MODULE 1
ENGINEERING MATERIALS

FUELS

They are combustible materials consisting mainly of Carbon and Hydrogen, which on burning in Oxygen (Combustion) give large quantity of heat energy which can be efficiently and economically utilized for industrial and domestic purposes. Examples are wood, coal, petrol, diesel, LPG, water gas. The main sources of fuels are coal and petroleum occur underground deep in the crust of earth. They are generally called "Fossil fuels "or Chemical fuels.

Classification.
According to occurrence, fuels are classified in to:

(a) Primary or Natural fuels-fuels which are found in nature.

(b) Secondary or Artificial fuels- fuels which are prepared from the natural fuels.

According to Physical State:

(a) Solid Fuels (b) Liquid Fuels (c) Gaseous Fuels.

Physical State	Occurrence	
	Primary Fuels	Secondary Fuels
Solid	Wood, Coal	Coke, Charcoal
Liquid	Petroleum or Crude Oil	Petrol, Diesel, Kerosene
Gaseous	Natural gas	Water gas, Producer gas

Constituents of a fuel

1. Combustible elements Carbon, Hydrogen and Sulphur (CHS)

2. Non-combustible element Nitrogen

3. Supporter of combustion Oxygen.

4. Moisture, Ash and volatile content.

Requirements of a good fuel

1. High Calorific Value,
2. Moderate Ignition Temperature. (The lowest Temp. to which a fuel is to be heated so that it starts burning smoothly)
3. Low moisture content.
4. Moderate combustion velocity.
5. Low ash content.

6. Harmless combustion products.

7. Low cost and availability.

8. No spontaneous combustion.

Calorific Value (CV). Defined as the total quantity of heat energy liberated by the complete combustion of unit mass or volume of the fuel. The unit of heat is calories or Kilocalories. Hence the units of CV are: Cals/Gram, Kcals/Kgm

Higher Calorific Value (HCV) or Gross Calorific Value. The total quantity of heat energy liberated by the complete combustion of unit mass or volume of the fuel and when the products of combustion are cooled back to room temperature.

Lower Calorific Value(LCV) or Net calorific value. The total quantity of heat energy liberated by the complete combustion of unit mass or volume of the fuel and when the products of combustion are allowed to escape.

The difference is in the amount of heat taken by the water produced during combustion to escape as steam. Hence:

LCV = HCV-Latent heat of steam.

= HCV- Mass of water produced x Latent heat of steam

= HCV- Mass of Hydrogen in the fuel x 9 x Latent heat of steam in Cals/gm
= HCV-H/100 x 9 x Latent heat of steam in Cals/gm.

= HCV-0.09 H x Latent heat of steam Cals/gm
ie. LCV = HCV-0.09 H x587 cal/g
(Where H is the Percentage of Hydrogen in the fuel)

Experimental Determination of Calorific Value.

Bomb Calorimeter Method. Used to find the CV of solids and Liquids.

- The apparatus consists of a strong cylindrical steel bomb in which the combustion of fuel is made to takeplace.
- The Bomb is closed by a lid, which can be screwed to the Bomb gas-tight. The lid is provided with an Oxygen valve and two stainless steel electrodes.
- To one of the electrodes,a small ring is attached which can act as support for a crucible.
- The Bomb is placed in a Copper Calorimeter containing aknown amount of water and the Calorimeter is provided with an electrical stirrer and a Beckman's thermometer which can read up to 1/100 of degree.
- Copper Calorimeter surrounded by air and water jackets to prevent the loss or gain of heat from the surroundings.

Working. About one gram of the fuel is accurately weighed and placed inside the crucible. The Mg wire is stretched and placed over the fuel. The bomb is tightly closed and filled with oxygen to a pressure of 25 atm. The Bomb is placed inside the Calorimeter in which a known mass of water is taken. The stirrer is operated and initial Temp. of water is noted. The battery is switched on. The fuel burns, heat is given out and is absorbed by the water in the calorimeter. The temp rises. Uniform stirring is continued till maximum rise in temperature is attained.

Calculation

Mass of fuel =X g

Initial Temp. =T_1 Degree.

Final Temp. =T_2Degree.

Mass of water in the Calorimeter = W g

Water equivalent of Calorimeter = w.gm

HCV of the fuel = L Cals/gm

Heat given out by the fuel = XL Cals

Heat absorbed by the Calorimeter and water = (W+w) (T_2- T_1)

Heat lost = Heat gained.

XL=(W+w) x(TT)

HCV (L) = $\frac{(W+w)\ x(T^2-T^1)}{X}$ Cals/gm

For accurate results, Fuse wire correction, Cooling correction and Acid correction are applied.

HCV=$\frac{(W+w)(T2-T1+cooling\ correction)-(Acid\ correction+fuse\ wire\ correction)}{Mass\ of\ fuel}$

COAL

Coal is non-renewable energy sources formed from the remains of vegetable matter buried in the earth's crust for millions of years.Hence it is known as fissil fuel and is mainly composed of C,H and O.Apart from these elements it also contains minor amount of N,S and moisture.

Analysis of coal

The quality of coal can be assessed byi)Proximate analysis and ii)Ultimate analysis depending on the type of data required.

Proximate analysis

The data varies with the procedure adopted and hence it is called proximate analysis.It gives information about practical utility of coal.Proximate analysis of coal determines the moisture,ash,volatile matter and fixed carbon.

This analysis involves the following determinations.

1.Moisture:-Moisture content is determined by heating a known amount of coal to 105-110^{0}C in an electronic hot air oven for about one hour.After one hour it is taken out from the oven and cooled in a dessicator and weighed.Loss in weight of coal is reported as moisture content on percentage basis.

Percentage of moisture=$\frac{Loss\ in\ weight}{Weight\ of\ coal\ taken}$x100

Significance

- Moisture lowers the heating value of coal(calorific value).Hence lesser the moisture content,better quality of coal as a fuel.
- Excess of moisture is undesirable in coal(up to 10%is desirable).

2.Volatile Matter

It consists mainly of combustible gases such as H_2,CO,CH_4 and other hydrocarbons.It is determined by heating a known weight of moisture free coal sample in acovered platinum crucible at 950$\mp$20^{0}C for 7 minutes.The crucible is cooled,first in air,then inside a dessicator and weighed.Loss in weight is reported as

% volatile matter=$\frac{Loss\ in\ weight\ due\ to\ removal\ of\ volatile\ matter}{Weight\ of\ coal\ taken}$x100

Significance

- A high percent of volatile matter affects the furnace volume and arrangement of heating space.Hence ,lesser the volatile matter,better the quality of coal as a fuel.

3.Ash:-Ash content is determined by heating the residual coal left after the removal of volatile matter in an open crucible at 700-750^{0}C for hsif sn hour in a muffle furnace.Heating,cooling and weighing is repeated till a constant weight is obtained.

%ash=$\frac{Weight\ of\ ash\ formed}{Weight\ of\ coal\ taken}$x100

Significanc**e**

- Ash is useless,non-combustible matter,which reduces the calorific value of coal.It causes hindrance to the flow of air and heat,there by decreases the efficiency.

