

UNIT - 2: CHEMISTRY OF MULTI FUNCTIONAL MATERIALS

Engineering plastics: Definition, synthesis, properties and applications of PC, PTFE, and PMMA.

Conducting polymers: Definition, types and applications

Biodegradable polymers: Definition, classification, mechanism of degradation and applications.

Nano Materials: Introduction, size dependent properties (Colour, magnetic and electrical), method of synthesis – CVD, applications of Nano materialss.

Engineering Plastics (or) performance plastics

Engineering plastics are a group of plastic materials that have better mechanical and/or thermal properties than the more widely used commodity plastics (polystyrene, PVC, polypropylene and polyethylene).

These new polymer materials (*Engineering plastics*) represent an important driving force for technological progress. Engineering plastics have gradually replaced traditional engineering materials such as wood or metal in many applications. It is because of their high strength, high efficiency, high thermal resistant, high chemical resistant, low weight and low cost. Moreover, these new materials can be used much easier to manufacture, especially complicated shapes. This shows, that each Engineering plastics usually has a unique combination of properties that make the material of choice for some application. So, Engineering plastics are finding wide applications in demanding areas like automobiles, defence, electrical, electronics, telecommunications, textiles, satellites, robots, mountaineering, and computer components etc. As a result, the Engineering plastics global market is valued very high now a day.

General properties:

- a) High mechanical strength
- b) High load-bearing characteristics
- c) High Plasticity
- d) Readily moldable characteristics into complicated shapes
- e) High dielectric constants
- f) High abrasion resistance
- g) Do not absorb water
- h) Dimensional stability
- i) Thermal and chemical stability
- j) Light weight
- k) High performance properties
- l) Corrosion resistant
- m) Insect resistant
- n) Low maintenance cost: no protective paints required
- o) Can show optical properties due to their reflection and transmission behavior

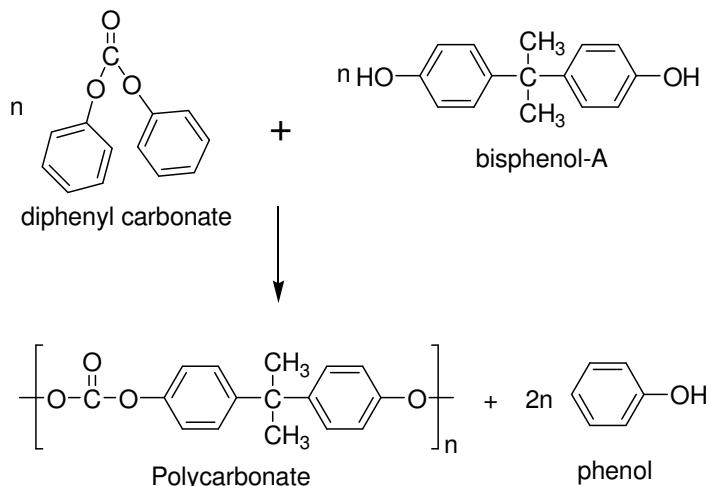
Engineering plastics offer many advantages over metal as a production material:

- Reduction in weight

- Good wear properties
 - Superior to corrosion
 - More chemical resistance
 - Ease to use in manufacture processing
 - Electrical and thermal insulation
 - Cost saving
- ❖ PC, PTFE, and PMMA are the some of the engineering plastics with special characteristics and their applications are given below.

Polycarbonates (PC): trade name 'Lexan' or Merlon

- PC are a group of thermoplastic polymers (on heating become moldable and harden on cooling) containing carbonate groups in their chemical structures.
- It is prepared by interaction of diphenyl carbonate with bisphenol-A [(2,2-bis(4-hydroxyphenyl) propane)].



Special characteristics of PC:

- Characterized by high tensile strength over a wide range of temperature
- Soluble in organic solvents and alkalis
- Polycarbonate is highly transparent to visible light, with better light transmission than many kinds of glass. **So it can use as a substitute for glass.**
- Polycarbonate can undergo large deformations without cracking or breaking.
- Polycarbonate is a durable material, shows high dimensional stability, stiffness etc.
- Show low scratch resistance and susceptibility under goes ultra violet degradation (yellowing)

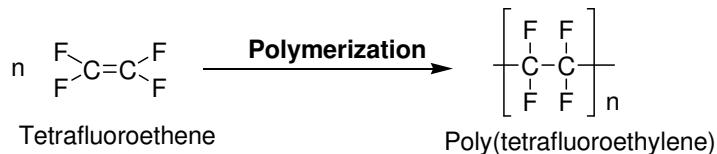
Applications of PC:

- For preparing moulded domestic ware, crash helmets.
- Being a good electrical insulator, heat-resistant and flame-retardant properties, it is used in various products associated with electrical and telecommunications hardware.
- A majorly in the production of CDs, DVDs, and Blu-ray Discs.

- d) Due to its low weight and high impact resistance, polycarbonate is the dominant material for making automotive, aircraft, and security components bullet-resistant windows in automobiles.
- e) For the making of Photographic films, binocular bodies, hair-drier bodies, sterilized transparent containers etc.

Poly(tetrafluoroethylene) (PTFE) or Teflon or Fluon

PTFE is obtained by polymerization of water-emulsion of tetrafluoroethene, under pressure in presence of benzoyl peroxide as catalyst.



Special characteristics of PTFE:

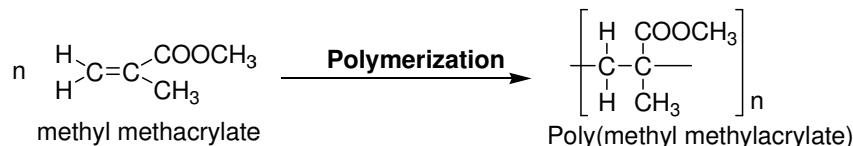
- i) Due to the presence of high electronegative fluorine atoms and the regular configuration of the polytetrafluoroethylene molecule results in very strong attractive forces between the different chains. This strong attractive force makes Teflon to possess extreme toughness, very high softening point (about 350 °C).
- ii) Extremely good mechanical properties,
- iii) Shows excellent chemical resistant
- iv) Very low coefficient of friction, waxy touch
- v) Very good electrical insulator
- vi) Due to their insoluble nature in solvents and cannot exist in a true molten state. However, around 350 °C, it gets viscous, opaque mass, which can be moulded into certain forms by applying high pressure.

Applications of PTFE:

- a) Due to toughness, high mechanical strength and high softening point they are in use as coating materials in making of kitchen utilizes
- b) Due to their chemical resistant, they used in making of chemical carrying pipes, tubing, containers etc
- c) Due to low coefficient of friction, high mechanical strength they widely used for making of non-lubricating bearings, non-sticking stop-cocks etc
- d) Very good electrical insulator, so they are widely used as electrical insulating material in motors, cables, transformers, electrical fittings

Poly(methyl methacrylate) (PMMA) or Lucite or plexiglass or acrylic or acrylic glass

PMMA is a linear thermoplastic polymer. It is obtained by polymerization of methyl methacrylate, in presence of acetyl peroxide or hydrogen peroxide.



