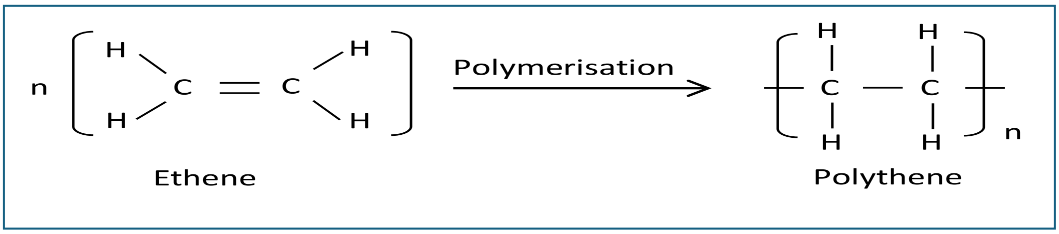
Unit 2

Materials Chemistry

Polymers

1. Introduction to polymer

The word *polymer* is derived from two Greek words, poly and meros, where *poly* means many and *meros* means parts. Polymers are giant molecules formed by the combination of several simple molecules having two or more binding sites linked through covalent bonding.



The simple molecules which are repeating units of the polymer are called monomers.

Eg: Polythene is formed by the combination of several ethene (ethylene) molecules.

Degree of polymerization (DP): Degree of polymerization is the number which expresses the total number of repeating units (n) in the polymer chain. Polymers with large number of repeating units are called high polymers and those with lower number of repeating units are called oligomers.

DP is used to determine the molecular weight of the polymer by multiplying the number of repeating units (n) with the molecular weight of repeated unit.

Functionality: The total number of functional groups, bonding sites or reactive sites present in the monomer is called the functionality of the monomer. The reactive functional groups can be

–OH, -COOH, $-NH_2$, -SH , –NCO etc.

Eg: In CH_3CH_2OH one reactive - OH group is present, hence functionality is one (monofunctional)

HO- CH_2 -CH_2 – OH has two – OH groups hence bifunctional

HOOC CH_2 CH (COOH) CH_2 COOH has three -COOH groups, hence trifunctional

The presence of double or triple bonds in the molecule imparts polyfunctionality to the molecules.

Eg: Ethylene - due to the presence of a double bond, it can take on two atoms of hydrogen or halogens. Depending upon the functionality of the monomers used linear, branched or three dimensional cross-linked polymers are formed.

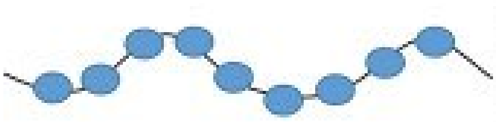
2. Classification of polymers based on molecular structure

Polymers can have different molecular structures, which significantly influence their physical properties and behavior. The three main types of polymer structures are linear, branched, and network (or cross-linked) structures.

2.1. Linear polymers:

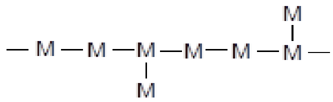
Linear polymers consist of long, unbranched chains of monomers linked together in a straight line. The monomers are connected by covalent bonds, forming a continuous backbone. Examples of linear polymers include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polyesters like polyethylene terephthalate (PET).Linear polymers tend to have high strength and stiffness due to the ability of the chains to align and crystallize. They also exhibit good resistance to solvents and chemicals, as well as relatively high melting and glass transition temperatures.If 'M' represents a monomer, the typical structure of a linear polymer is represented as:

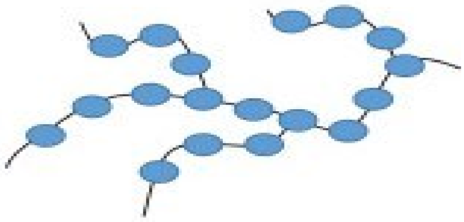
–M–M–M–M–M–M–



2.2. Branched polymers:

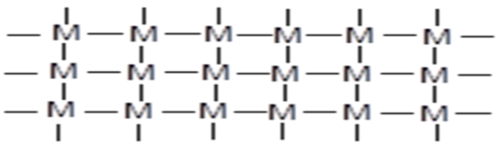
Branched polymers have a main linear backbone with additional side chains or branches attached to it. The branches can be short or long, and they can be evenly distributed or randomly placed along the main chain. Examples of branched polymers include low-density polyethylene (LDPE), polyisobutylene, and certain types of polypropylene. Branched polymers generally have lower densities and lower crystallinity compared to their linear counterparts. They exhibit improved flow properties, making them easier to process and mold. Additionally, branched polymers tend to have better impact resistance and flexibility due to the disruption of chain packing caused by the branches. The typical structure of a branched-chain polymer may be represented as:

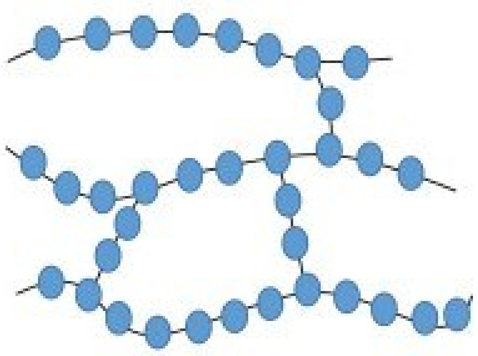




2.3. Network (cross-linked) polymers:

Network or cross-linked polymers are formed when linear or branched polymer chains are chemically connected at various points along their lengths, creating a three-dimensional network structure. The connections between the chains are typically covalent bonds, but they can also involve ionic or hydrogen bonding. Cross-linked polymers are highly resistant to solvents, heat, and chemicals due to their rigid network structure. They exhibit high strength, toughness, and dimensional stability, but they are also relatively inflexible and insoluble. Examples of cross-linked polymers include vulcanized rubber, thermoset resins like epoxy and polyurethane, and certain types of hydrogels. The typical structure of a cross-linked polymer is represented as:





The degree of cross-linking plays a crucial role in determining the properties of network polymers. Highly cross-linked polymers are more rigid and brittle, while those with lower degrees of cross-linking exhibit greater flexibility and elasticity. The molecular structure of polymers significantly affects their properties and applications. Linear polymers are used in packaging, textiles, and engineering plastics, while branched polymers find applications in film manufacturing and packaging. Cross-linked polymers are employed in various applications, such as tires, coatings, adhesives, and advanced composite materials.

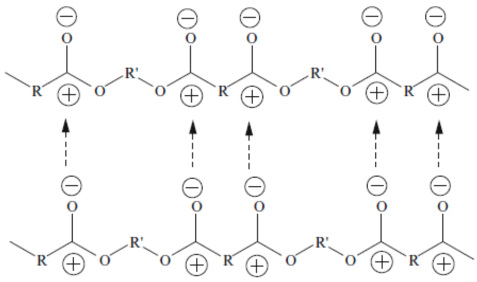
Structure and properties of polymers

The structure of a polymer has profound influence on some of the properties of polymers. The properties such as crystallinity, tensile strength, elasticity, resistance to chemicals and plasticity depend mostly on the polymer structure and are discussed below.

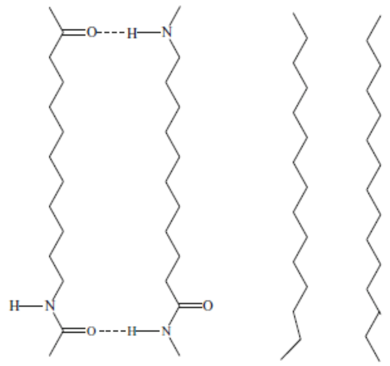
Strength: This property is discussed based on forces of attraction and slipping power.

Based on forces of attraction: Strength of the polymer is mainly determined by the magnitude and distribution of attraction forces between the polymer chains. These attractive forces are of two different types viz., primary or covalent bond and secondary or intermolecular forces.

In case of straight chain and branched chain polymers, the individual chains are held together by weak intermolecular force of attraction. But in these polymers, strength increases with increase in chain length (increase in molecular weight) i.e., attains mechanical strength if the chain length is greater than 150 – 200 carbon atoms in the chain. Less than these numbers, the polymers will be soft and gummy, but brittle at low temperature. Intermolecular forces can be increased by introducing polar groups like carbonyl & hydroxyl.