- Lower the ash content better the quality of coal.

4.Fixed Carbon:-The material left behind after the determination of moisture volatile matter and ash is known as fixed carbon.

% fixed carbon=100-% of(Moisture+Volatile matter+Ash)

Significance

- Higher the percentage of fixed carbon, greater is the calorific value and better the quality of coal.
- The percentage of fixed carbon helps in designing the furnace and the shape of the fire box,because it is the fixed carbon that burns in the solid state.

Knocking

Knocking is a sharp metallic sound similar to rattling of hammer which is produced in internal combustion engines due to immature ignition of fuel-air mixture.

In petrol engines, as the spark is given some portion of the fuel air mixture ignites spontaneously producing an explosive violence. It disturbs the harmony in which the piston moves up and down. The resulting shock waves produce a metallic knocking sound.

Knocking causes engine efficiency decreases.So a good petrol sample should have anti-knocking properties.

Octane Number

Octane number shows the amount of antiknocking properties in a sample of petrol. It is the rating of gasoline with respect to its anti-knocking properties. This rating is based on standard mixtures containing n-Heptane and iso-Octane. In a standard petrol engine n-Heptane-knocks very badly. So its antiknock value or Octane number is fixed as zero. But iso-Octane gives very little knocking, so the Octane number, is fixed as 100. Mixing these two a series of fuel mixtures with octane number 0-100 are prepared. Such mixtures are taken as standard and the given pètrol samples are compared to them regarding their antiknock property or octane number.

When we say a petrol has Octane number 80, it means that this petrol has the same anti-knocking property as an 80: 20. mixture of iso-Octane and n- Heptane. "Numerically octane number is the percentage by volume of iso- Octane in a mixture of iso-octane and n-Heptane, which just matches the petrol under test in knocking. Certain substances like Tetra Ethyl Lead [TEL] or Di- Ethyl Telluride are added in small quantities to petrol to increase the octane number.

Cetane Number. Diesels are rated by their Cetane Number shows the ignition quality of a given diesel. It is actually a measure of a fuels ignition delay. The time interval between start of ignition and start of combustion of a fuel is called ignition delay. The engine is working abnormally and known as diesel knock. It causes over-heating of the engine, efficiency decrease and structural damages to the piston and cylinder. Diesel knock depends on the chemical nature of the fuel and engine conditions.

Cetane Number is used to grade the diesel fuels. This rating is based on standard mixtures containing Cetane [Hexadecane] and. a Methyl Naphthalene.

Cetane is the best diesel fuel with minimum ignition delay while Methyl Naphthalene is the worst diesel with maximum-delay. Cetane number of cetane is fixed as 100 and that of a Methyl Naphthalene as 0. standard mixtures are prepared by mixing them with different Cetane numbers 0 - 100. The given Diesel is compared to those mixtures regarding its Ignition Delay. A Diesel with Cetane number 40 means it has the same Ignition Delay as 40:60 mixture of Cetane and a Methyl Naphthalene. So Cetane Number is the percentage of Cetane in a mixture of Cetane and a Methyl Naphthalene that has the same Ignition Delay as the fuel under test. Cetane Number can be increased by the addition of "DOPES" like Amyl Nitrate or Acetone Peroxide.

Biofuels

Biofuels are biologically produced fuels. Biofuels are renewable energy sources that can be used to replace fossil fuels in transportation. They can be produced from biomass, which is plant and animal products. Biofuels can be liquid, solid, or gaseous. The two most common types of biofuels in use today are ethanol and biodiesel, both of which represent the first generation of biofuel technology. Other examples are biogas, biohydrogen etc.

Biofuels have many characteristics, including:

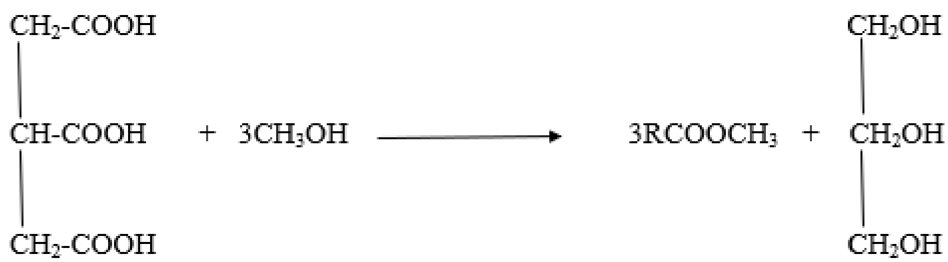
- Biofuels have similar combustion properties to fossil fuels, so they can be used in internal combustion engines with little modification.
- Biofuels are a renewable and biodegradable alternative to fossil fuels. They can be made from edible and non-edible sources.
- Biofuels are free from these substances such as Sulfur, aromatics, metals, and crude oil residues.
- Biofuels are more lubricating than petroleum diesel fuel, which can extend the life of diesel engines.
- Biofuels are non-flammable.
- Biofuel can provide economic independence and environmental safety.

Bio-Diesel. It is an efficient, clean, non-toxic and natural fuel. It is an alternative for Diesel from petroleum. It is free from Sulphur and Aromatics. Since 40% of the energy need is supplied by Diesel, Bio-Diesel helps to reduce the foreign exchange spent for import of crude oil or Diesel. Bio-Diesel can be made from any fat or vegetable oil. It can be used in diesel engines with little or no modifications. It is used in pure form or blended with petroleum diesel.

Bio-Diesels are Alkyl Esters of long chain fatty acids. It is made by "Trans Etherification Process" A fatty acid ester reacts with another lower alcohol to give ester of the lower alcohol. This interchange of alcohol portion of the ester is termed as Trans-esterification. If Methyl alcohol is used as the lower alcohol the product is called Fatty Acid Methyl Ester [FAME]

Animal fats and vegetable oils like sunflower, Palm, mustard and Jetropha are commonly used. It is treated with NaOH and Methanol to get Bio-Diesel and Alcohol or Glycerol.

$$\underset{\text{Oil}}{RCOOR} + \underset{\text{Lower Alcohol}}{R'OH} \rightarrow \underset{\text{Biodiesel}}{RCOOR'} + \underset{\text{Alcohol}}{ROH}$$



Fat(Glyceride) | Methyl Esters(Biodiesel) Glycerol

Biodiesel is an efficient solvent and it cleans the engine cylinders and increases the efficiency. It contains higher Hydrogen and oxygen content than petroleum diesel. So, it helps complete combustion and reduces emission of particulates like unburnt hydrocarbons and carbon.

Green Hydrogen

Hydrogen energy is emerged as an effective solution for global energy crisis. Approximately 80 million tons of hydrogen is produced world wide per annum. Major percentage of this hydrogen is produced from fossil fuels.