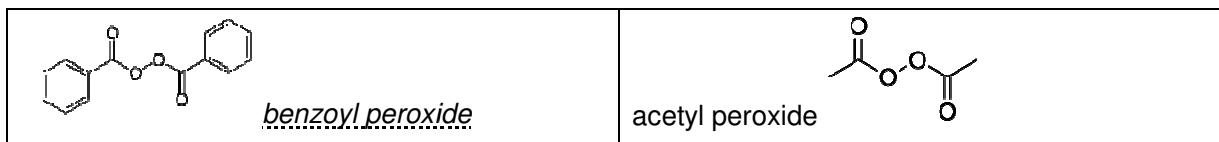
Special characteristics of PMMA:

- i) Physical and mechanical properties: PMMA has a lack of methyl groups on the backbone of carbon chain this makes that one chain can slide over each other easily, so the material becomes softer. Due to this, PMMA has high Young's modulus and low elongation at break and shows high scratch resistant. This gives high mechanical strength to PMMA. Further, PMMA exhibits low moisture and water absorbing capacity, due to this it shows good dimensional stability.
- ii) Electrical characteristics: Very good electrical insulator.
- iii) Thermal property: PMMA is a combustible material. Its resistance to small temperature changes is very good. However, it becomes rubber like at above 65°C, and shows high softening point of about 130-140 °C. This wide span of temperature accounts for its outstanding shape-forming property. Further, it can withstand temperatures as low as -70°C
- iv) Chemical resistance: It has low chemical resistance to hot acids and alkalis. It dissolves completely in organic solvents.
- v) PMMA exhibits very good optical properties: it transmits more light (up to 93% of visible light) than glass. Unlike glass, PMMA does not filter ultraviolet light. It transmits UV light and infrared light.

Applications of PMMA:

PMMA is an economical, versatile general-purpose material. It is available in sheet, rod and tube forms, as well as custom profiles. Acrylics used in wide variety of fields.

- **Optics:** Dust covers for hi-fi equipment, sunglasses, watch glasses, magnifying glasses. By considering its good degree of combined compatibility with human tissue, it can be used for making of contact lenses.
- **Vehicles:** for making of rear lights, indicators, tachometer covers, and warning triangles
- **Electrical engineering:** Lamp covers, switch parts, control buttons;
- **Office equipment:** Writing and drawing instruments, pens;
- **Medicine:** Packaging for tablets, capsules, urine containers, sterilizable equipment
- **Others:** Leaflets, shatter-resistant glass films, screen guard, shower cubicles, transparent pipelines, illuminated signs, toys.



Conducting Polymers (electro-active polymers)

Polymer –are macromolecules consisting of large number of (at least five)repeated chemical units (known as monomer[m]) joined together. Polymers usually contain morethan five monomers, and some may contain hundreds orthousandss of monomers in each chain.

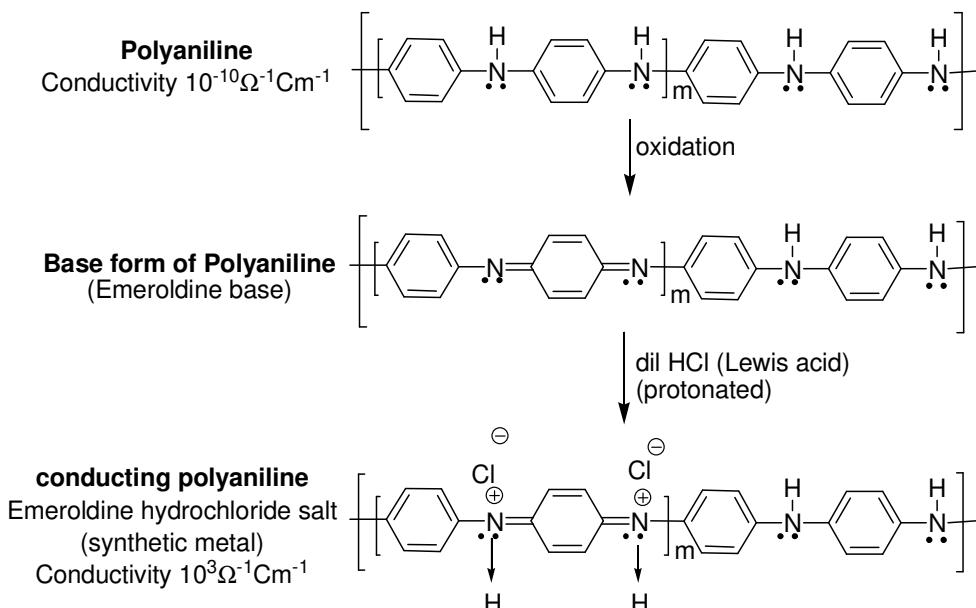
A small unit which combines with each other to form a polymer molecule is termed as **monomers**. The number of repeating units (n) in a polymer is known as “**degree of polymerization**”. The molecular weight of the polymer depends on its degree of polymerization, and most of the polymers show their molecular weight in the range of 5000 to 2 lakhs.

Polymers may be **natural** (ex. Cellulose, DNA) **synthetic** (Ex. nylon or polyethylene).

Conducting polymers (CP)

Def: *Conducting polymers are synthetic organic polymers that ‘conduct electricity’.* Such compounds may have conductivity same as Cu, Ag or can act as semiconductors.

Conducting polymers phenomenonwas first described in the mid-19th century by Henry Lethby, in polyaniline.



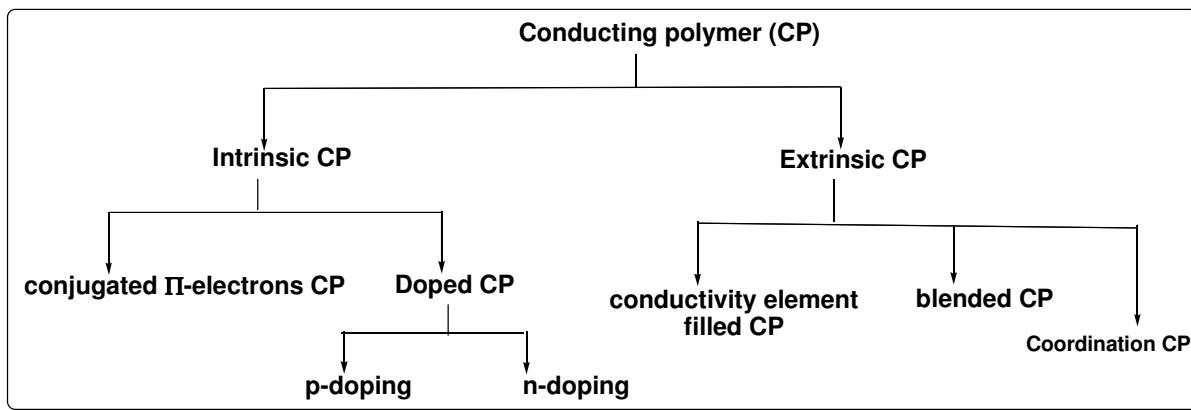
Polyaniline consisting of conjugated π -electron system is treated with a Lewis acid, there by oxidation takes place and creates positively charged sites on polymer backbone, which are charge carriers for conduction.

Polyaniline is more noble than copper and slightly less noble than silver which is the basis for its broad use in printed circuit board manufacturing (as a final finish).

