniques used as follows—

i) P-doping:-

It includes doping of TCP with a Lewis acid. Oxidation takes place & +ve charge is developed on polymer chain increasing conductivity.

Lewis acids like I_2 , Br_2 , $FeCl_3$, PF_6 , AsF_5 can be used as p-dopants.

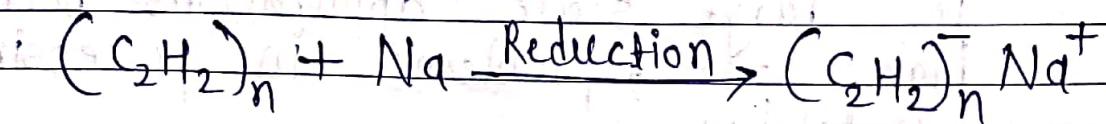


ii) N-doping:-

It includes treating of TCP with Lewis base. Reduction takes places & negative charge is developed on polymer chain, increasing conductivity.

Lewis base like lithium, sodium

metals etc can be used as N-dopants.



Polyacetylene

III) Extrinsically Conducting polymers :-

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

It can be done in two ways :

i) Conductive element filled polymer :-

Metallic fibres, metal oxides or carbon black can be mixed in the polymer during moulding process. Polymer acts as a binder to hold the conducting elements.

Conducting plastics containing carbon black finds uses in wires & cables, video discs etc.

ii) Blended conducting polymers :-

It is obtained by blending conducting polymer with conventional polymer, physically or chemically.

Applications :-

- i) In rechargeable light weight batteries,
- ii) In electronic devices such as transistors, photodiodes & light emitting diodes (LED)
- iii) In optical display devices
- iv) In telecommunication system
- v) In solar cells
- vi) In drug delivery system for human body.

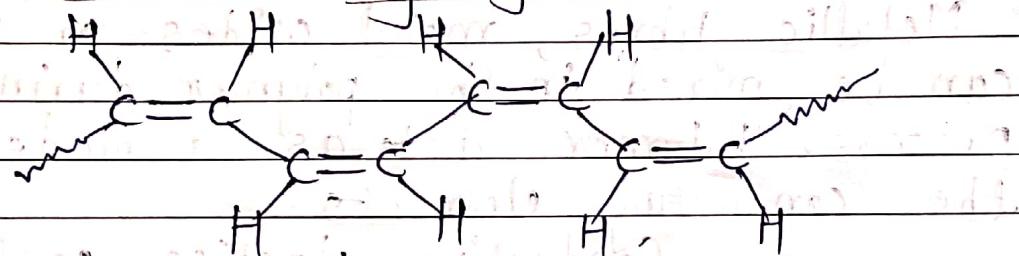
limitation —

Conducting polymer have only few large scale applications because of high cost, problems in processing & instability.

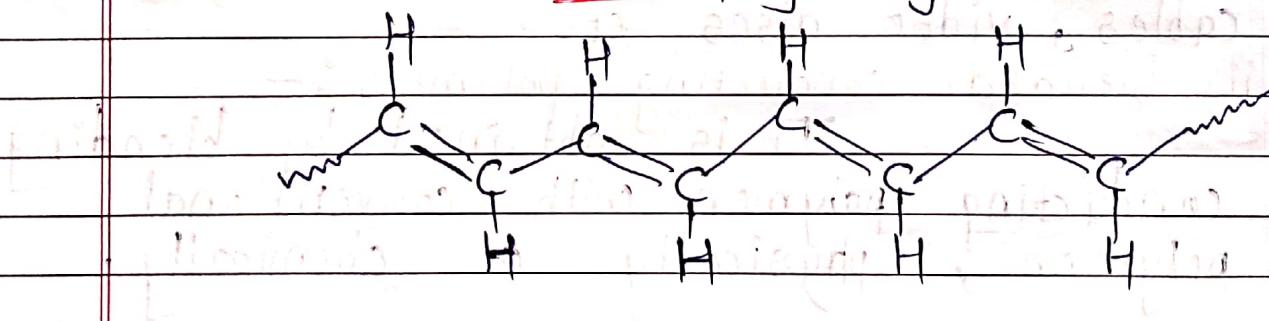
eg Polyacetylene :

STRUCTURE :

The polymer consist of a long chain of carbon atoms with alternating single & double bonds between them. Each carbon possesses one hydrogen atom.

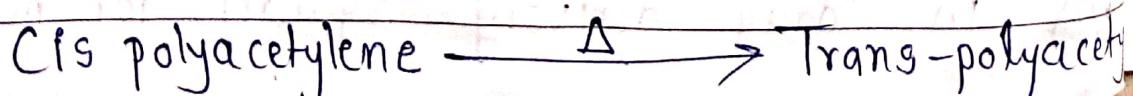


cis - polyacetylene



Trans - polyacetylene

Polyacetylene so formed has predominantly cis conformation. When formed at -78°C or raising the temperature to about 200°C isomerization to more stable trans form take place.