Based on the production methods, hydrogen is classified in to

i) Blue hydrogen: Hydrogen is produced through the partial oxidation of methane with O_2,and the CO_2 formed is then captured and stored.

ii) Grey hydrogen: Hydrogen is produced through the partial oxidation of methane with O_2,and the CO_2 formed is not captured.

iii) Brown hydrogen: Produce hydrogen and carbon dioxide using partial oxidation of coal.

iv) Pink hydrogen: Hydrogen is produced by the electrolysis of water using nuclear energy.

v) Green hydrogen: It refers to the hydrogen gas produced by the electrolysis of water using renewable energy sources. This results in the production of hydrogen without the emission of any greenhouse gases and hence it is otherwise mentioned as sustainable hydrogen. Unlike other hydrogen generation methods, green hydrogen generation is a zero-emission technology, making it more environmental friendly and plays a crucial role in addressing climate change.

Green hydrogen production is the electrolysis of water. Water splits it in to hydrogen and oxygen by passing electric current through it.

$$H_2O_{(l)} \rightarrow H_{2(g)}+O_{2(g)}$$

A typical water electrolysis cell is composed of an electrolyte and two electrodes which enables the decomposition of water molecules. Hydrogen gas is produced at the cathode and oxygen gas is produced at the anode. There are three types of electrolyzers based on electrolytes-separators used.

i) Alkaline water electrolyzer (AWE): Uses alkaline electrolytes such as KOH & NaOH

ii) Proton exchange membrane water electrolyzer (PEMWE): Uses solid polymer electrolyte membrane such as perflourosulphonic acid to conduct protons.

iii) Solid oxide water electrolyzer (SOWE): Uses solid oxide or ceramic electrolyte.

Solar energy, wind energy, geothermal energy, hydropower etc. can be used as the renewable energy source for green hydrogen production. It is also produced by electrolysis of water using renewable energy source like solar energy or by photolysis of water.

Applications

- can be used in industry for the production of ammonia, methanol, and steel,
- can be used as a backup energy source for renewable energy plants, providing a constant and reliable source of energy.
- can be used as heating and cooling systems in buildings and homes

Lubricants

Lubricants are substances which are used to reduce the friction ,wear and heat between two surfaces which are moving, sliding or rolling one over another. When one surface is moved relative to another surface with which it is in contact there is a frictional resistance to motion. This can be due to;

Interlocking of surface peaks and valleys

Intermolecular attraction

Formation of cold welded joints

Eletrostatic attracion between rubbing surfaces

As a result there is surface wear and loss of energy as heat. For reducing these two to a minimum in all kinds of machines, a lubricant is used to keep the moving surfaces apart.

Functions of a good Lubricant. A good lubricant reduces;

- It reduces surface wear and deformation
- It act as coolant to carry away heat.
- It prevents corrosion
- It icreases the efficiency of meshines
- It reduces Loss of material.
- It reduces Expansion by frictional heat.
- It reduces Loss of energy as heat.

Classification

Based on their physical state lubricants can be three types.

1. **Liquid lubricants.** Usually known as lubricating oils. They must have high boiling points, low freezing points, thermal stability, oxidation resistance and sufficient viscosity. They can be three types.

   a) Mineral oils: -They are obtained by fractional distillation of petroleum. They are refined to remove the unwanted ingredients, a number additives are added for oiliness, high viscosity index, corrosion resistance etc. These are the most widely used lubricants, because they are cheap, easily available and stable.

b) Animal and vegetable oils: - They have good oiliness and easily adsorbed on the surface. They are good for wet bearings and steam cylinders. They are blended with mineral oil to improve their performance. E.g., Olive oil, castor oil, Palm oil.

c) Synthetic lubricating oils: - They are used under severe operating conditions like high temperature, pressure and in places where ordinary oils cannot be used. E.g., Silicone oil, poly glycols.

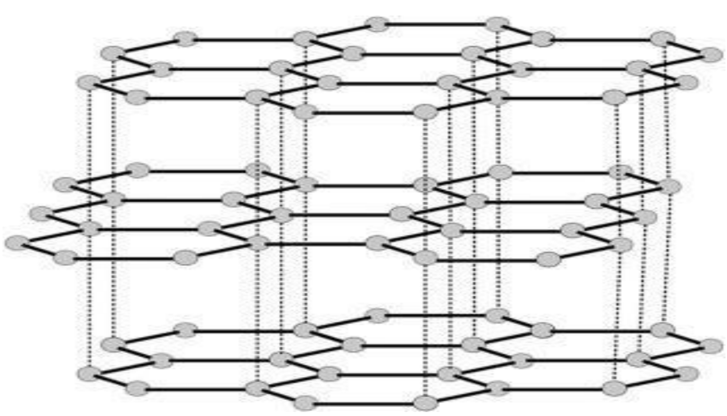
2. **Semi solid lubricants.** The most important semisolid lubricants are greases and vaselines. Grease is a semisolid combination of one or more mineral oils with one or more soaps. It is obtained by saponification of fats or fatty acids with alkali followed by the addition of hot mineral oils. Inorganic substances like clay, silica, carbon black are added to improve thermal resistance. Greases are classified according to the soap used.

- Calcium grease-Calcium soap is used, most common and cheap,
- Soda base grease-Sodium soap is used.It is soluble in water so these greases are water resistant. Good for ball bearings.
- Lithium base grease- Lithium soap is used. These greases are resistant to water and have good high temperature properties.
- Aluminum soap grease-Aluminum soap is used.

3. **Solid lubricants.** Used in places where oil or semisolids cannot be used because of high temperature and pressure, high load and speed. Most common are Graphite and molybdenum disulphide.

Graphite

Graphite has a layer structure made of hexagonal plates or layers of carbon atoms. The layers are held together by weak Vander walls forces. It is used in powder form or dispersed in water or oil. When graphite is dispersed in water is called aquadag and when it is dispersed in oil are called oildag. Graphite is soapy to touch, non-inflammable and resist oxidation. It is used in generators, motors and in foodstuff industry. Oildag is used in internal combustion engines.



Molybdenum disulphide.

It has sandwich like structure in which 'Mo' and'S' are separately arranged in different layers and are sandwiched alternatively.

Properties of Lubricants.

1. Viscosity Index. It is the most important property of a lubricating oil. It is the property which resist the flow of a fluid by cohesive forces between the layers. Viscosity changes with temperature. The rate of change of viscosity with temperature is known as Viscosity Index. High viscosity index means little change with temperature. Low viscosity index means large change with temperature. A good lubricant must have high viscosity index.

2. Cloud and Pour points. When an oil is cooled slowly, the temperature at which the oil appears cloudy or hazy is called cloud point. The oil may contain paraffin wax and resinous impurities. They may separate out at lower temperature. The temperature at which the oil just fails to flow or pour is called pour point. It gives the minimum temperature up to which the oil can be used for lubrication.

The oil is taken in a test jar cooled by a freezing mixture. The temperature falls. The temperature at which the oil appears cloudy is taken as cloud point. Cooling is continued. The jar is withdrawn periodically until the oil fails to flow even when the jar is kept horizontal for a few seconds. This temperature is taken as pour point.

3. Aniline point. It is the lowest temp at which the oil is Completely miscible with an equal volume of aniline. It gives an idea about the composition of the oil.

High aniline point...............High paraffin or low aromatic content.

Low aniline point--------- High aromatic and low paraffin content .

High aniline point is preferred for a good lubricating oil. Aromatic hydrocarbons may react with rubber and other synthetic surfaces.