In cross-linked polymers, monomeric units are held together only by means of covalent forces. Hence possess greater strength than straight and branched chain.



Based on slipping power**:** Slipping power is defined as movement of molecules one over the other. Eg: polyethylene molecule is simple and uniform, hence movement of molecule one over other is possible, i.e., slipping power is high. Hence it has lesser strength. But in case of polyvinyl chloride (PVC), bulky chlorine atoms are present along the chain length hence, movement is restricted, i.e., slipping power is less. Hence it has higher strength compared to polyethylene. But in case of cross-linked polymer, movement is totally restricted because of the presence of covalent bond. Hence these products are strong, rigid and tough.

Plastic deformation: When a polymer is subjected to some stress in the form of heat or pressure or both, permanent deformation in shape takes place, which is known as plastic deformation. This property actually helps in moulding of plastics. Slippage is more in case of linear molecules than branched and cross-linked, because of the presence of weak intermolecular forces and hence they show greatest degree of plastic deformation. At high pressure and temperature the vander Waal's forces acting between molecules become more and more weak. No slippage occurs in case of cross-linked polymers, because only strong covalent bonds are present throughout the entire structure. However, when considerable external force or temperature exceeding the stability of material is applied, it will result in total destruction.

Crystallinity: Based on the relative arrangement of polymer chains with respect to each other, polymer can exhibit amorphous and crystalline nature. An amorphous state is characterized by completely random arrangement of molecules and crystalline form by regular arrangement of molecules. The crystallization tendency of a polymer depends on the ease with which the chains can be aligned in an orderly arrangement. Crystalline regions of a polymer are formed when the individual chains are linear (without branching), contain no bulky substituents and are closely arranged parallel to each other. The chains of polymer may be held together by vander Waal's forces, hydrogen bonding or polar interactions. A polymer with high degree of crystallinity will have high tensile strength, impact and wear resistance, high density and high fusion temperature. Polymers with a long repeating unit or with low degree of symmetry do not crystallize easily, hence forms amorphous structure e.g., polystyrene. Crystallization imparts denser packing of molecules due to increase of intermolecular forces of attraction. Such type of polymers will have sharp softening point, greater strength and rigidity. e.g PVC, Polypropylene. Polymers are in general, amorphous with some degree of crystallinity.

Chemical Resistance: Chemical resistance of polymer depends upon the chemical nature of monomers and their molecular arrangement. A polymer is more soluble in structurally similar solvent. For example, polymers containing polar groups like – OH, - COOH, usually dissolve in polar solvents like water, alcohol etc but are chemically resistant to non-polar solvents. Similarly non-polar compounds like hydrocarbons dissolve only in non-polar solvents like benzene & toluene.

As a general rule, the tendency of solubility in a particular solvent decreases with increase in molecular weight of the polymer- (i) high molecular weight polymer on dissolving yield solutions of high viscosities (ii) crystalline polymers exhibit higher resistance than less crystalline polymers of similar chemical character (iii) greater the degree of crystallinity, lesser is its solubility.

Today several drugs and essential oils are stored in plastic bottles for long shelf life. If they disintegrate or change in their chemical composition they may render the drug ineffective or may cause it to react adversely when used, leading to specific disorder. Therefore, chemical resistance of plastic bottles is important to prevent drug polymer interactions.

Elasticity: Elastic nature in polymers results due to the uncoiling and recoiling of the molecular chains on the application of force. In an upstretched elastomer we can observe a peculiar configuration of irregularly coiled and entangled snarls in a random fashion, indicating the amorphous state. In a stretched state snarls disentangle and straighten out in a proper chain orientation, indicating the crystalline state. The crystallinity in a stretched rubber band can be observed from its opaqueness and warmth it produces when touched by lips. The main criteria for a polymer to show elastic nature is that , the individual chains should not break even after prolonged stretching. This can be done by introducing suitable crosslinking in the chains, by allowing nonpolar groups or side groups in the repeating unit.

Glass transition temperature Tg

Amorphous polymers do not have sharp melting points. They possess softening point. At low temperature, polymers exist as glassy substances. Since the molecular chains cannot move at all easily in this state, the solid tends to shatter, if it is hit. If the solid polymer is heated, eventually it softens and becomes flexible. This softness and flexibility is obtained at the glass transition temperature. After this temperature, crystalline and amorphous thermoplastic polymers behave differently. Heating has little effect on thermosetting polymers and at a high temperature, they are destroyed.

So the ***glass transition temperature*** can be defined as the temperature below which an amorphous polymer is brittle, hard and glassy and above the temperature it becomes flexible, soft and rubbery.

Glassy state $\longrightarrow$ rubber state
(Hard brittle plastic) (soft flexible)

In the glassy state of the polymer, there is neither molecular motion nor segmental motion. When all chain motions are not possible, the rigid solid results. On heating beyond T_g segmental motion becomes possible but molecular mobility is disallowed. Hence flexible,

Factors affecting glass transition Temperature

Glass transition temperature of a polymer depends on parameters such as chain geometry, chain flexibility, molecular aggregates, hydrogen bond between polymer chains, presence of plasticizers and presence of substrates in the polymer chains.

A polymer having regular chain geometry show high glass transition temperature, the bulky groups on chain increases the T_g of the polymer. E.g., polyethylene has T_g -110 °C. The T_g is quite low because there are no strong intermolecular forces and no bulky side groups are present, the side chain is only hydrogen atom. But nylon 6 has T_g 50 °C because of the presence of large number of polar groups in the molecule leading to strong intermolecular hydrogen bonding.

The T_g of a polymer is influenced by its molecular weight. However, it is not significantly affected if molecular weight is around 20000. With increase in molecular mass, the temperature (T_g) will be higher.

In crystalline polymers the polymer chains are arranged in a regular parallel fashion. Each chain is bound to the other by strong forces like H-bonding. Hence crystalline polymers have higher T_g than amorphous polymers.

The added plasticizers reduce the T_g of the polymer by reducing the cohesive forces of attraction between the polymers. e.g., dibutyl phthalate, diacetyl phthalate etc.,

The glass transition temperature is an important parameter of polymeric material. This helps in choosing the right processing temperature. It is a measure of flexibility of a polymer and also gives the idea of the thermal expansion, heat capacity, electrical and mechanical properties of the polymer.

Molecular weight of polymers

A polymer comprises of molecules of different molecular weights and hence, its molecular weight is expressed in terms of an 'average' value.

The molecular weight of a polymer can be expressed by the two most and experimentally verifiable methods of averaging –

(i) Number – average molecular weight and (ii) weight – average molecular weight

Number – average molecular weight: Number average molecular mass of a polymer can be defined as the total mass of all the molecules in a polymer sample divided by the total number of molecules present.

$$\overline{Mn} = \frac{\sum ni\,\mathrm{M}i}{\sum ni}$$

Weight – average molecular weight: The sum of the fractional masses that each molecule contributes to the average according to the ratio of its mass to that of the whole sample.