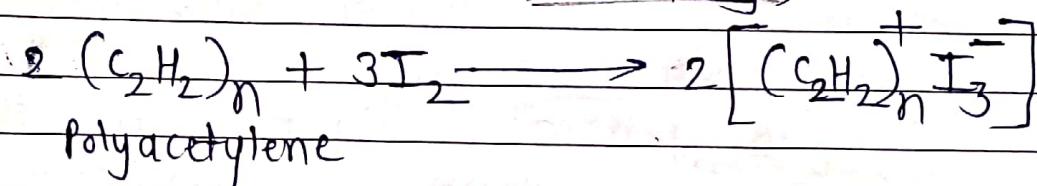
* Conductivity in polyacetylene —

Trans polyacetylene has higher conductivity than cis-polyacetylene. Doping of AsF_5 , I_2 increases conductivity.

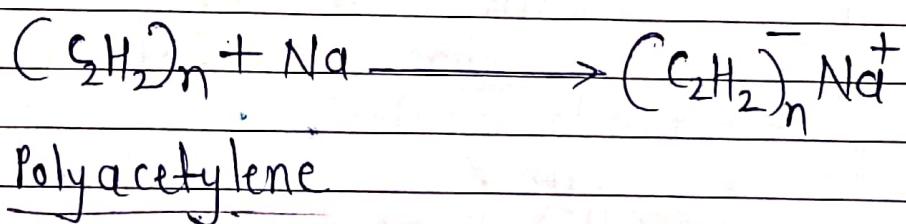
Polyacetylene in its original form is semiconductor. Doped polyacetylene has comparable conductivity to that of good conductor such as copper & silver.

There are two types of doping :

- Oxidation with I_2 (P-doping) —



- Reduction with alkali metal like Na (N-doping) —



Applications of polyacetylene : —

- Doped polyacetylene has high electrical conductivity therefore used as electric wiring or electrode material in light weight rechargeable batteries.
- Tri-iodide oxidized polyacetylene can be used as sensor to measure glucose concentration.

4) Electroluminescent polymers :-

Electroluminescent polymers are the polymers which emits light with response to the passage of an electric current or a strong electric field.

* Polymer Light Emitting Diode (PLED) :-

Construction :-

- i) Semiconducting polymers with π electron system such as PPV exhibit electroluminescence.
- ii) To generate light with these materials, a thin film of semiconducting polymer is sandwiched between two electrodes.
- iii) Indium Tin oxide is commonly used anode material & is transparent electrode material, deposited on glass/plastic substrate.
- iv) Metals like calcium, magnesium, aluminium are used for cathode.

Working :-

- i) Electrons & holes are injected from cathode & anode resp. in to polymer.
- ii) The charge carriers move through the polymer over certain distance.
- iii) The band gap (energy difference bet' valence band & conduction band) determine the wavelength & the colour of emitted light.

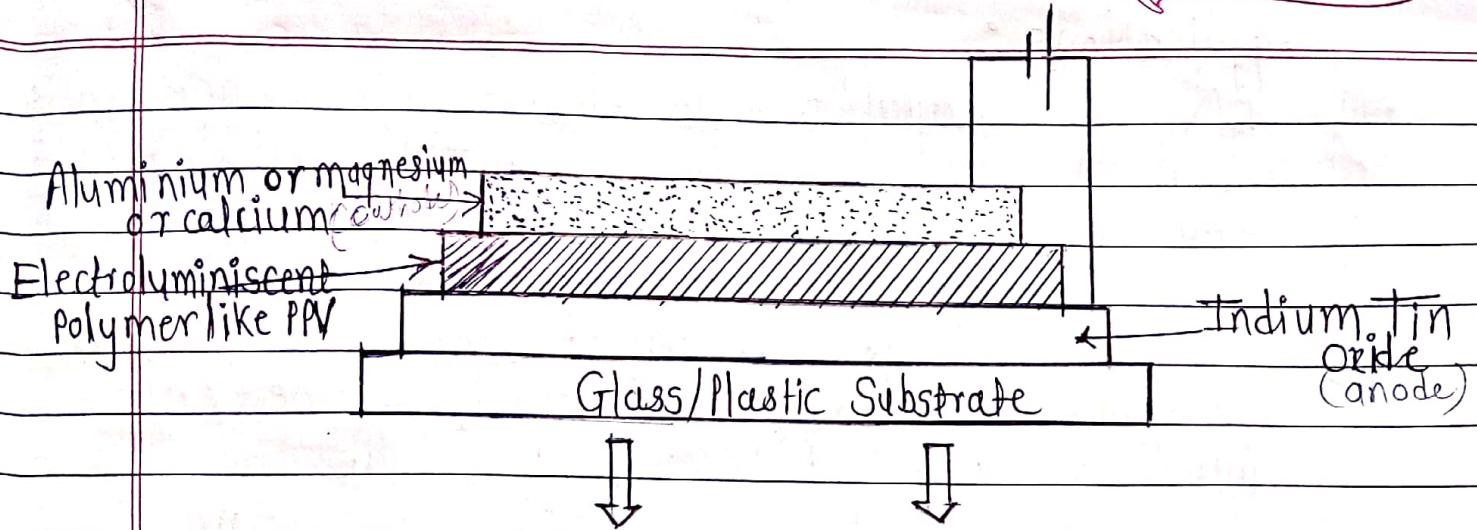


fig : Device structure of single layer polymer electroluminescent diode (Polymer LED)