4. Flash and fire points. Flash point is the lowest temperature at which the oil gives off enough vapours which will ignite for a moment or a flash is produced when a flame is brought near it. Fire point is the temperature at which the oil vapourises and burn continuously for a few seconds, when aflame is brought near.

Flash point gives the maximum temperature up to which the oil can be used for lubrication.

Flash and Fire points are determined using Pensky-Marten's apparatus.

Cement

Cement is defined as a binding agent that is used to bind various construction materials. Given its adhesive and cohesive properties, it is an essential ingredient of concrete and mortar. Cement is mixed with water to form a paste that binds aggregates like sand or crushed rocks.

Cements can be classified in to the following types

i) Natural cement

ii) Pozzolanic cement

iii) Slag cement

iv) Portland cement

v) Special cements

Portland cement

Portland cement is a finely ground powder that is the primary ingredient in concrete, mortar, stucco, and grout. It's made from limestone and clay or shale that are heated to create a clinker, then ground with gypsum. The name comes from the resemblance of the set cement to Portland stone, a limestone from the Isle of Portland, England.

Manufacture of Portland cement

The major raw materials required for the manufacture of Portland cement are:

1. Calcareous materials ($CaCO3$ containing materials such as limestone, chalk, marble etc.)
2. Argillaceous materials (Silicate containing materials such as clay, shale, slate etc.)
3. Powdered coal
4. Gypsum
5. Iron Oxide

The steps involve in the manufacturing process are as follows:

i) Mixing
ii) Burning
iii) Grinding

i) Mixing

The mixing of raw material is carried out either by the dry process or wet process.

Dry process:-If the lime stone and clay are hard,then the dry process is used.In this process limestone is first brocken in to small pieces.It is then mixed with clay and finally powderized.Then the raw mix is fed to a rotary kiln.

Wet process:- If the lime stone and clay are soft,wet process is used. In this process the raw materials are crushed and then ground in wash mills in the wet condition in presence of water.The muddy mixture formed is known as slurry.The slurry is then fed to rotary kiln.

ii) Burning(Calcination)

The dry powderized raw mixture or wet slurry is introduced in to a rotary kiln,which is steel tube kept in an inclined position,150-200 feet long and 10 feet in diameter lined with free bricks.The kiln is capable of rotating at one resolution per minute about its longitudinal axis.Burning fuel and air are injected at the lower end of the kiln.Along hot flame is produced,which heats the interior of the kiln up to a maximum temperature of about1750^{0}C.This is called burning zone and the mixture melts and forms clinkers.The clinker falls out from the lower end of the kiln in to clinker coolers where it is cooled by the atmospheric air which passes over it.

Chemical Reactions

a) Drying zone:- In this zone temperature raises to maximum 750 ^{0}C so that entire slurry gets evaporated.The clay is broken in to Al_2O_3 ,Fe_2O_3 and SiO_2.

Al_2O_3. 2SiO2.Fe_2O_3.$2H_2O$ → Al_2O_3 +2SiO2+ Fe_2O_3 + $2H_2O$

b) Calcination zone:When the temperature reaches at 1000^0C,the limestone is completely decomposed in to CaO.

CaCO3 → CaO.+ CO_2

c) Reaction zone(clinkering zone):-When the temperature reaches about 1600^0C,the mixture is partialy fused and chemical combinations between lime,alumina,ferric oxide and silica,resulting in the formation of calcium aluminates and silicates occur.

2CaO+ SiO_2 → 2CaO. SiO_2 (C_2S-Di calcium silicate)

3CaO+ SiO_2 → 3CaO. SiO_2 (C_3S-Tri calcium silicate)

2CaO+ Al_2O_3 → 2CaO. Al_2O_3 (C_2A-Di calcium Aluminate)

3CaO+ Al_2O_3 → 3CaO. Al_2O_3 (C_3A-Tri calcium Aluminate)

4CaO+ Al_2O_3 + Fe_2O_3 → 4CaO. Al_2O_3. Fe_2O_3 (C_4AF-Tetra Calcium Alumino Ferrite)

The aluminates and silicates of calcium then fuse together to form small hard,greyish stones called clinkers.These clinkers are very hot.it cooled and collected.

iii) Grinding :-The cooled clinkers are ground to a fine powder in ball mills.During final grinding a small amount of powdered gypsum is added so that resulting cement is does not quickly,when it comes in contact with water.The mixture of clinker and gypsum powder is known as cement.This cement is fed in to automatic packing mashines.

Chemical composition of Portland cement

Portland cements are composed of the following four components.

1.Dicalcium silicate

2.Tricalcium silicate

3. Tricalcium Aluminate

4. Tetra Calcium Alumino Ferrite

Setting and Hardening of cement

When cement is mixed with water and allowed to stand, it sets to a hard rigid mass by a series of complex reactions. The process of solidification consists of setting and hardening. Setting is the initial stiffening of the original paste due to gel formation and hardening is the development of strength, due to crystallization.

The important reactions taking place during setting and hardening are as follows

Initial setting of cement. – Paste is due to the hydration of tricalcium aluminate(C_3A) and gel formation of tetracalciumaluminoferrite.

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O$$

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

Tricalcium aluminate

$$4CaO.\ Al_2O_3.\ Fe_2O_3 \quad + \quad 7H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O \ + \ CaO.Fe_2O_3.H_2O$$

$$C_4AF \quad + \quad 7H_2O \longrightarrow C_3A.\ 6H_2O + CF.H_2O$$

Tetracalciumaluminoferrite

The dicalcium silicate present also undergoes hydrolysis to give tobermonite gel (which has very high surface area and very high adhesive property.)

$$2[2CaO.SiO_2] \quad + \quad 4\ H_2O \longrightarrow 3CaO.2SiO_2.6H_2O \ + Ca\ (OH)_2$$

$$C2S \quad + \quad 4\ H_2O \longrightarrow C_3S_2.6H_2O \quad + \quad Ca\ (OH)_2$$