Types of conducting polymers

Conducting polymers are many types and they are divided into two main category.

- a) Intrinsic conducting polymer
- b) extrinsic conducting polymer



a) Intrinsic conducting polymer

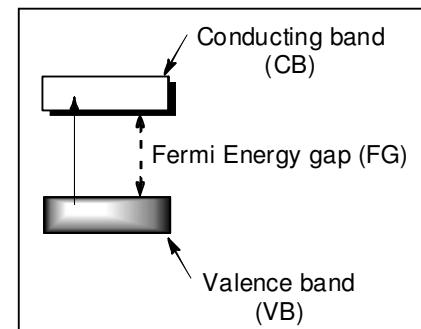
The conduction of electricity in this type of polymers is due to conjugation in the back bone of polymer. These polymers are characterized by intensive conjugation of double bonds in their structure. These intrinsic conducting polymers are further divided into two types.

1) *Conjugated π-electrons conducting polymer*

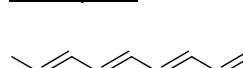
2) Doped conducting polymer

1) Conjugated π-electrons conducting polymer

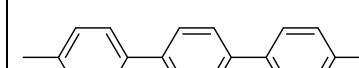
- Polymers having conjugated double bonds in the main chain show conductivity due to π -electrons (delocalized electron-pairs) or residual charges.
- Overlapping of orbital over the entire polymer chain results in the formation of valence bands and conducting bands which extend over the entire polymer molecule.
- The electrical conductivity takes place only after thermal or photolytic activation of the electrons. As a result of this activation, the activated electrons jump the Fermi energy gap and reach into conduction band.
- In an electric field, conjugated π -electrons of the polymer get excited, and can be transported through the polymer material.
- With increase of conjugated π -electrons in a polymer, its conductivity also increases
- These polymers exhibit low conductivity values which is around $10^{-10} \Omega^{-1} \text{cm}^{-1}$



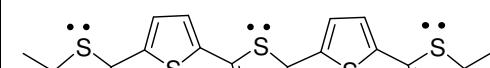
Examples:



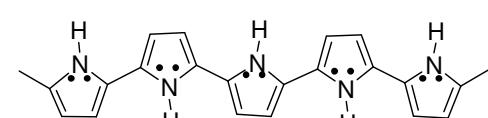
polyacetylene



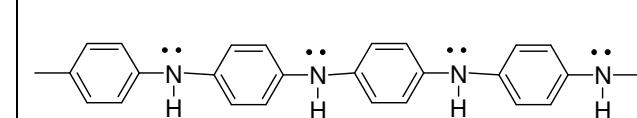
poly(p-phenylene)



polythiophene



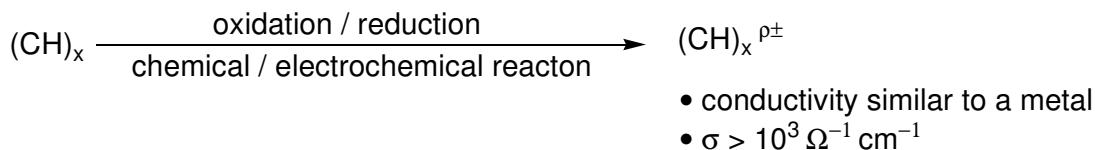
polypyrrole



Polyaniline

2) Doped conducting polymer

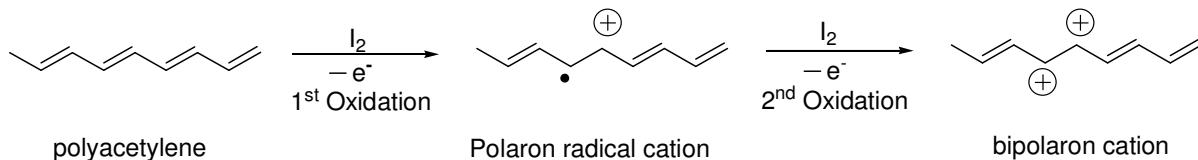
- i) *Conjugated π-electrons conducting polymers* possess low conductivity, their conductivity can be increased by creating either +ve or -ve charge (dopant) on the polymer chain by oxidation (removing of electrons) or reduction (adding of electrons).
 - ii) Conductivity increases very rapidly as dopant is added. Addition of dopant is called doping
 - iii) This doping is possible because, the *conjugated π-electrons conducting polymers* possess low IP and high EN, and so these can be easily oxidized or reduced.
 - iv) Doped conducting polymers can be obtained by exposing a polymer to a 'charge transfer agent' (oxidation/reduction) in either gas phase or in solution.



- v) There are two types of doping: A) *p*-doping B) *n*-doping

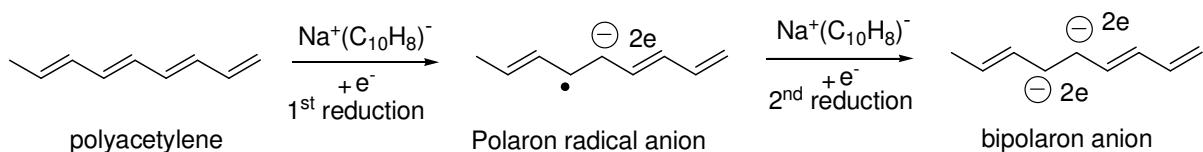
A) *p*-doping (or) oxidative doping

- When the *conjugated π -electrons* *conducting polymer* is treated with a lewis acid, thereby oxidation takes place and +ve charges are created on the polymer chain.
 - These +ve charges on polymer chain enhance the electrical conductivity.
 - Common p-dopants are I_2 , Br_2 , AsF_5 , PF_6



B) *n*-doping (or) Reductive doping

- When the *Conjugated π -electrons conducting polymer* is treated with a lewis base, thereby reduction takes place and –ve charges are created on the polymer chain.
 - These –ve charges on polymer chain enhance the electrical conductivity.
 - Common n-dopants are Li, Na, Ca, Naphthylamine, tetabutyl ammonium, and sodium naphthalide ($\text{Na}^+(\text{C}_{10}\text{H}_8)^-$) etc.



b) **Extrinsically conducting polymer**

The conductivity of these polymers is due to the presence of externally added ingredients in them. Again these extrinsically conducting polymers are divided into two types.

- i) Conducting element field polymers ii) blended CP iii) Coordination CP

i) Conducting element field polymers:

- The polymer acting as binder to hold the conducting elements such as carbon black, metallic fibers, metal oxides etc.
- With addition of the minimum concentration of conducting elements, conventional polymers show conductivity. This minimum concentration is known as '*percolation threshold*'.
- The main advantage of these *Conducting element field polymers* are i) low cost ii) low weight iii) mechanically stable iv) fabricated very easy to any design.
- The main disadvantage of *conducting element field polymer* is that addition of 10% carbon black will drastically decrease the tensile strength of the polymer material.

ii) Blended conducting polymers:

- The conventional polymer is blended with a conducting polymer either by physically or chemically charge.
- Such polymers can be easily processed.
- The obtained possess improve physical, chemical, electrical, and mechanical properties.