Applications of Electroluminescent polymers :-

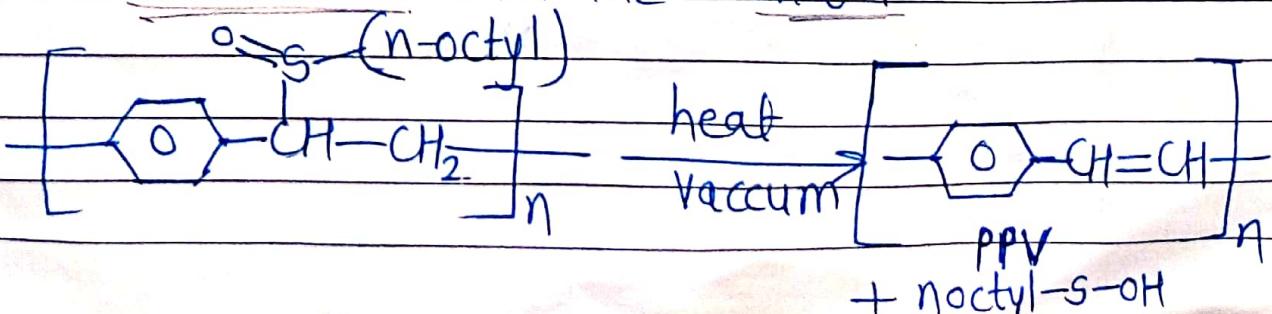
- i) Electroluminescent polymers have applications in light emitting diode (LED) devices.
- ii) Flat panel displays for computer monitors, television screens, mobile phone displays etc.

eg Polyphenylene Vinylene (PPV)

Polyphenylene vinylene (PPV) is a ~~electroluminescent~~ ^{electroluminescent} ~~plastic~~ ^{plastic} ~~conductive~~ ^{conductive} polymer.

Preparation -

- i) PPV is conveniently prepared from precursor polymer i.e. poly(α -n-octyl sulphinyloxyphenylene ethylene) by heating in vacuum.
- ii) Elimination of n-octylthiol introduces the double bonds in the chain.



Applications :

- i) PPV is capable of electroluminescence, so is used in organic light emitting diodes (OLED).
- ii) PPV is also used in organic solar cells, photovoltaic devices, sensors etc.
- iii) Used in the form of thin films for displays & ^{also} used in electroluminescent night lamps.
- iv) Used in light strips for decorating building & vehicle safety precaution.

Properties :

- i) PPV is dimagnetic material.
- ii) It gives bright yellow-green fluorescence on application of electric field.
- iii) It is water insoluble.
- iv) Its electrical conductivity increases by doping with iodine, ferric chloride, alkali metals etc.

★ 5) Polymer composites:-

Composites are formed by the combination of two or more different materials & the properties of resultant material superior to that of individual materials.

The components of composite do not merge or dissolve completely into each other but act together retaining their individual identities.

Defn:- Polymer composite is the material which is made up of polymer matrix & reinforcing material being put together with a defined interface.

Constituents of composites :-

There are two essential constituents of polymer composites are,

- A) Polymer matrix phase
- B) Reinforcement/Dispersed phase

A) Polymer matrix phase :-

It gives a continuous body constituents & is bulk form of composite. Commercial thermoplastic & thermosetting materials are used as polymer matrix.
eg - Epoxy resins, polyamides etc.

Polymer matrix materials can be of 2 types:

I) Thermoplastics —

Thermoplastics ~~are~~ can be made soft on heating & hard on cooling.

eg - Polyolefins, Vinylic polymers etc.

II) Thermosetting —

They get final shape which can not be changed on further heating

they decompose but do not become soft
eg Epoxy resins phenolic resins etc.

Functions of matrix phase are:-

- i) It binds the dispersed phase/reinforcement together.
- ii) It helps in distributing externally applied load to the reinforcement.
- iii) It prevents the development of cracks due to its plasticity & softness.
- iv) It protects the reinforcement/dispersed phase from chemical action & keep them properly oriented under the action of load.

B) Reinforcement/ Dispersed phase :-

Various reinforcements like fibres, particulates, flakes - etc are used in composites. ↗ (thin solid eg mica flakes)

i) fibres :-

long thin filaments of (glass, carbon, aramides) are added to matrix, to give high tensile strength, stiffness & low density.

II) Particulates:

Small (metallic or nonmetallic particles) can be added to polymer matrix to increase surface hardness & strength.