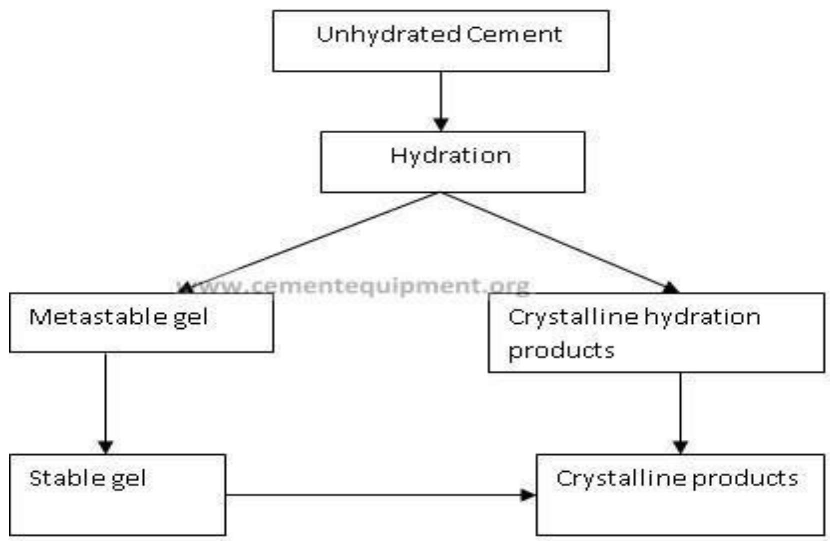
Dicalcium silicate tobermonite gel

Final Setting and hardening of cement

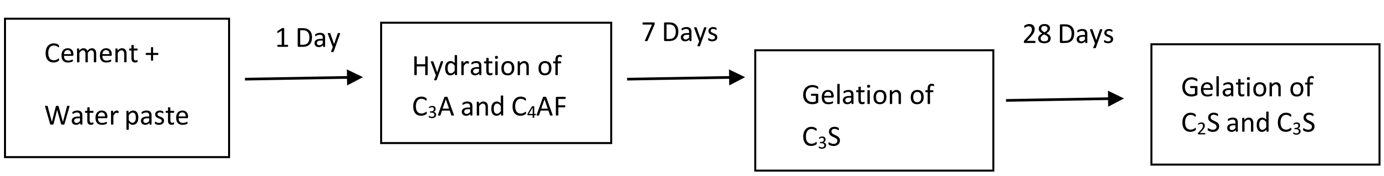
$$2[3CaO.\ SiO_2] \quad + \quad 6H_2O \longrightarrow 3CaO.2SiO_2.3H_2O \ + 3\ Ca\ (OH)_2$$

$$2C_3S \quad + \quad 6H_2O \longrightarrow C_3S_2.3H_2O \ + 3\ Ca\ (OH)_2$$

Setting and hardening of cement



The sequence of chemical reactions during setting and hardening of cement is shown below.



Nano materials

The materials which are created from blocks of nanoparticles or they are defined as" a set of substance where at least one dimension is less than approximately 100 nanometers" Nano materials are defined as materials with at least one dimension in the size range from approximately 1 - 100 nanometers.

Nanomaterials are of interest because at this scale unique optical, magnetic, electrical and other properties emerge. these emergent properties have the potential of great impacts in electronics, medicine and other fields. Nano carbon such as fullerenes and carbon nanotubes are excellent examples of Nanomaterials. The properties of Nanomaterials are entirely different from bulk materials. The reasons for this are 1. Increased relative surface area .2. Quantum effects.

<u>Classification of the Nanomaterials</u>

1. Classification based on dimension

Classification of the nanostructured materials and Systems essentially depends on the number of dimensions which lie within the nano metric range(1-100 nm)

a). Zero dimension (0 -D):Here all the three dimensions are in the Nanometric range.

E.g., quantum dots

b).One dimension(1-D): Here one of the dimensions is outside the nanometric range and the other two are within the range. E.g., Nano wires, nano tubes, nanofibers.

c). Two dimension (2-D):Here two of the dimensions are outside the nanometric range and one is within within the range. E.g. Nano film ,Nano layers, Nano coating.

d). Three dimension (3-D):Here all the dimensions are outside the nanometric range

E.g., Bundles of nano wires and nano tubes.

2. Classification based on materials

a) Carbon based Nanomaterials:- These are defined as materials in which the nano component is pure carbon. Eg. carbon nanotubes (CNT), wires, fullerenes.

b) Metal based Nanomaterials: -Metal based Nanomaterials are made of metallic nanoparticles like gold, silver, metal oxides etc. Eg.TiO 2 , SiO2 ,nano gold.
c) Nanocomposites: - Composite Nanomaterials contain a mixture of simple nanoparticles or compounds such as nanosized clays within a bulk material. The nanoparticles give better physical, mechanical or chemical properties to the bulk material.
d) Nano polymers or Dendrimers: - Dendrimers a nanosized polymers built from branch units. these are tree like molecules with defined cavities. They can be functionalized at the surface and can hide molecules in their cavities. A direct application of dendrimers is for drug delivery.
e) Biological Nanomaterials: - These Nanomaterials are of biological origin and are used for nanotechnological applications. The important features of these particles i) self-assembly properties and ii) specific molecular recognition. Example of DNA nanoparticle, nanostructured peptides. Various self-assembled peptides can be designed to release compounds under specific conditions and are used in drug delivery Systems.

<u>Synthesis of nanoparticles</u>

1. Hydrolysis

Nanoparticles of metal oxides can be prepared by the hydrolysis of their alkoxide solutions under controlled conditions .Eg. silica (SiO_2),Titania(TiO_2),alumina (Al_2O_3) are prepared by this method.

$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH$$

Hydrothermal synthesis and sol-gel method come under this category.

Sol-gel method

The sol-gel method is based on the phase transformation of a sol into a gel. A sol is a colloidal system of Nano solid particles dispersed in a liquid. A gel is a colloidal system in which liquid droplets are dispersed in solid nanoparticles. Hydrolysis of metallic alkoxides can give a sol at a suitable temperature and pH The sol contains many other impurities. In order to remove impurities so is transformed into a gel by changing the pH or other factors .The gel can be purified by filtration and washing with suitable solvents. The purified gel on drying give solid nanoparticles. For eg.Al2O3 nanoparticles are obtained by hydrolysis of aluminium oxide by sol-gel technique.

$$Al(OR)_3 + 3H_2O \rightarrow Al(OH)_3 + 3ROH$$

2.Reduction

Nanoparticles of gold and silver can be prepared by the reduction of their respective solutions using reducing agents, such as sodium borohydride(NaBH4),ascorbic acid, glucose etc.along with a protective agent like thyol,glucose etc. This method can be of two types;- reduction using reducing agent and electro reduction.

Reduction using reducing agents

- Silver nanoparticles can be prepared by this methode.
- 60 ml 1mM AgNO3 solution is taken in a beaker covered with a watch glass and heated in a hot plate with magnetic stirrer.
- On boiling the solution 60ml of1mM of trisodium citrate is added dropwise, about 1drop per second.
- The beaker is then closed and kept for some time, till the colour of the solution changed to a light golden colour.
- Then it is allowed to cool.The solvent can be removed by freeze-drying.

Applications of Nanoparticles

1.Magnetic nanocompsites are used as ferrofluids for high density information storage and magnetic refrigeration.

2.Nanostructured metal oxide thin films are use as gas sensors (CO,CO2,CH4 and aromatic hydrocarbons).

3.Carbon nanotube based transistors are used for miniaturizing electronic devices.

4.A mixture of carbon nanotubes and fullerenes is used for making solar cells.

5.Nanoparticles can be used as catalysts.

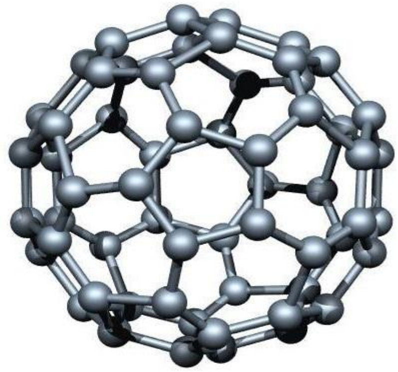
6.Nano-cadmium telluride exhibit different colour depending upon its size.It can be used for dyeing fabrics which never fades.