The formula to determine 'weight average molecular weight' of polymers is,

$$\overline{Mw} = \frac{\sum ni\,\mathrm{M}i^2}{\sum niMi}$$

1) A polymer sample contains 1, 2, 3 & 4 molecules having molecular weight 10^5 , 2X 10^5 , 3X10^5 and 4X 10^5 respectively. Calculate the number average & weight average molecular weight of the polymer.

$$\mathrm{Mn} = \frac{1(1X10^5)+2(2X10^5)+3(3X10^5)+4(4X10^5)}{1+2+3+4}$$

$= 3.0 \times 10^5$

$$M_w = \frac{1(1 \times 10^5)^2 + 2(2 \times 10^5)^2 + 3(3 \times 10^5)^2 + 4(4 \times 10^5)^2}{1(1 \times 10^5) + 2(2 \times 10^5) + 3(3 \times 10^5) + 4(4 \times 10^5)}$$

$= 3.3 \times 10^5$

2) Calculate the number average & weight average molecular weight of a polymer sample in which 30 % molecules have molecular mass of 20000, 40 % have molecular mass of 30000 & rest 30 % have molecular mass of 60000.

$$M_n = \frac{30 \times 20000 + 40 \times 30000 + 30 \times 60000}{30 + 40 + 30}$$

$= 36000$

$$M_w = \frac{30 \times (20000)^2 + 40 \times (30000)^2 + 30 \times (60000)^2}{30 \times 20000 + 40 \times 30000 + 30 \times 60000}$$

$= 43,333$

3) Polymers molecule with different degree of polymerization such as 500, 750, 950 and 1500 are mixed in molecule ratio1:2:3:4 in a sample of high polymer of ethylene. (Mole. Mass= 28). Calculate number average and weight average mol.mass.

$$M_n = \frac{1(28 \times 500) + 2(28 \times 750) + 3(28 \times 950) + 4(28 \times 1500)}{1+2+3+4}$$

$= 30380$

$$M_w = \frac{1(28 \times 500)^2 + 2(28 \times 750)^2 + 3(28 \times 950)^2 + 4(28 \times 1500)^2}{1(28 \times 500) + 2(28 \times 750) + 3(28 \times 950) + 4(28 \times 1500)}$$

$= 33761$

3) A polymer sample contains:

Polymer of DP	400	500	600	800	1000
Percentage	10	15	35	15	25

Calculate the average degree of polymerization.

Solution: $DP = \dfrac{10X400+15X500+35X600+15X800+25X1000}{10+15+35+15+25}$

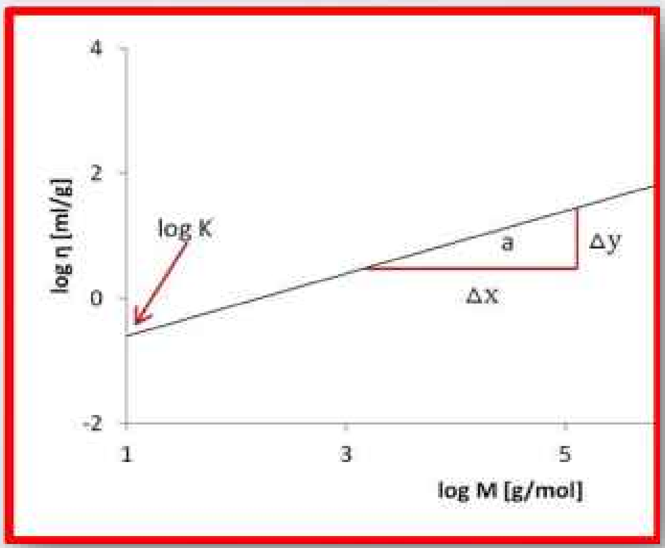
$= 695$

Determination of Molecular weight of polymers by viscometry

Viscometry: The molecular weight obtained by this technique is the viscosity average molecular weight, Mv. The viscosity of a polymer solution is considerable high as compared to that of pure solvent. The relationship between the viscosity of a polymer solution and molecular weight is given by Mark-Houwink equation-

$[\eta] = KM^a$

Where $[\eta]$ is the intrinsic viscosity, M- molecular weight and a and K are constant for a particular polymer/solvent/temperature system. Values of K and a are available for may known polymers.



A plot of log [η] against log M gives a straight line. From the graph, the value of K and a can be determined from their ordinate intercept and slope of the line.

. $[\eta] = KMa$ $\log [\eta] = \log K + a \log M$

Engineering Polymers

Introduction to Engineering polymers

An introduction to engineering polymers provides a foundational understanding of these advanced materials, their properties, and their diverse applications across various industries. Engineering polymers, also referred to as high-performance polymers, represent a specialized class of materials designed to meet stringent performance requirements in demanding applications.

Definition and Significance of Engineering Polymers:

Polymer engineering comprises the engineering discipline, focusing on the design, analysis, and modification of the polymer materials. It encompasses various facets of the petrochemical industry, including polymerization processes, polymer structure and characterization, polymer properties, compounding, and processing techniques, as well as the study of major polymers, their structure-property relationships, and diverse applications.

Key attributes of engineering polymers include:

- **Mechanical Properties**: Engineering polymers often exhibit high strength, stiffness, toughness, and impact resistance, making them suitable for structural applications where mechanical performance is crucial.

  Ex: ultra-high molecular weight polyethylene (PE)- have better tensile strength than steel, Fibers (KevlarTM , carbon fiber and nylon)

- **Thermal Stability**: These polymers maintain their properties over a wide range of temperatures, including both high and low extremes. They can withstand prolonged exposure to elevated temperatures without significant degradation.
  Ex: polybenzoxazoles (PSPBOs), poly phenyls
- **Chemical Resistance**: Engineering polymers are resistant to a wide range of chemicals, solvents, and environmental conditions, making them ideal for applications where exposure to harsh substances is common.

Ex: low density polyethylene (LDPE), Polytetrafluoroethylene (PTFE).

- **Electrical Properties**: Conducting polymers possess the ability to conduct electricity, which arise from the presence of delocalized π-electrons along the polymer backbone or within conjugated segments. Many engineering polymers possess excellent electrical insulation properties, making them suitable for use in electronic and electrical components where insulation and reliability are paramount.

  Ex: conducting polymers like polyaniline (PANI), Polypyrrole (PPy)

  Insulating polymers: silicone, Ethylene Propylene Diene Monomer (EPDM)

- **Dimensional Stability**: These materials exhibit minimal dimensional changes under varying environmental conditions, ensuring precision and consistency in critical applications. i.e., they have ability to maintain their size even in changing environmental conditions. A dimensionally stable shows low water absorption and thermal expansion.

  Ex: Polyether ether ketone (PEEK), Polyethylene terephthalate (PET), polyvinylidene difluoride (PVDF)

  - Flame Retardancy: Some engineering polymers are formulated to meet stringent fire safety standards, making them suitable for applications where flame resistance is essential. They are made by incorporation of aromatic rings or heterocycles. They are also called as fire safe polymers, and find applications in construction of small, enclosed space like in air plane cabins, skyscrapers etc.

    Ex: Polyimides, polybenzoxazoles (PBOs), polybenzimidazoles, and polybenzthiazoles (PBTs)

High-performance polymeric materials represent a specialized class of polymers engineered to exhibit exceptional properties and performance characteristics, surpassing those of conventional plastics. They have crucial role to play in various industries such as medical, aerospace, automotive, electronics and other industrial sectors because of their superior properties and performance.

Polyamides

Polyamides, commonly known as nylon, are a versatile class of engineering polymers with a wide range of applications across various industries. Polyamides are prepared by the melt polycondensation between di-carboxylic acid and diamines. Synthesis of Polyamides is shown in Fig. 1.

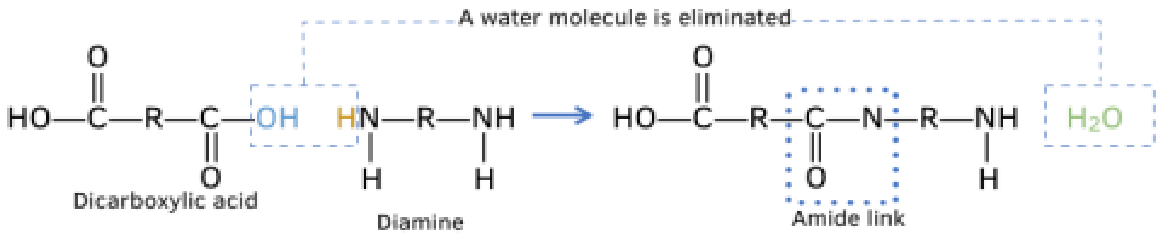


Fig 1. Condensation Reaction between a Dicarboxylic Acid and a Diamine to form a Polyamide.

Polyamides are synthetic polymers characterized by the presence of repeating amide (–CONH–) linkages along the polymer chain. These amide groups contribute to the material's strength, toughness, and chemical resistance.

The aliphatic polyamides are generally known as nylons.

Types of Polyamides: There are several types of polyamides, each with unique properties and applications and are usually indicated by numbering system. The no. gives the carbon atom present in the monomer molecules.

Some common examples include:

- Nylon 6 (polycaprolactam)
- Nylon 6,6 (polyhexamethylene adipamide)
- Nylon 11 (polyamide 11)
- Nylon 12 (polyamide 12)

Commercially, Nylon 6,6 and nylon 6,10 are extremely important.