* Classification of Composites :-

Based on reinforcement, composites can be classified as :

i) Particle reinforced composites

2) Fibre reinforced composites

3) Structural composites

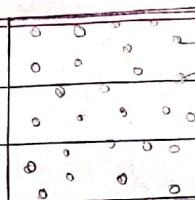
- a) Laminar composites
- b) Sandwich panels

1) Particle reinforced composites :-

- i) These are composed of particles distributed or embedded in the matrix body.
- ii) Metallic or nonmetallic particles can be added polymer matrix to improve mechanical strength.
- iii) eg - Carbon black reinforced rubber show improvement in tensile strength, toughness & are used in manufacturing automobile tyre.

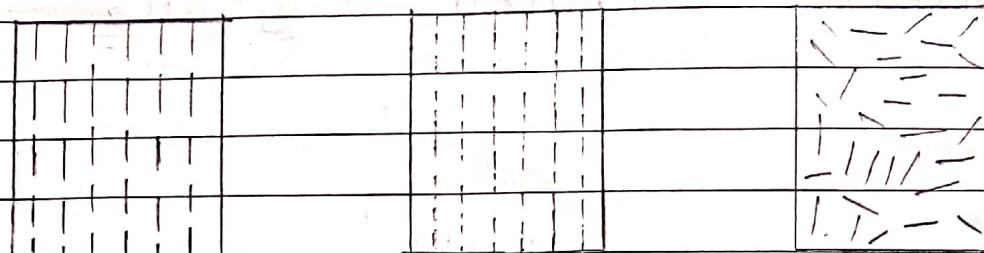
2) Fibre reinforced composites :-

- i) These are composed of fibres embedded in the matrix material
- ii) These can be further divided in to 3 categories - continuous aligned, discontinuous aligned, discontinuous randomly oriented fibre composites.
- iii) In case of discontinuous fibre composite its properties vary with fibre length. Whereas in case of continuous fibre composite the length of the fibre does not alter the properties.
- iv) eg - Glass fibres reinforced composite, Carbon fibres reinforced composite, Aramid fibre reinforced composite.



Partides

fig - Particle reinforced composite



(a) Continuous aligned composite

(b) Discontinuous aligned composite

(c) Discontinuous randomly oriented composite

3) Structural Composites :-

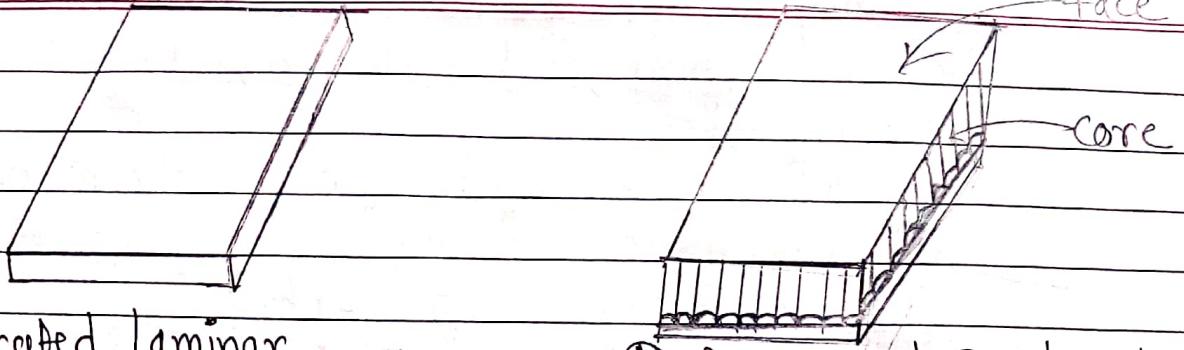
Properties of structural composites depends not only on the constituent materials but also on geometrical design of composite.

a) Laminar Composites —

A laminar composite is made of lamellar sheets that have high strength along the direction of alignment of fibres eg - Wood.

b) Sandwich panels Composites :-

Sandwich panels consists of two strong outer faces separated by a layer of less dense core. (Face material is generally fibre reinforced material) whereas core material can be synthetic rubber. These type of materials are normally used in air craft wings, roofs, floors, walls etc.



a) Fabricated Laminar composite

Properties of polymer composites :-

- i) High tensile strength
- ii) High stiffness
- iii) High thermal stability
- iv) cheap & easily available
- v) Low thermal expansion.
- vi) High oxidation resistance.

Applications of composites :-

- i) In automobile body parts, engines, pumps, valves etc
- ii) In fabrication of roofs & floors, furniture
- iii) In marine applications for making shafts, propellers etc.
- iv) In components of rockets, aircrafts, helicopters etc.
- v) In manufacturing sports goods (rackets), toys, musical instruments.
- vi) In electronic applications - communication antenna, electronic circuit board etc.

* Fibre reinforced plastic (FRP) : (composites)

Fibre reinforced plastic is a composite material made of a polymer matrix reinforced with fibres.

Properties of FRP :

Commonly used reinforcement fibres are — glass, carbon, aluminium, asbestos, wood fibres etc.

Commonly used polymer matrix are —

Thermoplastic such as nylon, polyethylene etc

Thermosetting such as epoxy & phenolic resins.