7.Nanomaterials are used as targeted delivery, gene therapy, photo imaging, antioxidant activity etc.
8.nanoparticles are used in water treatment like removal of toxic pollutants, heavy metals, oli droplets, pesticides, insecticides etc.

Fullerenes

The discovery of fullerenes in 1985 by Curl,Kroto,and Smalley culminated in their Nobel Prize in 1996.Fullerenes,or Buckminister fullerenes,are named after Buckminister fuller the architect and designer of the geodesic dome and are sometimes called bucky balls.

Fullerenes are allotrope of carbon having cage like structure.The most well-known fullerene is buckminsterfullerene (C60), which has a spherical structure with 60 carbon atoms arranged in 20 hexagons and 12 pentagons.The geometry is same as that of soccer football. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.Each carbon atom is bonded to three others and is SP_2 hybridised.Other fullerenes include C70 and C80.



Properties

• Fullerenes are spirangly soluble in many solvents.

• Harder than steel and diamond.

• Higher fullerenes have variety of colours.

• They are electrical insulators

Applications

1. Exhibit pholochromic effect
2. They are powerful antioxidant
3. They are very good medium to make H_2 fuel
4. Can be used as fillers
5. Used as drug delivery tools
6. Act as catalyst in organic reactions and water purifications
7. On organic photovoltaics
8. It inhibits HIV virus

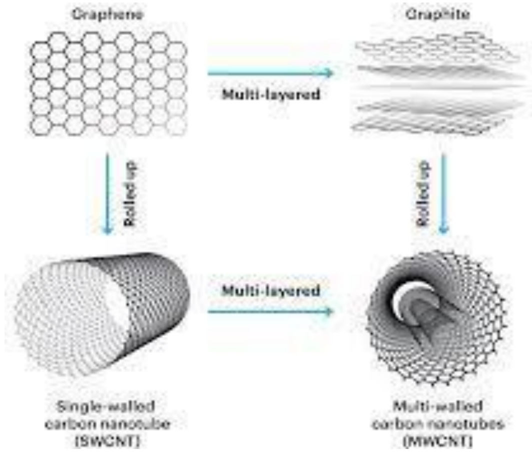
<u>Carbon Nanotubes</u>

CNTs were discovered in1991 by the japanese electron microscopist Sumio lijima who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes.

Carbon Nanotubes are allotropes of carbon having hollow cylindrical structure. They have a diameters of a few nanometers (as low as 1nm) made up of lattices of carbon atoms. Carbon atoms are linked by covalent bonds. Because of SP 2 hybridisation,they have unique strength and novel properties. There are two types of CNTs.Single walled carbon nanotubes and Multi walled carbon nanotube.

Single walled carbon nanotubes (SWCNT): It is a one atom thick sheet of graphite rolled up in to a cylindrical form.They have a few nanometers in diameter and several centimeters length.

Multi walled carbon nanotubes (MWCNT): It consist of multiple layers of graphite. The distance between the layers is approximately 3.4A0.



Properties

Carbon nanotubes (CNTs) are cylindrical structures made of carbon atoms arranged in a hexagonal lattice. Their unique properties have made them a subject of intense research and development. Here are some of the key properties of CNTs:

Mechanical Properties:

- High tensile strength: CNTs are among the strongest materials known, with tensile strengths several times that of steel.
- High modulus: They also exhibit high modulus, meaning they resist deformation under stress.
- Lightweight: CNTs are extremely lightweight, making them ideal for applications where weight is a critical factor.

Electrical Properties

- High electrical conductivity: CNTs can be either metallic or semiconducting, depending on their structure. Metallic CNTs have high electrical conductivity, making them promising for electronic applications.
- High electron mobility: CNTs have high electron mobility, which is a measure of how quickly electrons can move through the material. This property is crucial for high-performance electronic devices.

Thermal Properties

- High thermal conductivity: CNTs are excellent heat conductors, making them suitable for thermal management applications such as heat sinks and cooling systems.
- Low thermal expansion: CNTs have a low thermal expansion coefficient, meaning they expand or contract very little with temperature changes.

Optical Properties

- Nonlinear optical properties: CNTs exhibit nonlinear optical properties, which can be used for applications such as optical switching and frequency conversion.
- Strong light absorption: CNTs can absorb light strongly, making them potential materials for solarcells and optical sensors.

Chemical Properties

- High surface area: CNTs have a very high surface area to volume ratio, which makes them excellent for adsorption and catalytic applications.
- Chemical inertness: CNTs are generally chemically inert, making them resistant to corrosion and degradation.

Applications

Carbon nanotubes (CNTs) have a wide range of potential applications:

• Electronics: They can be used in transistors, computers, and other electronic devices.

• Materials: They can be added to other materials to make them stronger, lighter, or more durable.

• Energy: They can be used in batteries, solar panels, and fuel cells.

• Medicine: They can be used to deliver drugs, treat diseases, and create artificial organs.

• Environmental: They can be used to clean up pollution and filter water.

• They can be used in many other areas, such as sports equipment, clothing, and cosmetics.

Polymers

Polymers are large molecules built up of a number of smaller molecules.A polymer is made up of identical monomers are called homoplymers.eg; polyethylene,PVC etc. A polymer is made up of two or more different monomers are called co-polymers. .eg:- BS,ABS

ABS-Acrylonitrile Butadiene Styrene

• It is a copolymer • Formed by copolymerizing styrene and acrylonitrile in presence of butadiene.

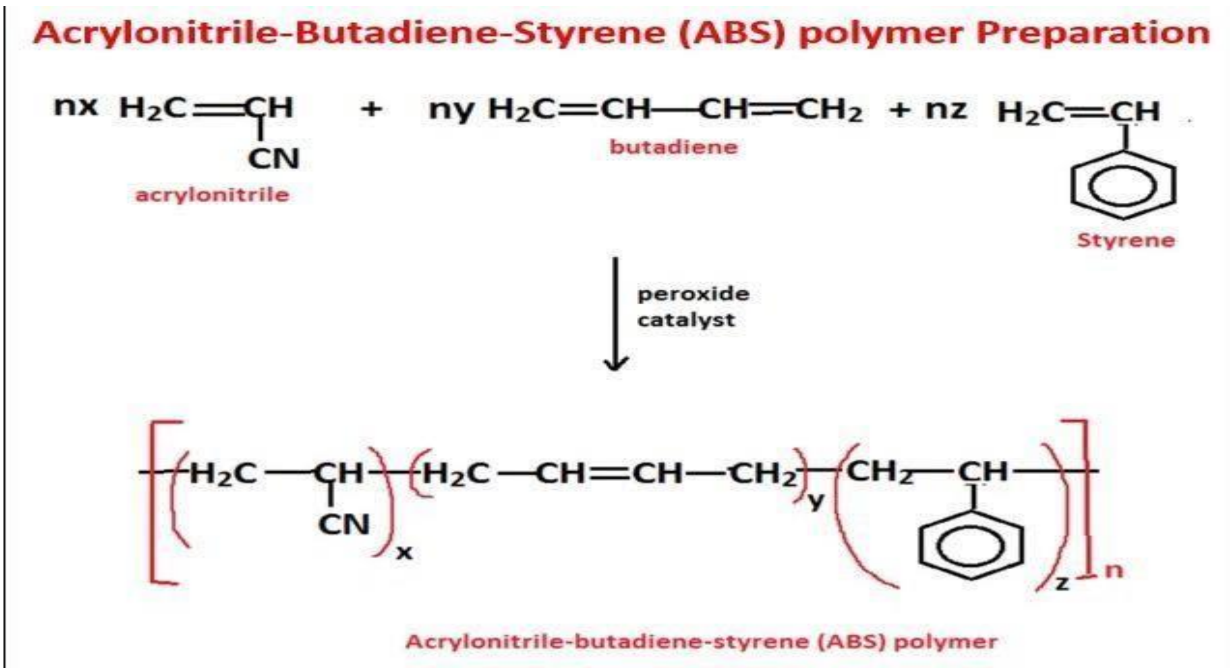
• Acrylonitrile -15 to 35%.................rigidity