Ex: 40% of polypyrrole in a conventional polymer shows high conductivity.

iii) Coordination conducting polymer (inorganic polymer)

- They are charge transfer complex containing conducting polymer obtained by combining a polymer with a polydentate ligand.
- Their use is limited because of their low degree of polymerization (≤ 18), and further show corrosion characteristics.

Factors influencing the conductivity of conducting polymers:-

Conductivity increases

- i) with increase the conjugation
- ii) with increase of doping levels, but after some time it becomes constant
- iii) with increase of temperature, but after some time it becomes constant

Advantages of conducting polymers

- i) these polymers possess good conductivity
- ii) they can store a charge
- iii) easy to fabricate to any design
- iv) good environmental and thermal stability

Applications of conducting polymers:

Since the discovery of the conducting polymers in the late 1970s, many scientists have been working on finding applications for the newly discovered conducting polymers. Conducting polymers have attracted attention due to their inexpensive and potentially processable nature.

Polymer chemists did not find a practical application, but drew the attention of scientists and engineers to the rapid growth of the field. Since the late 1980s, organic light-emitting diodes (OLED) have emerged as an important application for conducting polymers.

- a) Polymer light-emitting diodes (LED): consists of a conducting polymer layer. This LED operate at a low bias voltage
- b) Conducting polymers can be used in high sensitive organic solar cells, and for printing electronic circuits
- c) In rechargeable and light weight batteries: Lithium ion batteries doped with polyacetylene are light in weight and fit a variety of designed configuration. Further their power density is 12 times higher that of ordinary lead acid batteries _____.
- d) Conductive Polymers in Photography: little electric sparks generated huge losses during the production of photofilm. Traditionally, inorganic salts used as an antistatic coating failed to work when the humidity dropped below 50%. Today photographic film has been coated with the conducting polymer, polythiophene.
- e) Color change devices: This is due to change in chemical structure of polymer in presence of radation/heat electronic devices can exhibit various colors. poly-phenylene-vinylene polymer is used as the emissive material, which gives color varied from green to orange-red.
- f) Conducting Polymers in Sensors: The chemical properties of conducting polymers make them very useful for use in chemical/ gas sensors _____
- g) Conducting Polymers inside the Human Body (biosensors): Due to the biocompatibility of some conducting polymers, they may be used to transport small electric signals through the body, i.e., act as "artificial nerves" so these conducting polymers are named as "Artificial Muscles".
- h) New Plastic Circuits: Conducting polymers (polyaniline) can replace silicon resulting IC's are lower in cost when compared with their silicon counterparts. These are used in radio frequency (RF) identification.
- i) Antistatic Fabrics: The fiber is coated with conductive polymer material help military equipment and personnel from near infrared and radar detection.
- j) For Medical Applications: ECG electrodes manufactured from highly conductive materials.
- k) Corrosion Control: As a coating additive to control corrosion.
- l) Molecular wires: In making 'molecular wires' (or molecular nanowires) which conduct electrical current. They are the fundamental building blocks for molecular electronic devices
- m) In making electronic displays and optical fibers _____
- n) In making smart screens and non-linear optical materials
- o) In telecommunication systems
- p) Conducting polymers can absorb harmful electromagnetic radiation. So these can be used to coat on the cases of computer monitors and cell phones as electromagnetic screening systems.

- q) In electronic devices such as transistors and diodes
 - r) In making aircrafts and aerospace machines. In these cases polypyrrole is approved one.
 - s) As new modified electrode materials for the manufacture of super capacitors which are widely used in hybrid electric vehicles.
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Biodegradable polymers

Today polymer/plastic industry is causing environmental problems. Each year millions tons of plastics are produced from petroleum. Most of these plastics will remain in landfills for years under standard environmental conditions. Further, they are causing significant health risks to animals; however, the average person's lifestyle would be impractical without them. One solution to this conundrum lies in biodegradable polymers. These new type polymers have the distinct advantage that over time they will break down.

Biodegradable polymer(BDPs):“A biodegradable polymer / Plastic is one in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae.”

“Biodegradable polymers are a specific type of polymer that breaks down after its intended purpose to result in natural byproducts such as gases (CO₂, N₂, CH₄), water, biomass, and inorganic salts”.

Biodegradable polymers have a long history and many are natural products. The precise timeline of their discovery and use cannot be accurately traced. One of the first medicinal uses of a biodegradable polymer was the catgut suture, which dates back to at least 100 AD. The first catgut sutures were made from the intestines of sheep, but modern catgut sutures are made from purified collagen extracted from the small intestines of cattle, sheep, or goats.

Common properties of BDPs:

- 1) All biodegradable polymers should be stable and durable enough for use in their particular application, but upon disposal they should easily **break down**.
- 2) Shows extremely strong carbon back bones that are difficult to break, such that degradation often starts from the end-groups.
- 3) Crystallinity is often low
- 4) A high surface area is common as it allows easy access for either the chemical, light, or micro organism
- 5) A low degree of polymerization is normally seen.
- 6) brittle in nature
- 7) Low thermal stability

- 8) These polymers show hydrophilicity nature. _____.
- 9) Low water vapor permeability
- 10) Should have non-toxic nature and products of degradation also need not to be toxic

Classification of BDPs:

The biodegradable polymers can be classified according to their origin, chemical composition, and synthesis method, etc.



1) Natural biodegradable polymers: (NBDP)

- NBDP are directly extracted from biomass.
- NBDP are polymers formed in nature during the growth cycles of organisms,
- NBDP typically formed within cells by complex metabolic processes.
- Most common NBDP are:
 - i) Polysaccharides -- starch and cellulose.....
 - ii) Proteins --- silk (made with amino acids) and poly (2-glutamic acid).....
 - iii) Hydrocarbons -- natural rubbers

2) Synthetic biodegradable polymers:(SBDP)

- The concept of (SBDP) was first introduced in the 1980s. _____.
- Synthetic polymers that undergo degradation in presence of enzymes are called as (SBDP)
- These SBDP can be prepared in two ways.
 - i) Can be obtained from renewable resources such as agricultural and food processing wastes.
 - ii) Non-degradable conventional synthetic polymers are converted into biodegradable polymers by means of adding suitable additives or by proper treatment.
- The properties of SBDP are determined by their exact structure. However, there are some common properties for SBDP.
 - i) A higher hydrophilic/hydrophobic ratio is better for degradation.
 - ii) Straight chain or low branching is preferable, _____.
 - iii) Lower molecular weight polymers are more likely to biodegradation.
 - iv) Non-crystallinity _____ (non-crystalline form may show large surface area) • due to large surface area in case of non-crystalline amorphous state
- Synthetic biodegradable Polymers are divided into two types based on the back bone
 - a) Polymers with carbon backbones
 - b) Polymers with heteroatom chain backbone

a) Polymers with carbon backbones:

Ex: polyethylenes, vinyl polymers, polyvinyl alcohol, polylactic acid

Polymers with carbon backbones will naturally fragment and biodegrade, but it can take many decades to do this. But this problem can be resolved and can convert conventional polymers as SBDP.