Nylon 6,6

Preparation: The synthesis of Nylon 6,6 is shown in Fig. 2. Nylon 6,6 is prepared by the polycondensation of adipic acid and hexamethylenediamine at high temperatures, forming a polymer with the elimination of water.

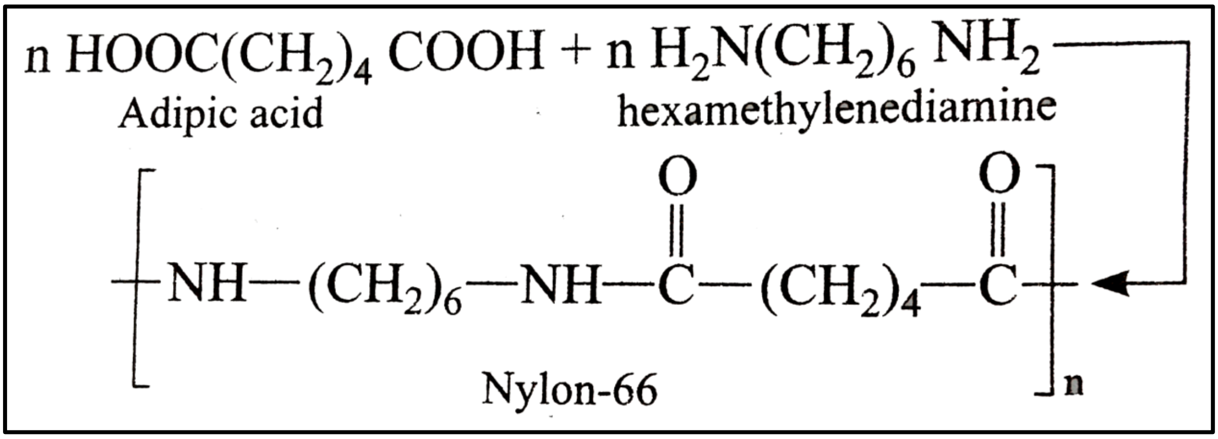


Fig.2. Synthesis scheme for Nylon 6,6

Applications of Nylon 6,6:

- Nylon 6,6 is used as plastic as well as fiber. It has a good tensile strength, abrasion resistance and toughness up to 150 ̊C. Also, it resists many solvents. However, formic acid, cresols and phenols dissolve this polymer.
- It is used in the production of tyre cord, monofilaments, and ropes.
- Used in the manufacturing of textile fibers.
- Being a tough plastic, it is a good substitute for metals in gears and bearings.
- Used to manufacture articles like brushes.

Polyesters:

Polyester is a category of polymers that primarily includes polyethylene terephthalate (PET). It is widely used in textiles, packaging, and many other applications due to its strength, durability, and resistance to shrinking and stretching. However, traditional polyester is derived from petrochemical sources and is not biodegradable, contributing to plastic pollution and environmental degradation.

Types of Polyesters: The specific arrangement of the atoms in a polyester molecule can affect its properties. For example, the strength and stiffness of a polyester fiber can be controlled by varying the length of the chains and the degree of crystallinity.

Polyesters are a category of polymers that contain the ester functional group in their main chain. They are widely used in a variety of applications due to their versatile properties. Some common types of polyesters are:

1. *Polyethylene Terephthalate (PET):*

It is Strong, lightweight, transparent, and resistant to impact and moisture. They are used in Bottles, food packaging, fibers for clothing (such as Dacron), and films.

2. Polycarbonate (PC) (often classified with polyesters):

They are high impact resistance, transparency, and heat resistance polymers. They are employed in Eyewear lenses, optical disks (CDs, DVDs), and bulletproof glass.

3. Polytrimethylene Terephthalate (PTT):

They have good elasticity, stain resistance, and softness. They are used in Carpets, textiles, and apparel.

4. Polycyclohexylenedimethylene Terephthalate (PCT):

They are High temperature and chemical resistance polymers. They exhibit high-performance engineering plastics, especially in the electronics industry.

5. Polyester Polyols:

They find application in the production of polyurethane foams and elastomers.

They are used in Flexible foams for cushions, rigid foams for insulation, and elastomers for adhesives and coatings.

Polyethylene terephalate (PET)

The most common type of polyester is polyethylene terephthalate (PET), which is used in a variety of applications, including clothing, food packaging, and plastic bottles. PET is made from the reaction of ethylene glycol and terephthalic acid.

Synthesis: Polyethylene terephthalate (PET) is typically prepared through a polycondensation reaction between terephthalic acid and ethylene glycol. Here are the steps involved in its preparation.

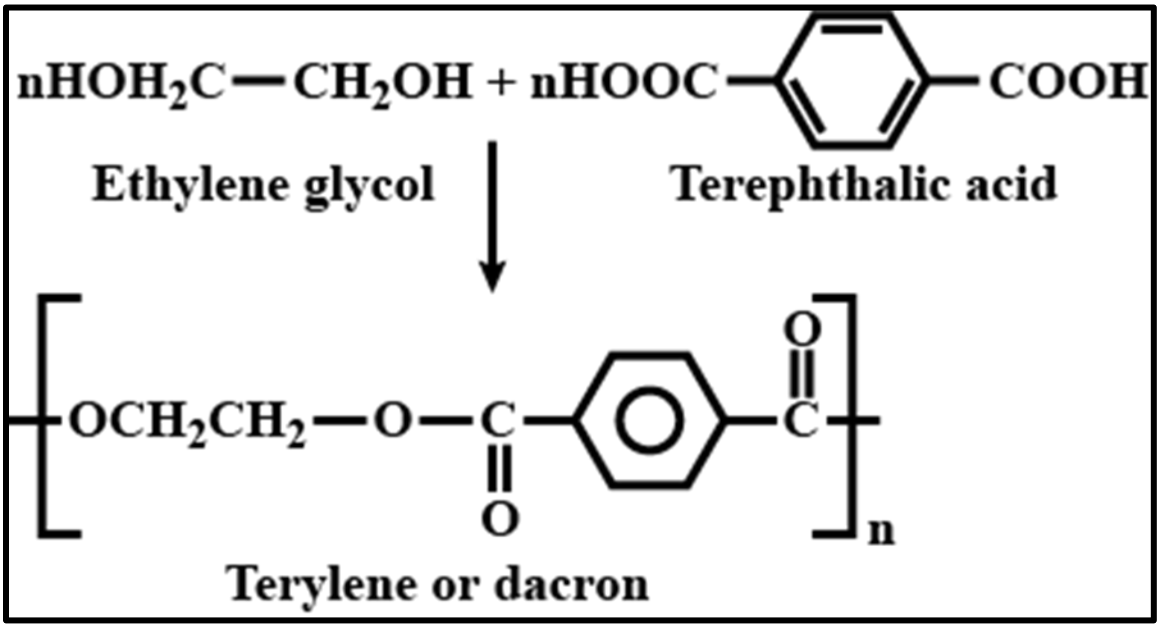


Fig 3. Synthesis of PET (terylene or dacron)