• Butadiene-5 to 30%...................... resilience

• Styrene-40 to 60%....................... Shiny appearance

• Amorphous thermoplastic polymer

• Glass transition temperature – 1050C



Properties

❑ Tough, Hard and Rigid

❑ Good chemical resistance

❑ Light weight

❑ High tensile strength and stiffness

❑ Excellent ductility

❑ Excellent high and low temperature performance.

Applications

✓ Manufacturing of TV cabin

✓ Computer monitor body

✓ Computer key board

✓ Mobile phone body

✓ Musical instruments

✓ Medical devices for blood access

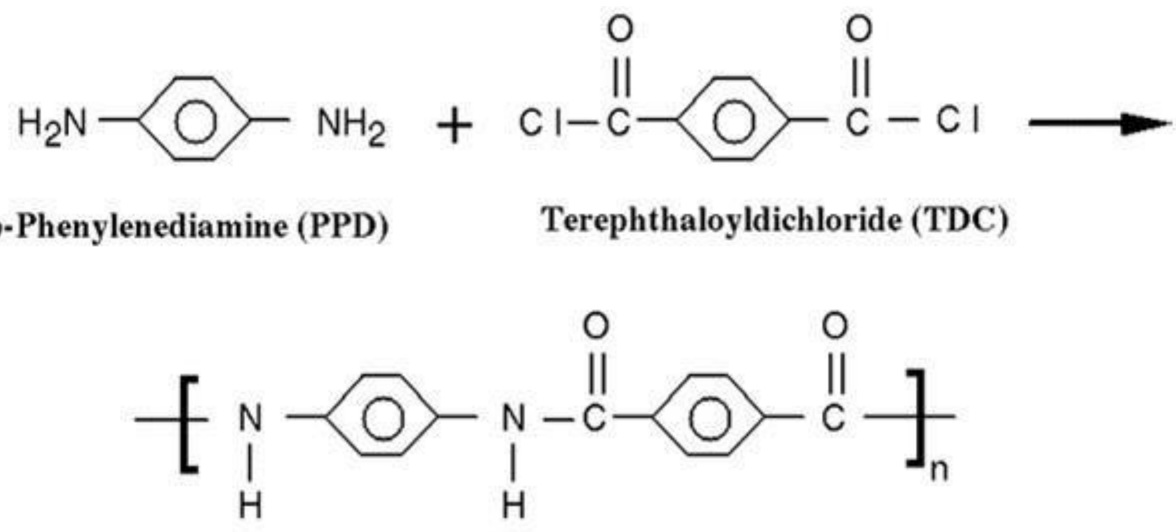
✓ Enclosures for electrical and electronic assemblies

KEVLAR (Poly- paraphenylene terephthalamide)

• Synthesized by the condensation of polymersation of monomers 1,4 phenylene diamine and terephthaloyl chloride giving HCl as byproduct.

• It is an aromatic amide polymer with alternate benzene ring and amide group.

• The polymer chain can be oriented in the form of fiber.



Properties

• Five times stronger than steel

• Light weight • Does not corrode

• High chemical resistance

• Structurall rigidity

• Heat and flame resistant

• Keep its strength down to cryogenic temperature(-1960C).

Applications

• Parts of aircrafts and ships

• Bullet proof vest and helmets

• Fibre optic cables

• Sports equipments-race car parts,sports shoe,skate board etc.

• Heat resistant gloves

• Ropes and cables.

<u>Conducting polymers</u>

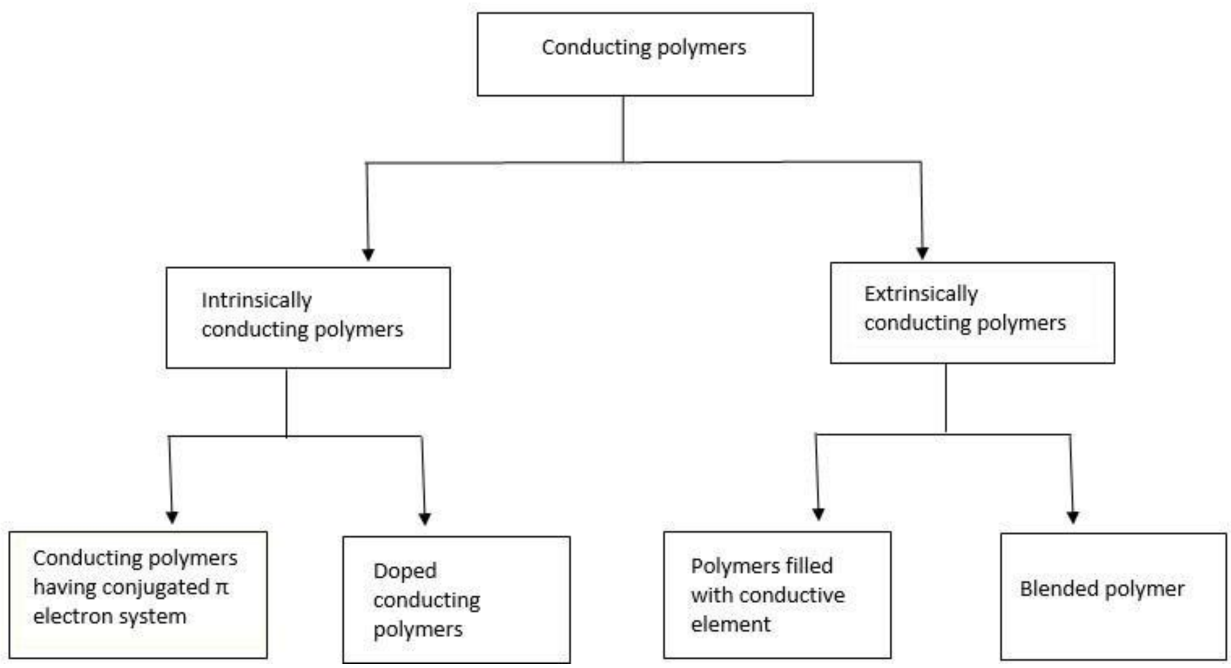
In general polymers are insulators. Organic polymers which can conduct electricity are called conducting polymers .Most conducting polymers are polyacetylene, polyaniline and polypyrrole.