General properties of FRP —

- i) High tensile strength
- ii) High stiffness
- iii) Lower density
- iv) High thermal stability
- v) Low cost production

Some important types of fibre reinforced composites are :-

A) Glass^{Fibre} reinforced polymer composite —

In this (glass fibre) reinforced in polymer matrix containing nylon, polyesters etc Glass fibres are obtained by forcing melt glass through small holes & rapidly pulling it & after cooling get fibres.

Advantages:

- i) High tensile strength
- ii) Low densities
- iii) Excellent resistance to corrosion & chemicals.

Limitations:

- i) Polymer matrix flows at high temp, they shows applications in limited temp range.
- ii) Sometimes the materials do not possess desired stiffness, & rigidity

Applications: —

- i) They are used in automobile parts storage tanks, industrial flooring, plastic pipes etc
- ii) They are extensively used in automobiles to reduce vehicle weight & boost fuel efficiency.

B) Carbon fibre reinforced polymer composites—
They use carbon fibre reinforced in polymer matrix like epoxy resins.
Carbon fibre are obtained by pyrolysis of cellulose/acrylonitrile in an inert atmosphere.
Advantages :—

- i) Excellent resistance to corrosion.
- ii) Low density
- iii) High temperature resistance.

Applications :—

- 1) They are used as structural components of air crafts & helicopters.
- 2) They are used in making sports goods, laptops, fishing rods, musical instruments, etc

Unit 3

Nanomaterials

Introduction —

Nanomaterials are characterized by a very small size in the range of 1–100 nm. Nanomaterials can be metals, ceramics, polymeric materials or composite materials. Nanomaterials have created high interest in recent years by their unusual mechanical, electrical, optical & magnetic properties.

Important applications of nanomaterials—

- i) Nano Zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is oftenly used in sunscreen lotions.
- ii) Clay nanoparticles when incorporated into polymer matrices increases re-inforcement & leading to stronger plastics.
- iii) Nanoparticles are hard & impart their properties to the polymer (plastic). Nanoparticles have also been attached to textile fibres in order to create good clothing.

- iv) Nanotechnology is highly (multi-disciplinary field). It includes field such as applied physics, material science colloid science & electronics etc.
- v) Nanotechnology is (also used in food technology), medical products & medicines.
- vi) Magnetic nanocomposites have been used for high density information storage.
- vii) Nanostructured semiconductors are known to show unique optical properties & are used as window layers in solar cell.
- viii) Nanophase ceramics are of particular interest because they are more ductile at elevated temp. e.g. nanophase silicon, which differs from normal silicon in physical & electronic properties could be applied to macroscopic semiconductor process to create new devices.
- ix) Nano sized metallic powders are used for production of gas tight materials & for porous coating.

* Defination : -

Nanomaterials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers.

- Nanomaterials are of interest because at nano scale unique optical, magnetic, electrical & other properties emerge. These properties arises at nanoscale have great impacts in electronics, medicine, energy storage & other fields.
- Some nanomaterial occurs naturally but of particular interest are engineered nanomaterials which are designed for commercial products & processes.

* Reasons for different properties in nanomaterials than their bulk materials -

These properties are mainly due to nanometer size of the materials which are responsible for following properties.

- It has large fraction of surface atoms.
- They have high surface energy.
- They have special confinement.
- They have reduced imperfections.

The properties of nanomaterials are different & special from their bulk materials is due to following reasons.

- a) ~~Much~~ Increased relative surface area—
As a particle decreases in size, a greater proportion of atoms are found at surface compared to atoms inside. e.g. a particle size of 30 nm has 5% of its atoms on its surface, at 10 nm 20% & at 3 nm 50%. Thus nanoparticles have much greater surface area per unit mass compared with other materials.

e.g.— (Metallic nanoparticles) can be used as very active catalysts. Chemical sensors from nanoparticles enhance the sensitivity.

- b) Quantum effect—

<The nanometer sizes of nanoparticles materials also have spatial confinement effect on the materials, which bring the quantum effects>

annealing — heat treatment

As the size of nanomaterials \downarrow the band gap \uparrow So change in excitation of energy of electrons from valence band to conduction band such effect is known as quantum effect.

The energy band structure & charge carrier density in the materials can be modified quite differently from their bulk material & modify the electronic & optical properties of materials eg \rightarrow lasers & light emitting diodes (LED), High density information storage using quantum dot devices.

c) Reduced imperfections:

Nanostructures & nanomaterials favours a self-purification process in that the impurities & intrinsic material defects move near the surface on thermal annealing which in turn increases the perfection in materials & thus affects the properties of nanomaterials.

eg - The chemical stability for certain nanomaterials may be enhanced, as a result the mechanical properties of nanomaterials becomes better than the bulk materials.