Structure: Polyethylene Terephthalate

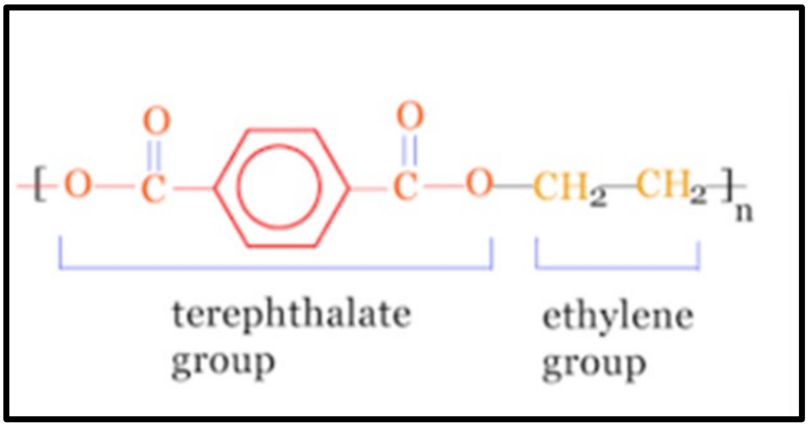


Fig. 4. Terephthalate group and ethylene group of PET with ether linkage

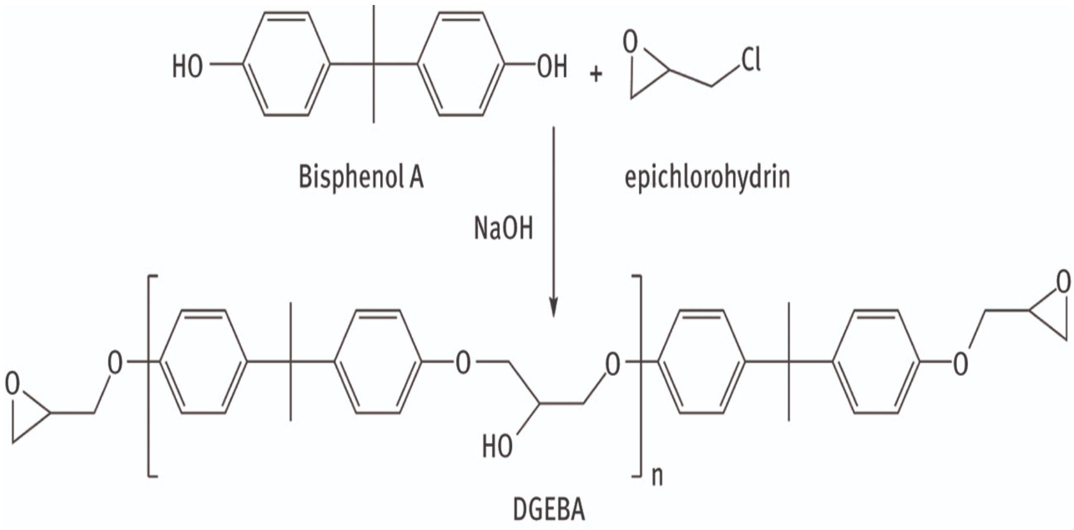
Each type of polyester has unique properties that make it suitable for specific applications, ranging from everyday consumer products to specialized industrial components.

Epoxies :

They are a class of reactive prepolymers and polymers which contain epoxide groups. They are known for their excellent mechanical properties, strong adhesion, and resistance to chemical and environmental degradation. Here are some key types of epoxies and their applications:

Structure: Epoxy resins are formed from a long chain molecular structure similar to vinyl ester with reactive sites at either end. In the epoxy resin, however, epoxy groups instead of the ester groups form these reactive sites. The absence of ester groups means that the epoxy resin has particularly good water resistance.

Fig: Synthesis of Epoxy resin from Bisphenol A and Epichlorohydrin



Types of Epoxies

1. *Bisphenol A Epoxy Resins*

Properties: High mechanical strength, good thermal and chemical resistance, and excellent adhesion.

Uses: Coatings, adhesives, electrical and electronic components, composites, and laminates.

2. *Novolac Epoxy Resins*

Properties: Superior chemical resistance, high temperature performance, and excellent mechanical properties.

Uses: Chemical-resistant coatings, high-performance composites, and applications requiring high thermal stability.

General Properties of Epoxies:

- High bonding strength to a variety of substrates including metals, ceramics, glass, and plastics
- Excellent protective properties, resistance to corrosion, chemicals, and abrasion
- High strength-to-weight ratio, durability, and resistance to environmental factors.

- Excellent insulation properties, thermal stability, and protection against moisture and contaminants
- Clear, glossy finish, and ability to embed object

Biodegradable Polymers

Biodegradable polymers are a class of polymers that can be broken down by microorganisms, such as bacteria, fungi, and algae, into harmless byproducts like water, carbon dioxide, and methane, under aerobic or anaerobic conditions. This makes them a more environmentally friendly alternative to traditional plastics, which can take hundreds or even thousands of years to decompose and contribute significantly to plastic pollution.

Biobased Biodegradable Polymers: derived from renewable resources such as plants, animals, or microorganisms.

Eg. Polylactic acid (PLA), polyhydroxyalkanoates (PHA).

Synthetic Biodegradable Polymers: created through chemical synthesis but designed to degrade under specific environmental conditions.

Eg. polycaprolactone (PCL) and polybutylene succinate (PBS)

Poly(lactic acid) (PLA) is a biodegradable and bioactive thermoplastic derived from renewable resources such as corn starch, sugarcane, or cassava roots, reducing dependence on fossil fuels.

Mechanism of Degradation of PLA

The degradation of polylactic acid (PLA) involves both physical and chemical processes, primarily hydrolysis, which leads to the breakdown of its polymer chains into smaller, more biodegradable molecules. The main stages of PLA degradation are

1. Water Absorption and Hydrolysis
   - The first step in PLA degradation is water absorption. PLA is hydrophilic (water-attracting), so when it's exposed to moisture, water molecules begin to penetrate the polymer structure.
   - This water interacts with the ester bonds in the polymer backbone, initiating hydrolysis, where the ester bonds (–COO–) break down and release oligomers and eventually lactic acid monomers (lactic acid is a smaller molecule than the original polymer chain). This is called as chain scission which leads to the shortening of the polymer chains.
2. Microbial Degradation (Biodegradation)

- After the polymer has undergone significant chain scission, the smaller oligomers and monomers (primarily lactic acid) can be metabolized by microorganisms (like bacteria and fungi) in the environment.
- Microbes can use lactic acid as a carbon source, breaking it down through biochemical processes, converting it into carbon dioxide (CO_2), water (H_2O), and microbial biomass.
- This microbial activity is an essential part of the biodegradation of PLA, and it happens more effectively in environments like industrial composting facilities, where temperature, moisture, and microbial populations are optimized.

3. End Products of Degradation

- The final products of PLA degradation are carbon dioxide, water, and microbial biomass. The carbon dioxide is released into the atmosphere, and the water can return to the environment.
- In some cases, if PLA is exposed to anaerobic (oxygen-lacking) conditions, the degradation might result in methane (CH_4) instead of CO_2, but this is less common.

Environmental Conditions

- PLA's degradation rate depends heavily on environmental conditions. In natural environments like soil or water, degradation is slower because of lower temperatures, reduced microbial activity, and limited moisture. In industrial composting settings, which provide optimal conditions (higher temperatures, moisture, and controlled microbial activity), PLA can degrade more quickly, typically within a few months.

Advantages

- Renewable Resources: Made from renewable biomass, reducing reliance on fossil fuels.
- Biodegradability: decomposes into lactic acid, a naturally occurring substance, under composting conditions, reducing environmental pollution.
- Low Toxicity: Safe for food contact and medical applications.

Disadvantages

- Low Thermal Resistance
- Brittle and less impact-resistant compared to some traditional plastics.
- Degradation Conditions: Requires industrial composting facilities to be biodegradable effectively, which may not be available everywhere.

Uses

- Production of biodegradable plastic films, containers, cups, and utensils.
- Popular material for 3D printing due to its ease of use, low printing temperature, and minimal warping.
- for sutures, stents, and drug delivery systems due to its biocompatibility and biodegradability.
- PLA fibers are used in clothing, upholstery, and non-woven fabrics.
- used in mulch films and other agricultural applications.

Polyhydroxyalkanoates (PHAs) are a class of biodegradable and biocompatible polymers produced by various microorganisms. PHAs are gaining significant attention for their potential to address environmental and sustainability challenges associated with traditional petroleum-based plastics.

Mechanism of degradation of PHA

1. Hydrolytic Degradation

Similar to PLA, PHAs are susceptible to hydrolysis, which is the process where water breaks the ester bonds in the polymer backbone.

2. Microbial Degradation

- After the polymer chains break down into shorter oligomers and monomers, **microorganisms** (bacteria, fungi, and actinomycetes) secrete enzymes like **PHA depolymerases** that specifically break down the polymer into smaller monomeric units, such as **hydroxybutyrate** (for PHB) or **hydroxyvalerate** (for PHBV).
- These monomers are then metabolized by microorganisms as a carbon and energy source. In aerobic conditions, they are converted into **carbon dioxide** (CO_2), **water** (H_2O), and microbial biomass. Under anaerobic conditions, **methane** (CH_4) may be produced instead of CO_2.