Polyethylenes: their degradation property enhanced, by adding plasticizers **or** low molecular weight impurities

Vinyl Polymers: To improve biodegradability of vinyl polymers, photosensitive groups like ketones are introduced into the vinyl polymers.

b) Polymers with heteroatom chain backbone:

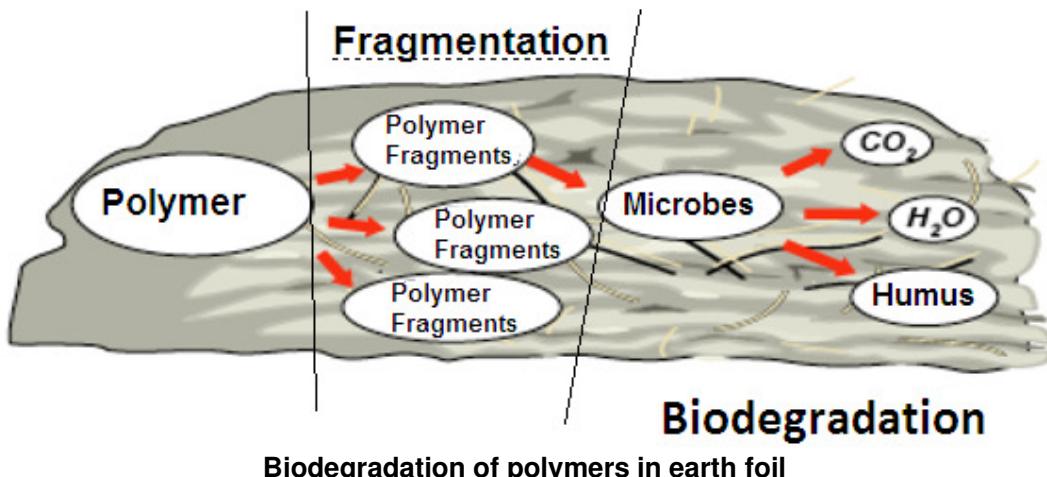
Ex: polyamides, polyethers, polyacetates etc.

- i) These types are more likely to biodegrade than polymers with carbon backbones.
- ii) It is due to the development of new polar centers with the introduction of heteroatom in the carbon chains of carbon backbone polymers.
- iii) These, polar centers, accelerates the biodegradation by the environmental conditions like temperature, pH, moisture, oxygen, nutrients, microbial population etc.

Mechanism of degradation of biodegradable:

Polymer Degradation:

- Polymer degradation means bringing a change in the properties like molecular weight, density, tensile strength, colour, shape, etc of a polymer or polymer based product.
- Normally these biodegradable polymers (BDPs) comprised of monomers linked to one another through functional groups and have unstable links in the backbone. These BDPs broke down into biologically acceptable molecules in presence of naturally occurring microorganisms
- In general, BDPs break down to form gases (CO_2 , N_2 , CH_4), water, biomass, and inorganic salts under aerobic or anaerobic conditions and the action of living organisms and this process is called mineralization.
- Factors affecting the biodegradation process.
 - i. The composition of polymer means bond type, structure, solubility, chain length, functional groups and copolymers among others.
 - ii. The disposal environment included pH, temperature, light, microorganisms present, nature of the soil, marine environments and water
- Biodegradation is typically two-step process in earth foil, as shown in figure given below.



- 1) **Degradation/fragmentation:** This process is initiated by heat, moisture or other environmental factors like oxygen, sunlight etc. These factors shorten and weaken polymer chains, resulting in fragmentation.
- 2) **Biodegradation:** The short carbon chains formed in above step are consumed by microorganisms as a food and energy source and converted into biomass, H_2O , CO_2 , CH_4 etc. This step can be further broken down into *aerobic* and *anaerobic processes*

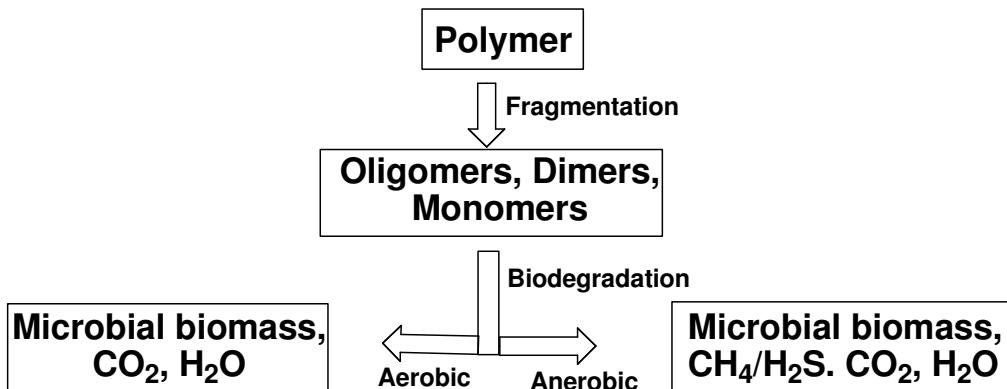
a. **Aerobic biodegradation:** The following general reaction takes place in presence of O_2



b. **Anaerobic processes:** The following general reaction takes place in absence of O_2



In the above two reactions, C_{residue} represents smaller fragments of the initial polymer such as oligomers and C_{biomass} represents total quantity of organisms.



Polymer degradation under aerobic and anaerobic conditions

Dimmers: contains two monomers

Oligomers: contains few monomers (5-7)

Applications and uses of Biodegradable polymers:

Biodegradable polymers are having waste applications both as nondurable and as durable agents.

Nondurable applications:

They are widely used in packaging, agriculture, and medicine because of their nondurable nature.

For Packaging

- i) This biodegradable material used for making of shopping bags or trash bags is very common. Ex. starch based biodegradable bags are available commercially but they are expensive compare to conventional polymers.
- ii) Trays and containers for fruit, vegetables, eggs and meat, bottles for soft drinks and dairy products and blister foils for fruit and vegetables are also widely manufactured from biodegradable polymers now a days.
- iii) One of the most commonly used polymers for packaging purposes is *poly(lactic acid)* (PLA)

In Agricultural applications

- In agricultural, in gardening sector (flower pots) much foils made of biodegradable plastics are widely used due to their low lifespan. These products can simply decompose, after which they are ploughed in to the soil. Further, these BDPs may act as supplement to the current nutrient cycle in the soils, upon degradation.

As Medical Products

- i) Biodegradable polymers are widely used for surgical sutures (surgical thread) Ex: Dexon (synthetic suture material) is made of *poly(glycolic acid)* (also known as *poly(glycolide)*)
- ii) They are used as sanitary products such as disposable gloves and diaper foils.
- iii) Orthopedic applications:
 - *For bone - fixation:* biodegradable implants can adjust to the dynamic processes of bone healing through decreasing amounts of weight - bearing material. Over a few months the introduced material disappears and there is no need to operate on a patient to remove it.
 - *poly(lactic acid)* is used to make screws and darts to repair broken bones
 - *poly(glycolic acid)*, *poly(lactic acid)*, *polyhydroxybutyrate* can be used as biocompatible cement in the fixation of prostheses (an artificial body part) and in the replacement of joints.
 - *poly(2-hydroxyethyl-methacrylate)*, *poly(ethylene glycol)* are used extensively in the repair of ligaments, and tendons.
- iv) In tissue engineering:
 - Artificial skin substitutes and wound dressings made of biodegradable polymeric materials have been developed to treat burns by Tissue engineers.
 - Tissue engineers can grow tissues (artificial skin) and cells *in vitro* by using a biodegradable scaffold to construct new structures and organs *in vitro*. Because, a biodegradable scaffold is obviously preferred as it reduces the risk of immunological reaction and rejection of the foreign object.