* Classification of Nanomaterials based on dimension:-

The most typical way of classifying nanomaterials is according to their dimensions. This classification based on dimensions which are not confined to the nanoscale range ($< 100\text{ nm}$)

1) Zero dimensional (0-D) :

These are the materials having all the dimensions are measured within nanoscale.

eg - Nanoparticles, quantum dots,
Zero dimensional quantum dots
are extensively used for LED's,
solar cells, lasers etc

2) One-dimensional (1-D) :

These are the materials having two out of three dimensions are measured within the nanoscale.

eg - Nanowires, Nanotubes,
nanorods etc

3) Two dimensional (2-D)

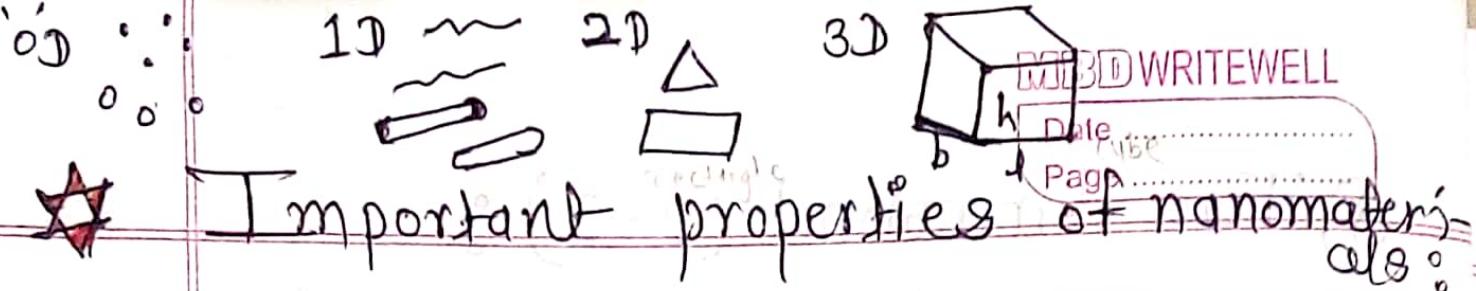
These are the materials having only one out of three dimensions is measured within nanoscale.
eg nanocoatings, nanofilms.

4) Three dimensional (3-D)

These are the materials having all the three dimensions not measured within the nanoscale. These nano materials are also known as bulk nano materials.

eg - Nanocrystals, nanocomposite materials.

<u>Nanomaterial type</u>	<u>Nanoscale dimension</u>	<u>Dimension not in nano-scale</u>	<u>examples</u>
0-D	All (x, y, z)	Nil	<u>nano particles</u>
1-D	<u>Two dimensions</u> (x, y)	<u>length</u> .	<u>Nanowire</u> <u>nanorods</u> <u>etc.</u> <u>nanotubes</u>
2-D	<u>one dimension</u> (z)	<u>$x & y$</u>	<u>Nanocoating</u> <u>& nanofilms</u>
3-D	<u>Nil</u>	<u>$x, y & z$</u>	<u>Nanocrystals</u> <u>& nanocomposites</u>



Important properties of nanomaterials:

a) Optical properties -

- One of the most useful property of nanomaterials is their optical properties. Nanomaterials use in optical detector, laser, sensor, imaging, display, solar cell & biomedicine.
- The (optical) properties of nanomaterials depends on parameters such as size, shape, surface characteristics & other variables including doping & interaction with surrounding environment or other nanostructures.
eg → Simple change in size of cd-se semiconductor to nanosize particles changes the optical properties of ~~cds~~ cdse nanoparticles.

b) Electrical properties —

- Electrical properties of nanomaterials are different than their bulk materials
- In nanomaterials especially nanotubes/nanowires with decreasing diameter of the wire, the number of electron wave mode contributing to the electrical conductivity becomes increasingly smaller
eg — In electrical conducting carbon nanotubes only one electron wave mode is observed which transports the electric current.

c) Mechanical properties —

- Mechanical properties of nanomaterials are influenced by porosity & the fillers used.
eg Filling of polymers (with nanoparticles or nanorods or nanotubes resp.) leads to significant improvements in their mechanical properties. Such improvements depends mainly depends on the type of the filler & the way in which filling is conducted.
eg — Composites consisting of polymer matrix & nanoparticles fillers (silicate) exhibit excellent mechanical properties.

- d) Magnetic properties :-
- Bulk gold & Pt are non-magnetic but at their nano size they are magnetic.
 - Bulk atoms can also be modified by interaction with other chemical species by capping them with nano particles
 - e.g. Magnetic nanoparticles of Pd, Pt & Au are obtained from non-magnetic bulk materials. This changes associated with size effect.



Carbon based Nanomaterials —

Carbon based nanomaterials composed entirely of sp^2 bonded graph carbon are found in all reduced dimensionalities including zero dimensional fullerenes, one dimensional carbon nanotubes, two dimensional graphene. The properties of carbon nanomaterials are strongly dependent on their atomic structures & interactions with other materials.

~~defⁿ~~-Graphene is a single layer of carbon atoms organized in a hexagonal lattice.