Key Differences in PHA and PLA Degradation:

- **Hydrophobicity:** PHAs are generally more hydrophobic than PLA, so they may not absorb water as readily, making hydrolysis somewhat slower in the initial stages.
- **Microbial Action:** PHAs are more readily utilized by a wide variety of microorganisms compared to PLA, which means the microbial degradation phase is usually faster for PHAs.

Advantages:

Biodegradability: broken down by microorganisms in natural environments such as soil, marine environments, and composting facilities. This reduces the accumulation of plastic waste in landfills and oceans.

Renewable Resources: produced from renewable resources, including agricultural waste, plant oils, and sugars, thus reducing reliance on fossil fuels and contributing to a circular economy.

Reduced Carbon Footprint: Production of PHAs results in lower greenhouse gas emissions compared to conventional plastics, contributing to climate change mitigation efforts.

Disadvantages:

- High Production Cost
- Production Complexity: The production process of PHAs is more complex and energy-intensive, requiring specific microorganisms and conditions.
- Feedstock Limitations: The production of PHAs often relies on specific feedstocks, such as sugar or plant oils, which can lead to competition with food resources.

Uses:

- Biocompatibility: non-toxic and biocompatible, making them ideal for medical applications.
- Packaging: production of biodegradable packaging materials, helping to reduce plastic pollution.
- Agriculture: in agricultural films, controlled-release fertilizer coatings, and biodegradable plant pots, promoting sustainable agricultural practices.
- Consumer Goods: disposable items, textiles, and personal care products.

Conducting polymers

Introduction:

Conductive polymers are organic polymers that conduct electricity. Such compounds may be true metallic conductors or semiconductors. It is generally accepted that metals conduct electricity well and that organic compounds are insulating, but this class of materials combines the properties of both. The biggest advantage of conductive polymers is their processability. Conductive polymers are also plastics (which are organic polymers) and therefore can combine the mechanical properties (flexibility, toughness, malleability, elasticity, etc.) of plastics with high electrical conductivities. Their properties can be fine-tuned using the methods of organic synthesis.

Classification of conducting polymers based on nature of conductivity:

1. **Intrinsically conducting polymers or conjugated π −electron conducting polymers**

It is a polymer whose backbones or associated groups consist of delocalized electron pair or residual charge.Such polymers essentially contain conjugated π-electrons backbone, which is responsible for electrical charge. In an electric field, conjugated π-electrons of the polymers get excited, thereby can be transported through the solid polymeric material. Overlapping of orbitals (of conjugated pi-electrons) over the entire backbone results in the formation of valence bands as well as conduction bands, which extend over the entire polymer molecule. Presence of conjugated π -electron in a polymer increases its conductivity to a larger extent.

Examples: Polyacetylene , Polyaniline, Polypyrrole, Polythiophene

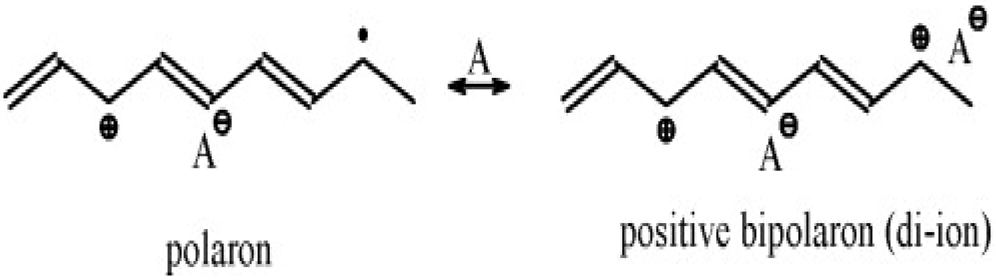
Doped conducting polymers: It is obtained by exposing a polymer to a charged transfer agent in either gas phase or in solution. Intrinsically conducting polymers possess low conductivity ($10^{-10}\,\Omega^{-1}cm^{-1}$), but these possess low ionization potential and high electron affinities, so these can be easily oxidized or reduced. Consequently, the conductivity of ICP can be increased by creating either positive or negative charges on the polymer backbone by oxidation or reduction. This technique, called doping (an analog with semiconductor), is two types:

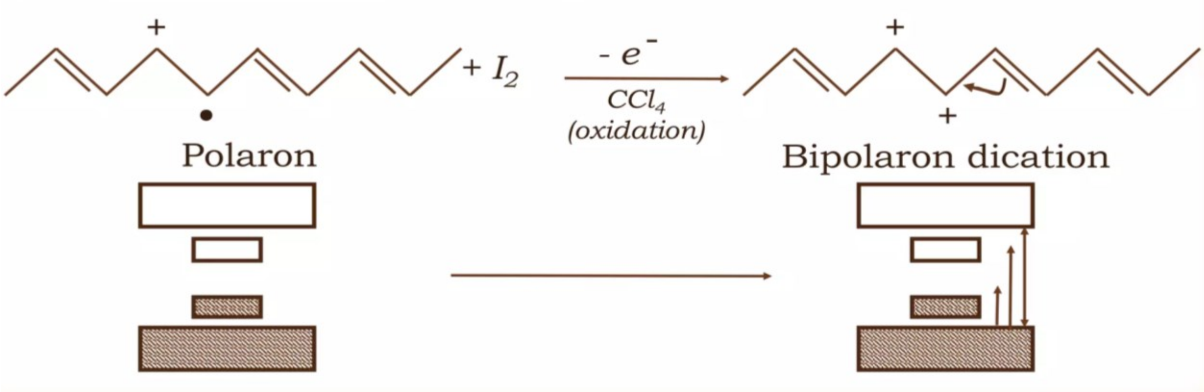
i) **p-doping:** It involves treating an intrinsically conducting polymer with a Lewis acid, thereby oxidation process takes place and positive charges on the polymer backbone are created. Some of the common P-dopant used are I_2, Br_2, AsF_5, PF_6, naphthylamine, etc. used for example

$$-(CH=CH)_n- \; + 2\,FeCl_3 \longrightarrow -(CH=CH)_n^{+} \quad FeCl_4^{-} + FeCl_2$$

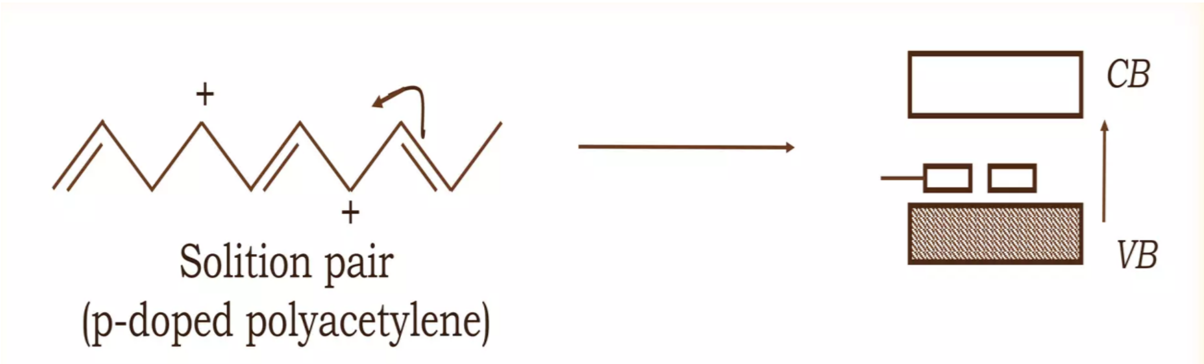
$$-(CH=CH)_n- \; + \; 3\,I_2 \longrightarrow 2-(CH=CH)_n^{+} - I_3^{-}$$

During oxidation process the removal of π electrons from polymer backbone led to the formation of a delocalized radical called ion called polaron having a hole in between valence band and conduction band. The second oxidation of the polaron results in the two positive charge carriers in each chain called bipolaraon, which are mobile due to delocalization. These delocalized charge carriers are responsible for conductance when placed in electric field.





The bipolaron is represented by the paired energy levels, where both levels are occupied within the band gap.