- polyglycolic acid and polylactic acid are used for making engineer vascular tissue, arteries and vessels for heart repair.
- v) For drug delivery:
- Biodegradable polymers are widely in use for drug delivery, because they act as target agents, as a result decreases the toxicity of the drug on healthy cells.
 - The great benefit of a biodegradable drug delivery system is the ability of the drug carrier to target the release of its payload to a specific site in the body and then degrade into nontoxic materials.
 - Normally, polylactic acid, poly(lactic-co-glycolic) acid, and poly(caprolactone) are used to carry anti-cancer drugs.

Durable applications: These type of biodegradable polymers show long durability under working conditions, but they undergo biodegradation upon their entry into earth foils.

1. Biodegradable polymers have found applications in interior automobile parts. (ex: interior car parts made using biodegradable polymers).
2. They have also found potential application in electronic devices such as mobile cases. These electronics produce less e-waste than non-degradable polymers.

Introduction

Nano-chemistry is new branch of chemistry related with the synthesis and characterization of materials including organic, in-organic and metallic compounds of nano-scale size.

Scientifically speaking, the nano-scale goes between 1 and 1000 nanometers, i.e. approximately between 10 and 10,000 atoms.

Nano-science & nano-technology are the study and application of nano materials across all the other science fields, such as chemistry, biology, physics, material science, and engineering.

Nano-science is often referred as "the science of small". The prefix "nano" comes from the Greek and means "Dwarf" (very small). $1 \text{ nm} = 10^{-9} \text{ m}$ ($1 \text{ A}^{\circ} = 0.1 \text{ nm}$ or 10^{-8} cm or 10^{-10} m).

- Although modern nano-science and nanotechnology are seems to be quite new, nano-scale materials were used by our ancients. **Mahabharata** (Sabha Parva 52, 2-4) mentions Pipilika Gold, which is a superior quality Gold obtained from the ant hills or termite mounds. Ants dig the earth and makes hills. In these hills gold is brought as particles and deposited in heaps. Mainly the kings between Meru and Mandarachala hills presented this very special Gold to Yudhishtira. This Pipilika Gold is equivalent to the present day nano-gold which has enormous applications in chemistry as well as industry and in Society.
- It is surprise to notice the nano painting in Ajanta and Ellora caves (Aurangabad district of Maharashtra) developed in the 2nd century of BCE to about 480 or 650 CE.
- Alternate-sized gold and silver particles used to create colors in the stained glass windows of medieval churches of Europe hundreds of years ago.

Todays' scientists and engineers are finding a wide variety of ways to make materials at the nano-scale to take advantage of their enhanced properties such as higher strength, lighter weight, increased control of light spectrum, and greater chemical reactivity than their larger-scale counterparts.

Abnormal physical changes can be seen in nano size compare with bulk size.

Nano Cu – transparent

Nano Al – combustion

Nano Pd – nano size is chemically reactive (in bulk size is non-reactive)

Nano Si – conductor (in bulk size act as insulator or semi conductor)

Different types of nanomaterials and their sizes:

Diameter / thickness	Type of nanomaterial	Example
1– 10 nm	Nano-films	Metals, oxides, nitrides, sulfides etc.
1– 50 nm	Nano-crystals	"
1– 100 nm	Nano-wires	"
1– 100 nm	Nano-tubes	Carbon, inorganic materials
0.5 – 10 nm (pore size)	Nano-porous solids	Phosphates, Zeolites

A nanocrystal is huge for a molecule but tiny for a human cell, and an individual nanowire cannot be seen by eye, but a massive parallel assembly of them could span a square centimeter can be seen. Due to the tiny nature, the nano particles are impossible to see with the naked eye and even with ordinary microscopes. However, they can visualize using the Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), Scanning Tunneling Microscope (STM) and the Atomic Force Microscope (AFM).

TEM is like photography but done in vacuum with an electron beam of wavelength smaller than the size of an atom and SEM can be carried out under near ambient conditions, with moderate electron energies.

STM and AFM can be used to see objects of size from a fraction of nanometer to tens of nanometers to study their properties. These two are modern microscopes.

Applications of nanotechnology: Nano-materials are backbone of any technologies

The potential applications of nanotechnology in different fields are the following:

- **Nano-cosmetics:** Nano particles act as carrier or delivery bags. This property made them to use in cosmetics.
 - As delivery bags:** These nano particles can penetrate through the outer layer of the skin and deliver the nutrient materials below the outer layers. As result the cosmetic formulations are effectively absorbed. This leads to production of new cells, therefore the skin remains soft and wrinkle free and keeps the humans with young look.
 - As carry bags:** Nano particles also act as carry bags and eliminates waste products from the cells.

The nano-cosmetics are nanoemulsions and **nano pigments**.

- a) **Nanoemulsions** are Oil-in-water type emulsions. They contain **oil droplets** reduced to nanometric size to increase the content of nutritious oils. Because of the tiny size, these nanoemulsions penetrates through skin easily (penetrate epithelial mucosol layers such as in the eye, skin, nasal, lung, tumor, blood-vein, and brain).
- b) **Sun-screen lotion:** Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing **nano-ZnO** and **nano-TiO₂** provide enhanced sun protection. The Sun-screen lotions with nano materials reflect and scatter UV light thus protecting human skin from skin-burns and cancer.

- **In Textiles:**
 - Textile scientists have produced wrinkle proof and stain proof textile materials by coating the fabric with a thin layer of hydrophobic **silicone nano-filaments**. Because of these hydrophobic silicone nano-filaments the cloths obtained 100% water proof. In addition to water proof, the silicone filament creates a permanent layer of air by trapping air between the layers of the nano-filaments. This trapped layer of air prevents wrinkles. _____.
 - The clothes made by using **nano-Polytetrafluoroethylene** coated fabrics give protection from rain, snow and wind.
 - The clothing impregnated with **silver nanoparticles** are useful in inhibiting the growth of bacteria and fungi which cause toe nail infections, foot odor and painful cracks in the heel.

- **Nanosensors:**

nanosensors are devices that use biological, chemical or mechanical sensory point to detect and convey the information about the nano regime (microenvironment) under investigation.

- Biological nanosensors:* By using nanoscale sensors it is easy to make various measurements in the microenvironment of an individual cell. Nanomaterials gives change in colour (**nano-Cd**, **nano-Se**, **nano-Ag** or **nano-Au** particles) are used for detection of anthrax, HIV, hepatitis, lung cancer, asthma attacks, different common virus such as the influenza virus, or the parasite responsible for malaria etc.
- Chemical nanosensors:* **Carbon-nano tubes** used as sensors to detect glucose levels and **ZnO nano tubes** used to measure concentration levels of ethanol.
- Gas nanosensors:* Commonly used gas sensors are metal oxides. Eg: **Tungsten oxide** (WO_3). The gas sensors detect nitrogen oxides, ammonia, hydrocarbons (LPG) etc.
- Mechanical nanosensors:* these are based on the principle of measuring the electrical changes. Sensors used in airbags in cars measure the changes in the capacitance. **Carbon nanotube** based sensors work in this way. _____.