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Graphene

Structure of graphene -

- i) It is a single layer of carbon packed in hexagonal lattice with a carbon-carbon bond distance of 0.142 nm . It is the first truly two-dimensional (crystalline) material.
- ii) In graphene every carbon in hexagonal lattice undergoes sp^2 hybridization.
- iii) A pencil contain graphite when it is moved on paper, the graphite is cleaved in to thin layers on ^{the} paper. A small fraction of these thin layers will contain only few layers or even a single layer of graphite is known as graphene.
- iv) Geim, Novoselov & their collaborators succeeded in isolating graphene.

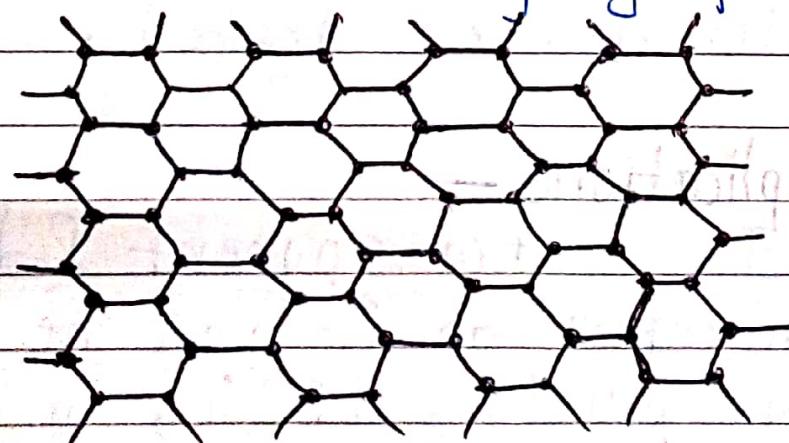


fig - Graphene

Properties —

- i) It is about 200 times stronger than the strongest steel & light weight because it is only one atom thick.
- ii) It is efficiently conduct heat & electricity & is nearly transparent.
- iii) It is the only form of carbon in which every atom is available for chemical reaction from two sides (due to 2D structure)
- iv) The impressive mechanical properties of graphene is stiffness, strength & toughness are one of the reasons that make graphene as good reinforcing agent in composites.
- v) Defect-free, monolayer of graphene is considered to be the strongest material ever tested.

Applications —

- 1) It is transparent & flexible conductor so it can be used in solar panels, LED's, smart phones (touchpanels)
- 2) It's powder can be used in making polymer composites.

- 3) Used in capacitors, batteries, 3D printer materials.
- 4) As sensor for gas detection.
- 5) Energy storage materials.
- 6) As filtration materials.

* Carbon Nanotubes —

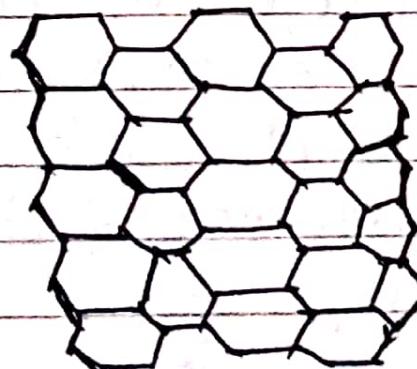
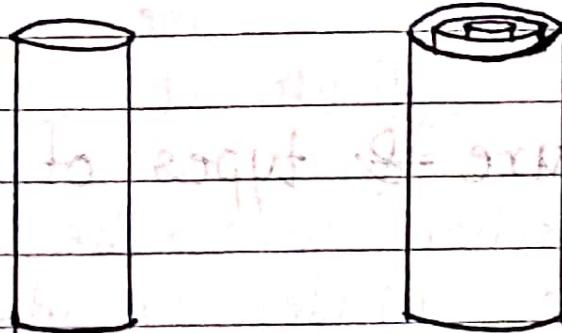
These are allotrops of carbon with a cylindrical nanostructure.

Structure & types of carbon nanotube-

- i) The carbon nanotubes can be considered as the cylinders made up of graphite sheets.
- The structure of carbon nanotube is formed by a layer of carbon atoms that are bonded together in hexagonal manner. This one atom thick layer of carbon is called graphene & it is wrapped in the shape of cylinder & bonded together to form a carbon nanotube.

- Nanotubes can have a single outer wall of carbon or they can be made up of multiple walls.

- Depending on the number of concentrically (rolled-up graphene) sheets, CNT are also classified to single walled (SWNT), double-walled (DWNT) & multi-walled CNT (MWNT)?
- Single walled carbon nanotube (SWNT) can be formed in three different designs: Armchair, Chiral, & Zigzag.



Armchair

Properties:-

- i) They have moderate chemical stability, high electrical conductivity & extraordinary thermal conductivity.
- ii) Carbon nanotubes are the strongest & stiffest materials in terms of tensile strength.
- iii) CNT shows fluorescence properties.
- iv) CNT can be made conducting by making its compounds with alkali metals.

Applications:-

1) Structural applications —

- i) Textile - CNT's can produce waterproof fabrics
- ii) Concrete CNT in ~~concrete~~ increases its tensile strength. CNT may be able to replace steel in making bridges
- iii) Used in making golf balls, stronger & lighter tennis rackets, etc.