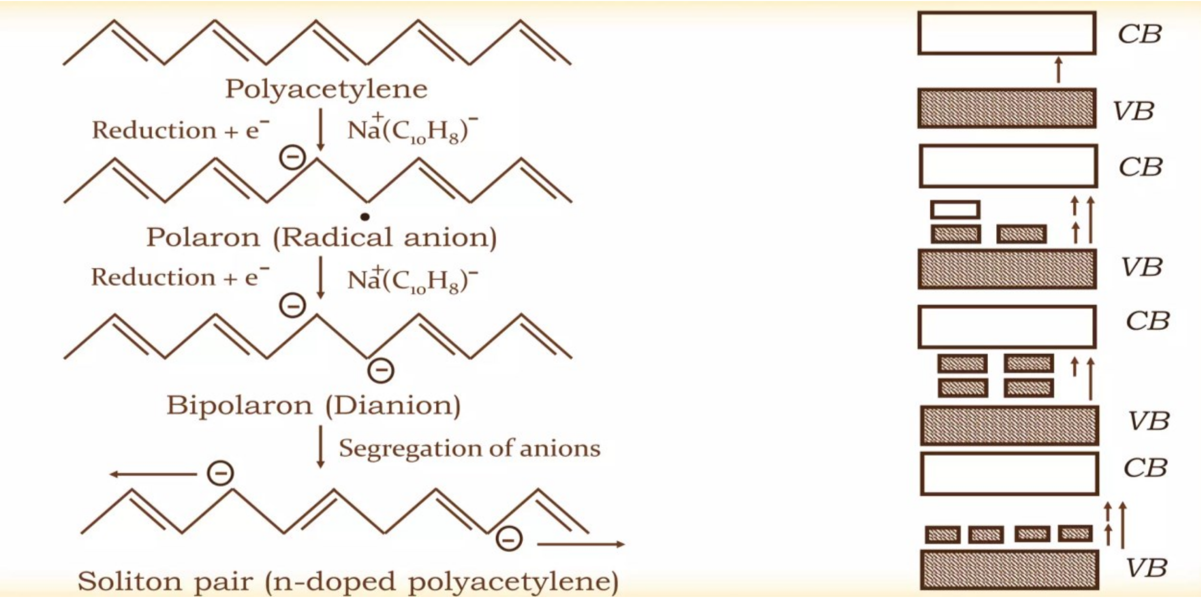


In p-doped polyacetylene, doping introduces holes (positive charges) into the polymer chain, which can lead to the formation of solitons.

(i) **n-doping:** It involves treating an intrinsically conducting polymer with a lewis base thereby reduction process takes place and negative charges on the polymer backbone are created. Some of the common n-dopant used are Li/Na naphthylamine, sodium naphthalide.

For example:

$$-\!\!(CH{=}CH)_n + Na^{\oplus}(C_{10}H_8)^{\ominus} \longrightarrow Na^{\oplus}(CH{=}CH)_n^{\ominus} + C_{10}H_8$$



Extrinsically CONDUCTING POLYMERS (ECPs)

These polymers possess their conductivity due to the presence of externally added ingredients in them.

These are of two types:

1. Conductive element filled polymers

The polymer acts as the binder to hold the conducting elements (such as carbon black, metallic fibers, metallic oxides etc.) together in the solid entity. Minimum concentration of conductive filler, which should be added so that polymer starts conducting is known as percolation threshold. Because at this concentration of filler or conducting element, a conducting path is formed in polymeric material.

2. Blended conducting polymers

These polymers can be obtained by blending processes. They are created by combining a conventional polymer with a conducting polymer, either chemically or physically. They possess better physical, chemical, electrical and mechanical properties and can be easily processed. Example-Polyacetylene and thermoplastic polymers composite

Applications: - Conducting polymers are finding increased use because they are light weight, easy to process and have good mechanical properties. Some of the important applications of conducting polymers are

i) In rechargeable light weight batteries based on perchlorate doped polyacetylene-lithium system. These are about 10 times lighter than conventional lead storage batteries. Such batteries are sufficiently flexible to fir a variety of designed configuration.

ii) ii) In optically display devices based on polythioplene. When the structure is electrically biased (1 to 3V), the optical density of the film changes. i.e., its colour changes. Such electrochromic system produce coloured displays with faster switching time and better viewing than conventional liquid crystal display devices (LED).

iii) wiring in aircrafts and aerospace components.

iv) telecommunication systems

v) antistatic coatings for clothing.

vi) electromagnetic screening materials.

vii) electronic devices such as transistors and diodes.

viii) solar cells, drug delivery system for human body, etc.

ix) photo voltaic devices, e.g., Al /polymer / Au photovoltaic cells.

x) non-linear optical materials.

xi) molecular wires and molecular switches.

Smart polymers:

Smart polymers, also known as stimuli-responsive or intelligent polymers, are materials that can undergo reversible changes in their physical or chemical properties in response to external stimuli such as temperature, pH, light, electric field, or solvent composition. These materials have attracted significant attention due to their potential applications in various fields including drug delivery, tissue engineering, sensors, actuators, and controlled release systems. The responsiveness of smart polymers allows for precise control over their behavior, making them highly versatile and promising for innovative technological advancements.

Temperature responsive polymers

Thermosensitive polymers are a class of intelligent materials capable of adjusting their properties in response to temperature variations. They achieve this by leveraging the controlled and easily measurable stimulus of temperature, which triggers the expansion or contraction of their polymer chains. This transformative process leads to transitions between solution and phase states. The crucial factor in this transition lies in the equilibrium between the hydrophilic (water-attracting) and hydrophobic (water-repelling) segments along the polymer chain, coupled with the overall energy dynamics of the system. These polymers exhibit distinct temperature thresholds known as the upper critical solution temperature (UCST) and lower critical solution temperature (LCST). In the case of LCST polymers, they dissolve readily at lower temperatures but become insoluble as the temperature rises. Conversely, UCST polymers dissolve at higher temperatures yet lose solubility at lower temperatures.

Examples

LCST: Poly (vinyl amide), poly (*N*-substituted acrylamide), poly (N vinylcaprolactam), cellulose, chitosan, xyloglucan and PLGA–PEG– PLGA triblock copolymers

UCST: poly (2-dimethyl) methacryloxyethyl-ammonium propanesulfonate

Applications:

- **Drug Delivery:** Thermoresponsive polymers are used to create drug delivery systems that release medication at specific body temperatures. For example, a polymer could be designed to release a drug when the local temperature rises due to inflammation.
- **Smart Textiles:** Fabrics made with temperature-sensitive polymers can change their properties (such as breathability or color) in response to environmental temperature changes.

Electro-responsive polymers:

Electro-responsive or electroactive polymers (EAPs) represent a specialized category within smart polymers capable of dynamically adjusting their physicochemical characteristics upon exposure to electric signals. Through the conversion of electrical energy into mechanical energy, they exhibit reversible changes in shape, including swelling, shrinking, or bending. These alterations depend on various parameters of the electric current, such as its magnitude, duration, and frequency.

Mechanism of working of Electro-responsive polymers:

- **Conductivity Change:** Some electroresponsive polymers change their electrical conductivity when subjected to an electric field. This can happen through doping (adding or removing electrons), which alters the polymer's electronic structure, making it conductive.
- **Electrostriction:** This refers to the change in the shape or size of the polymer when an electric field is applied. The polymer may expand, contract, or bend in response to the electric field, making it useful in applications like actuators or artificial muscles.
- **Ion Migration:** In some polymers, the application of an electric field causes ions within the material to move, leading to changes in the material's properties. This movement can cause swelling, deformation, or changes in conductivity.

Applications:

- **Actuators and Artificial Muscles:** Electroresponsive polymers can act as actuators, converting electrical energy into mechanical motion. This makes them ideal for use in robotics, particularly in the development of artificial muscles that can mimic natural muscle movements.
- **Smart Windows and Coatings:** Electroresponsive polymers can be used in smart windows that change their transparency in response to an electric field, allowing for controlled light and heat entry. Similarly, they can be used in coatings that change their properties based on electrical inputs.