- **In Drug delivery:**

The more specific drug targeting and delivery, and reduction in toxicity while maintaining therapeutic effects are most important part in drug delivery system.

The pharmaceutical sciences are using nanoparticles to reduce toxicity and side effects of drugs. Because, of the size, the nanoparticles can easily cross the various biological barriers within the body. Ex: Dendrimers. **Dendrimers** are special nano particles containing many hooks. The hooks enable the molecule to attach itself to cell in the body. As result, these dendrimers are using for the drug delivery.

- **In Cancer Therapy:** In chemotherapy and radiation therapy are not effective in treating the cancer because of their non-specific nature.

- Carbon nanotube** based drug are used in killing cancer cells.
- The injected **Cadmiumsolenoid** quantum dots into a cancer patient body seep by cancer tumors only and these areas are glow when the patient body exposed to UV light. This procedure is used during surgery, to locate tumor accurately and remove it. _____.
- Kanzius radio frequency therapy:** this is an alternative to radiotherapy. In this **gold nanoparticles** are injected into patient body and only the cancer cells absorb the gold

nanoparticles. Nanoparticles attached to cancer cells are subjected to radio waves. As the metal absorbs the energy from radio waves more efficiently, the gold nano particles get heated faster and efficiently and the cancer cells are cooked inside the body and killed while the healthy cells are left unaffected.

- **MRI with magnetic nanoparticles:**

Nanoparticles of **manganese oxide** (MnO_2) or **magnetite** (Fe_3O_4) are used as contrast agents for MRI (magnetic resonance imaging). This manganese oxide nanoparticle allows doctors to see inside living brain tissues, liver tissues, kidney and spinal imaging.

- **In tissue engineering:**

Scaffold is an artificial, 3D temporary structure that allows cells to create their own microenvironment. The new tissue can be developed from the isolated cells by using scaffold. The seeded cell nutrients diffuse in presence of the scaffold. **Carbon nano materials** can be used as scaffold materials to heal broken bones.

- **For water purification:**

Nanosilver particles disperse in water to form silver ions and these silver ions prevent the growth of bacteria and algae in water reservoirs.

Water filters with silver nanoparticles coated on the inner porous surface of ceramic candles are used in purification of water.

- **In lighting:**

LED (light emitting diodes) OLED (organic light emitting diodes) are set to provide cheaper, energy efficient and environment friendly light sources. LED and OLED with a layer of nanocrystals are effective.

eg: LEDs with a layer of nanocrystals '**CdSe**' on '**ZnS**' produces a bright white light by using very low voltage (1.5 V).

- **Nanocomputers:**

A nanocomputer is a computer whose basic parts are only a few nanometer sizes. Nanocomputers use nano-electronics to fabricate transistors and integrated circuits. Y junction **carbon nanotubes** have been used as transistors and nanolithography for integrated circuits in fabricating a nanocomputer.

Disadvantages of Nanomaterials

- (i) **Instability of the particles:** obtaining a nano particle is highly challenging, because at nano size, Nanomaterials are thermodynamically metastable and lie in the region of high-energy local-minima. Hence they undergo transformation.
- (ii) **Explosives:** Fine nano particles act as strong explosives owing to their high surface area coming in direct contact with oxygen. Their exothermic combustion can easily cause explosion.
- (iii) **Impurity:** Because nanoparticles are highly reactive, they inherently interact with impurities as well. So the synthesis of pure nanoparticles becomes highly difficult. Formation of oxides, nitrides, etc can also get aggravated from the impure environment/ surrounding while synthesizing nanoparticles.
- (iv) **Biologically harmful:** Nanomaterials are usually considered harmful as they become transparent to the cell-dermis. Toxicity of nanomaterials also appears predominant owing to their high surface

area and enhanced surface activity. Nanomaterials have shown to cause irritation, and have indicated to be carcinogenic. If inhaled, their low mass entraps them inside lungs, and in no way they can be expelled out of body. Their interaction with liver/blood could also prove to be harmful. However, this aspect still needs much more experimental support.

- (v) **Difficulty in synthesis, isolation and application:** It is extremely hard to retain the size of nanoparticles once they are synthesized in a solution. Hence, the nanomaterials have to be encapsulated in a bigger and stable molecule/material.
- (vi) **Recycling and disposal:** Still sufficient techniques are not available for the fast and safe disposal of nanomaterials and also the possibility of the recycle.

Properties of Nanomaterials:

Shrinking a body not only lead to size reduction, but also bring modifications in physical and chemical behavior.

Particle Size	Property
< 5 nm	act as catalyst
< 20 nm	Magnetic moment changes
< 50 nm	Refractive index changes
< 100 nm	Obtain mechanical strength

The nanomaterials exhibit following peculiar properties:

a) **Chemical reactivity:**

The ability to react with other species should also depend on size. Nanoparticles are highly reactive, because of their small particle size. As particle size is small, greater is the surface area; so reactivity can be enhanced with rise in reacting centers. A nanomaterials of size 10 nm has 20% of its atom on its surface and at 3 nm has 50% of its atoms. This makes nanomaterials more chemically reactive.

Ex: metallic Palladium is chemically inert, but nano palladium is chemically reactive

b) **Catalytic activity:**

Nanomaterials exhibit a prominent catalytic activity in wide variety reactions, both in homogeneous and heterogeneous phase. Due to the large surface, nanoparticles made of transition metal compounds exhibit interesting catalytic properties.

Ex: i) nano Pd-widely used in various carbon-carbon coupling reactions.

ii) Gold nanoparticles are used in selective oxidation reactions.

iii) nano MoS₂ used for methanation of CO_x + H₂ at low temp.

c) **Magnetic behavior:**

- Nanomaterials due to their tinny size exhibits permanent magnetism. The large surface area to volume ratio results in coupling of atoms with neighboring atoms differ in magnetism and leads to formation of nano clusters having magnetic behavior.
- It is assumed that the nano-clusters are single domain and the magnetic moment of each atom in that clusters interacting with the moments of the other atoms and this can force all the moments to align in one direction with respect to some symmetry axis of the cluster and the cluster has a net magnetic moment and is magnetized.

- As cluster size decreases the ferromagnetic behavior disappears and gains super paramagnet behavior due to large surface energy.

Ex: Bulk gold and platinum are non-magnetic but at their nano size, they show magnetic behavior.

d) Mechanical properties:

- They exhibit low density due to large size to volume ratio
- By reducing the grain size, lighter materials with enhanced mechanical properties can be produced.
- Nanomaterials exhibit unusual mechanical properties. They are strongest and stiffest fibers known.
- The extended surface area gives sliding behavior as a result they show high plasticity.
- Nano-grains are more mechanical resistant since they have no defects inside and no impurity precipitates.

Ex: • Nanocrystalline copper is 50 times more mechanical resistant than usual copper.
• The tensile strength of carbon nano tube is about 100 times higher than that of steal.

e) Optical Properties:

- Nanomaterials exhibit better optical properties due to their large surface area.
- Silicon nanowires show *strong photoluminescence* character. _____.
- Zinc oxide nanowire exhibits *ultraviolet laser action* at room temperature. _____.

f) Colour: Nanoparticles exhibits different colours depend on particle size.