2) Electronics applications —

- i) A strong magnetic field can be generated using multi-walled CNT coated with magnetite
- ii) Electromagnetic antenna - CNT can act as an antenna for radio & other electromagnetic

devices due to its durability, light weight & conductive properties.

iii) CNT can be used as alternative to tungsten filaments.

③ Medical application:-

- i) CNT can be used as drug delivery mediator.
- ii) CNT can be used for glucose detection biosensors.

4) Chemical applications:-

A) Air pollution filter —

CNT are one of the best material for air filters because they possess high adsorption capacity & large surface area. The conductance of CNT changes when polluted gas comes in its contact. This helps in detecting & filtering the polluted air. CNT membranes can successfully filter carbon dioxide CO_2 from power plant emission.

b) Water filter —

Water

CNT membranes can be used in filtration. It can reduce distillation costs by 75%. These tubes are so thin that small particles can pass through them, while blocking larger particles. CNT have high active site & controlled distribution of pore size on their surface.

c) Sensors —

CNT based sensors can detect temp. air pressure, chemical gases (CO_2 , NH_3 etc).

Quantum Dots (QDs) :-

2-10 nm size, zero dimensional

Defn — Quantum dots are semiconductor nanoparticles that glow a particular colour after being illuminated by light.

Types of Quantum dots —

There are three main types of quantum dots

Gr III-V Semiconductor quantum dots —
They are made up of elements

from gr III of the periodic table of elements (boron, aluminium, gallium, indium) & from gr IV (nitrogen, phosphorous, arsenic, antimony, bismuth).
eg - GaAs it is used as a light source in optical data processing.

2) Gr II-VI Semiconductor quantum dot -
They are made up of elements from gr II i.e transition metals (Zn, Cd) & from gr VI (Oxygen, sulphur, selenium, tellurium).
eg CdSe, CdTe. They shows outstanding fluorescence properties & widely used in electronics & biomedicine.

3) Silicon (Si) quantum dots -
They are made up of elements like silicon, which is standard material of semiconductor. It is used as component of optical chip, optical sensors etc.



Properties of quantum dots -
Silicon (semiconductor nanoparticles)

The specific colour glow of quantum dots depends on size of the nanoparticle & the energy difference between valence band & conduction band.

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- 1) Many semiconductor substances can be used as quantum dots. Nano-particles of any semiconductor substance have the properties of quantum dot.
- 2) Commonly used semiconductor materials for preparing quantum dots are silicon, cadmium sulphide, cadmium selenide & indium arsenide. These materials behave differently as quantum dots.
- 3) The gap betⁿ the valence band & the conduction band which is present for all semiconductor materials, causes quantum dots to fluorescence.
- 4) The main property of quantum dots is they show (colour glow) when illuminated by U.V light. This is because when they illuminated by U.V light, some of the electrons receive enough energy & conduct electricity. When these electrons drop back in to the outer orbit, they emit light. The colour of the light depends on the energy difference betⁿ the conduction band & valence band.

* The specific colour glow of quantum dots depends on —

a) Size of nanoparticle :

When the bulk material is reduced to the size of nanoscale, the energy band is broken into discrete levels. Hence by varying the size & composition of quantum dot different colour emission can be obtained.

e.g. — Larger QDs's of 5–6 nm diameter emit longer wavelengths with colours such as orange or red (whereas smaller QDs (2–3 nm) emits shorter wavelengths with colours like blue, green). Specific colour depends up on size & composition of QD.

b) The (energy difference) betⁿ the conduction band & the valence band —

The (smaller) nanoparticles have (higher) energy difference betⁿ the valence band & conduction band which results in deeper blue colour & for (larger) nanoparticles the energy difference betⁿ valence band & conduction band is (lower) which

results in red colour.

* Applications of quantum dots —

Quantum dots have various applications in several areas such as solar cells, transistors, LEDs, medical imaging etc.

1) Optical applications —

Quantum dots can emit any colour of light from the same material by changing the dot size.

a) light emitting diodes —

Quantum dot light emitting diodes (QD-LED) & QD-white LED are very useful when producing the displays for electronic devices.

QD-LED displays can give colours very accurately & use much less power than traditional displays.

b) Photodetectors —

Quantum dot photodetectors (QDP's) are produced from traditional single crystalline semiconductors & are widely used in integrated circuits, spectroscopy & for industrial inspection.

related to the production of electric current at the junction of two substances exposed to light

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3) Photovoltaics

Quantum dot solar cells can be produced using simple chemical reactions & can help to save manufacturing costs.

2) Biological applications —

The small size of quantum dots allow them to go anywhere in the body making them suitable for biological applications such as medical imaging & biosensors.

- Quantum dots can target specific cells or proteins to study the behaviour of the cells.
- Quantum dots can be used for producing images of cancer tumour.

3) Other applications —

- Quantum dots are being used to produce (miniature) lasers for communication devices.
- Quantum dots can be used in TV or computer displays. Displays using quantum dots should be thinner, lower power consumption than current ^{traditional} displays.