The conductance is due to two facts.

1. Conjugated double bonds.

2. Doping

Classification



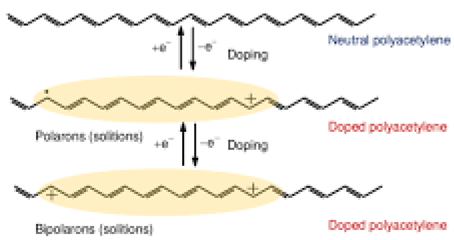
Intrinsically conducting polymers-The have continuous conjugation in the polymer backbone. it can be divided into two. They are

1. Conducting polymers having conjugated π electron system-They have conjugated double bonds along the polymer back bone. The P orbital of the conjugated π electrons overlap over the entire polymer back bone. As result valence and conductance bands are formed over the entire polymer molecule. These bands are separated by a large band gap. So conduction will occur only when electrons from balance band are excited to conduction band thermally or photolytically.Eg: Polyaniline,Polyacetylene.

2. Doped Conductive polymers .Conducting polymers with conjugated π electrons in their back bone can be easily oxidised or reduced. Their conductivities can be increased by creating positive or negative charge on the polymer backbone by oxidation or reduction. This process is called "doping".

P-doping: This is done by oxidation.Some electrons from the conjugated double bonds are removed. The holes so created can move along the polymer chain and it becomes conductive.Oxidation is done by Lewis acid like FeCl3.

n-doping: This is done by reduction Some electrons are added into the polymer chain having conjugated double bonds. The negative charge is created can move along the polymer chain and it becomes conductive. Reduction is done by Lewis bases.



p-doping and n-doping

Extrinsically conducting polymers: Conductivity is due to externally added ingredients.

1.Conductive Element filled Polymer: The polymers are filled with conducting elements like carbon black metallic fibres .Polymer act as a binder to hold the conducting elements. Hey have low cost, light weight, durability and strength. Can be made into desired shape.

2.Blend conducting polymers: They are made by blending conductive polymers with ordinary polymers. Good mechanical, physical and chemical properties.

Applications of conducting polymers

• Small size rechargeable batteries

• Used in electrochromic displays

• Used in electroluminance displays like TV,Mobile etc.

• Analytical sensors for pH,glucose,O2,N02 etc

• Photovoltaic devices

• In electronics like LEDs and electron beam Lithography

<u>Supercapacitors</u>

Supercapacitors or ultracapacitors are energy storage devices having high-capacity, with a capacitance value much higher than solid-state capacitors and batteries are energy storage devices. A capacitor contains two metal plates separated by a dielectric material whereas a super capacitor generally consists of electrodes, electrolyte, separator and collector.

Electrode: Materials with good conductivity and high stability like porous active carbon coating are generally used as the electrode material. Carbon based nanoparticles(eg:-carbon nanotubes,graphene,carbon

quantum dots etc.) metal oxide nanoparticles, nanowires, quantum dots, conducting polymer-based com-posites etc. are used electrode materials in supercapacitors. Nanomaterials enhances the performance of the supercapacitors by increasing the capacitance, energy density and cycling stability of the supercapac-itors.

Electrolyte: Capacity of the capacitor depends mainly on the dielectric constant of the electrolyte. Either solid or liquid can be used as the electrolyte. For commercial application solid electrolytes are preferred since they are leak-free and possess high ionic conductivity. Generally, a solvent mixed with

conductive salts such as tetraalkylammonium or lithium salts acts the solid electrolyte. Sulphuricacid, KOH solution etc can act as the liquid electrolyte.

Separator: Electrolyte membranes will act as the separator. It prevents short-circuiting between the electrodes but allows the electrolyte ions to pass through. Polymer-based and paper-based are found tobe durable and economical.

Collector: Electrons are collected at the collector. Carbon fibre, metal like Al, Pt, Cu, Ni etc. are the commonly used collectors. Binders, such as polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN),act as adhesives to hold the active material and current collectors together.

Advantages

- Longer cycling time and higher service life compared to the battery.
- High efficiency, higher charging rates and high power density.
- Low resistance which enables them to produce high load currents.
- Small sizes and lightweight which makes them easily installed in small areas.
- Environment friendly.

Graphene

Graphene is a material that is extracted from graphite and is made up of pure carbon, one of the most important elements in nature and which we find in daily objects like the lead of a pencil. It is an allotrope of carbon consisting of single layer of atoms arranged in a honeycomb nano structure .The name is derived from “graphite”and the suffix-ene ,reflecting the fact that graphite allotrope of carbon contains numerous double bonds in a two Dimensional sheet. It is a allotrope of carbon in the form of a plane of sp^2-bonded atoms with a molecular bond length of 0.142nm.in a graphene sheet ,each atom is connected to its three nearest carbon neighbors by bonds, and a delocalized π-bond, which contributes to a valence band. Graphene is worlds thinnest material. It is only one atom thick, one million thinner than human hair. However it is very stronger than steel and diamond.

Properties

- Electrical Conductivity:Graphene conducts electricity because its delocalized electrons can move freely throughout the sheet of carbon atoms.This property makes graphene useful in electronics.
- Large Surface area:Graphene's large surface area makes it useful for energy storage,sensor sensitivity and water purification.
- Strength and lightweight:Graphene's thermal conductivity supports efficient heat management.
-
- Optical Properties:Graphene absorbs only 2.3 of incident light over a broad wavelength range and hence make it suitable for applicationsin transparent electrodes for display,solar cells,touch screens etc.
- Mechanical strength and elasticity: They possess high elastic modulus and strength. It is 200 times stronger than steel. Graphene is highly is flexible and can be stretched by up to 20
- Thermal Conductivity: Graphene exhibits excellent thermal conductivity and is highly effi cient for heat dissipation and thermal management applications. Graphene is chemically inert, stable and biocompatible also.

Applications of Graphene

1. Electronics:
   a) Due to its lower resistance and higher transparency, graphene-based thin film ca be used in touchscreens, which is found to be superior than indium tin oxide.
   b) Smaller size transistors can be developed using graphene which shows better pe formance.
2. Energy storage:
   a) Graphene incorporated lithium-ion batteries have longer life span, faster chargin time and higher capacity.
   b) It can improve the efficiency of hydrogen fuel cell by lowering fuel cross over (fu permeating through the electrolyte or membrane to the opposite side of the fu cell).
   c) Graphene is used in supercapacitors to provide high energy density.
3. Biomedical:
   a) Suitably functionalized graphene can be used to carry chemotherapy drugs to can cells.
   b) Graphene-based biosensors are highly sensitive when detecting DNA, ATP, dopam etc.
4. Composites and coating:
   a) By combining graphene with paint, a unique graphene coating is formed which v effectively prevent rusting.
   b) Graphene in the carbon-fibre coating of aircraft's wing resists impact better a consumes less fuel.
   c) Graphene-based composites and coatings could play a significant role in improvi sports equipment for skiing,cycling etc.