Example-1:

- Gold nanoparticles of >20 nm exhibit yellow color
- Gold nanoparticles of 10-20 nm exhibit purple color
- Gold nanoparticles of 2-5 nm exhibit red color. In small monodisperse gold nanoparticles the '*surface plasma resonance phenomena*' is responsible for an absorption of the blue-green portion of the spectrum (~450 nm) while red light (~700 nm) is reflected, producing a red color. _____.

Example-2:

The smallest (~2 nm) CdSe particles emit blue while the largest (~5 nm) emit red.

g) Electrical properties:

In nanomaterial with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity increases. _____.

Nanomaterials shows electrical properties vary between semiconducting to metallic depending upon the diameter and chirality of the molecules. Further, the high conductivity of nanotubes is due to negligible amount of defects and as a result they show low electrical resistance.

Ex: i) carbon nano tubes reveal electrical properties and act as semiconducting and metallic nature on the basis of chirality and diameter of a tube.
ii) Nanotubes of MoS_2 , WS_2 show semiconducting nature at low temperature.

Reason for the anomalous behavior of Nanomaterials:

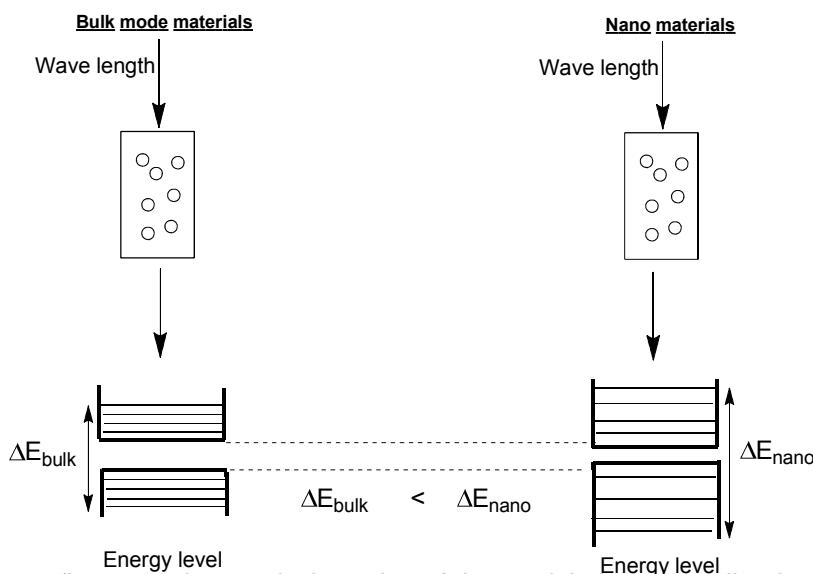
Mainly, the properties of nanomaterials depend on particle size, crystal structure and surface characteristics. However, the following two properties of nanomaterials keep them differ significantly from other materials. **1) Greater surface area to volume ratio**

2) Quantum confinement

1) Greater surface area to volume ratio:

- Generally as the size of the material decreases, surface area increases. Due to increase in surface area more fractions of atoms in nanocrystals will appear at surface compared to those inside.
- i) Chemical reactivity ii) Catalytic activity iii) Mechanical properties iv) Color of a nanomaterials depends on the size of the nanoparticles.

2) Quantum confinement:



- *Quantum confinement* observed when size of the particle is too small to be comparable to the wavelength of the electron.
- As the system size is reduced, it tries to show or obtain *de-Broglie wave nature of the electron*.
- The Quantum confinement means to confine the particular energy levels (discreteness) to the moving particle
- When atoms are isolated their 'energy levels are discrete'. For materials contain large number of close atoms (Bulk molecules), the *energy levels 'split and form a fully discrete energy spectrum'*. Nanomaterials are intermediate to the above cases. When the material size is reduced to nano-scale the energy levels of electron change. *i.e.* the energy levels discrete and this increase or widens up the band gap and ultimately the band gap energy also increases

- This Quantum confinement ... affects the optical, electrical and magnetic properties of nanomaterials. Normally, these properties of materials can be studied based on the energy levels.

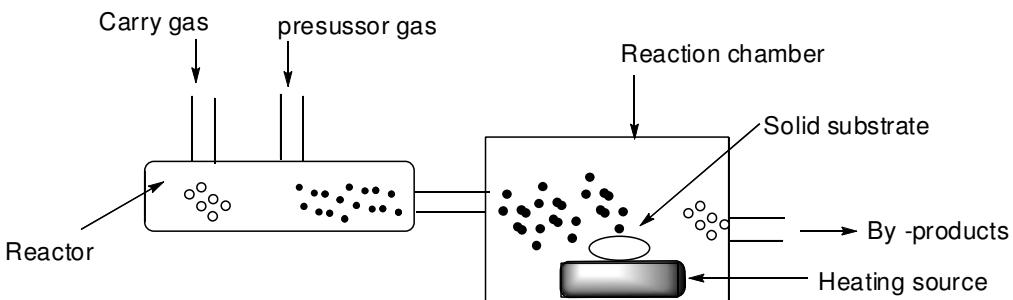
Gas phase synthesis of nanomaterials:

The gas-phase synthesis methods are of increasing interest because of the following advantages

- ✓ An excellent control of size, shape, crystallinity and chemical composition
- ✓ Highly pure materials can be obtained
- ✓ Multicomponent systems are relatively easy to form
- ✓ used to produce high quality, high-performance, nano materials
- The conventional example for gas-phase synthesis is Chemical Vapour Deposition (CVD) synthesis.
- CVD is a process whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface.
- By varying the experimental conditions like “substrate material, substrate temperature, composition of gas mixture, total pressure, gas flows, etc.” materials with different properties can be grown.
- In CVD the solid material is obtained as a coating, a powder, or as single crystals.

Basic principle of CVD:

- In CVD, gaseous reactants (precursor gas) are admitted into a reactor. Then gases reactants are diluted by carry gas in the reaction chamber at approximately ambient temperature. As gases reactants pass over or come into contact with a heated source, they deposited on the source.
- Whereas gases like NH_3 , N_2 or H_2 will be used as carrier gases or process gas.



- CVD processes frequently proceed by complicated chemical reaction schemes.
- $\text{Gaseous reactants} \longrightarrow \text{Solid material} + \text{Gaseous products}$
- Normally in CVD, *Thermal decomposition reactions or pyrolytic reactions* are main. In this case, that a gaseous compound AX is thermally dissociated into A (a solid material) and X (a gaseous reaction product).



Use of thermal decomposition reactions normally results in relatively pure coatings. Examples of some thermal decomposition reactions are given below:



- A carbon-carrying vapor species e.g., methane, acetylene, ethylene, and ethane can be used as precursor gases. For example Methanethen decomposes in principle according to



Advantages of CVD:

- Enabling the production of coatings of uniform thickness
- Properties with a low porosity even on substrates of complicated shape.
- Another characteristic feature is the possibility of *selective* deposition, on patterned substrates.
- Used in the microelectronics industry to make films serving as dielectrics, conductors
- The production of optical fibers, as well as corrosion-, and heat resistant coatings