Photo-responsive polymers:

Photoresponsive polymers are materials that undergo changes in their physical or chemical properties when exposed to light. These changes can include alterations in shape, color, solubility, or mechanical properties, and they are typically reversible, meaning the polymer can return to its original state when the light stimulus is removed or altered.

Mechanism of working of Photoresponsive polymers:

Photoisomerization:

- **Mechanism:** This is one of the most common mechanisms in photoresponsive polymers. Certain molecules within the polymer structure, known as chromophores, can switch between two different forms (isomers) when exposed to specific

wavelengths of light. The most well-known example is azobenzene, which can switch between a cis and trans configuration upon exposure to UV or visible light.
- **Effect:** This change in molecular configuration can lead to macroscopic changes in the polymer, such as bending, stretching, or changes in optical properties. The process is reversible, so the polymer can switch back to its original state when exposed to a different wavelength of light.

Applications:

- **Smart Coatings:** Photoresponsive polymers can be used in coatings that change their properties, such as color or hydrophobicity, in response to light. This can be applied in windows that adjust transparency or surfaces that change their wettability.
- **Soft Robotics and Actuators:** Light-induced changes in shape or mechanical properties can be harnessed to create soft robots or actuators that move or change form in response to light, allowing for remote and precise control of their movements.

FILTRATION MEMBRANES

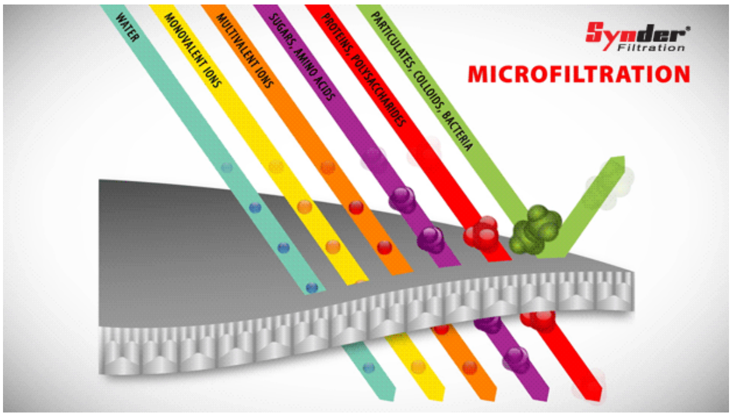
The non-biodegradable polymers contribute to the accumulation of plastic waste in landfills, oceans, and other natural environments, posing threats to wildlife, ecosystems, and human health. Hence, Sustainable biodegradable or recyclable polymers offer solutions to mitigate plastic pollution and promote responsible waste management practices. Hence, filtration membranes are important to overcome this problem.

Polymers are sometimes preferred for membrane filtration because they are more flexible, eas ier to handle, and less expensive than inorganic membranes fabricated from oxides, metals and ceramics.

A membrane is a semi-permeable thin layer of material capable of separating contaminants due to their physical/chemical characteristics. It is a thin layer of material that will only allow certain compounds to pass through it. Usually, the membrane filtration method separates components that are dissolved or suspended particles in a liquid. Membrane filtration is a physical procedure for particle separation of particles using semi-permeable membranes. Membrane filtration is a rapidly expanding field in water treatment. Many different types of filters are available in a wide range of pore sizes and configurations. In addition, there are numerous possible applications for membrane filtration ranging from removing relatively large particulate material to removing dissolved compounds.

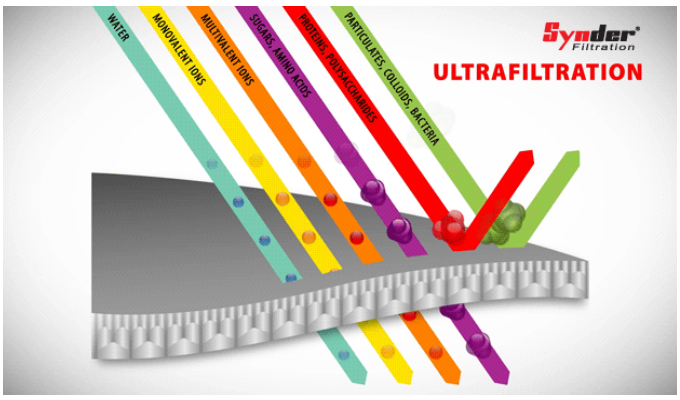
Types of filtration membranes

(a)Microfiltration: Microfiltration membranes have the most open pore sizes of all polymeric membranes. With a pore size range of 0.1 to 10μm, microfiltration membranes are capable of separating large suspended solids such as colloids, particulates, fat, and bacteria, while allowing sugars, proteins, salts, and low molecular weight molecules to pass through the membrane. The PVDF microfiltration membrane filters are manufactured to sustain excellent chemical and heat resistance. They are available in both spiral-wound and flat sheet configurations, to provide more flexibility for customization around specific process applications.



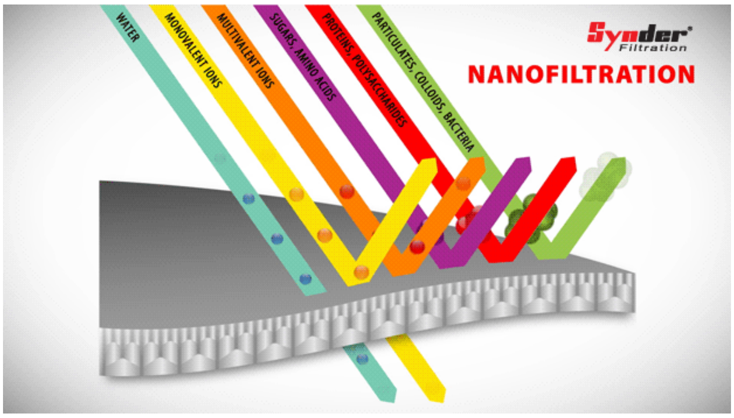
(b)Ultrafiltration membranes: These membranes have pore sizes of 0.01 to 0.1μm, between that of nanofiltration and microfiltration. which contributes to the production of high-quality water. Ultrafiltration membranes are capable of separating larger materials such as colloids, particulates, fats, bacteria, and proteins while allowing sugars and other low molecular weight molecules to pass through the membrane.

Example: Polyethersulfone (PES)



(c)Nanofiltration

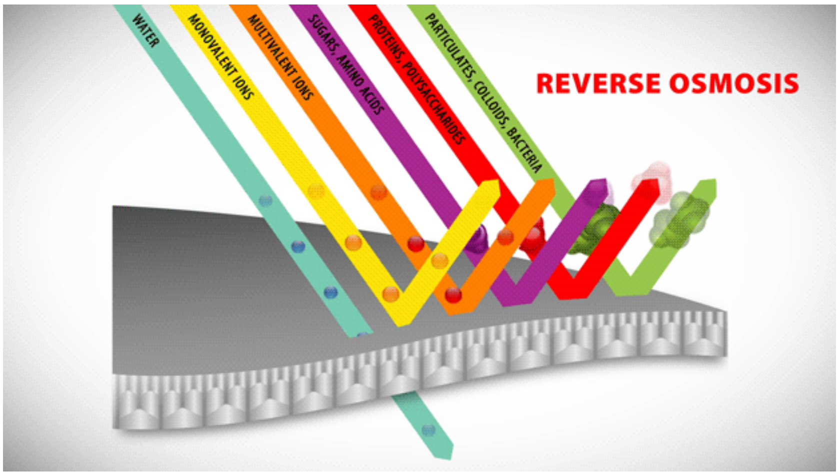
Nanofiltration is a separation process characterized by organic, thin-film composite membranes with a pore size range of 0.1 to 10nm. Unlike reverse osmosis (RO) membranes, which reject all solutes, NF membranes can operate at lower pressures and offer selective solute rejection based on both size and charge. Nanofiltration membranes allow water and some salts to pass through the membrane while retaining multivalent ions, low molecular weight molecules, sugars, proteins, and other organic compounds.



The nanofiltration technique lies between ultrafiltration and reverse osmosis techniques, and it is considered a low-cost process and is capable of removing pesticides, organic matter, desalination of sea water, oil process and pollutants from industrial wastewater.

(d) Reverse osmosis

Reverse osmosis is a membrane treatment process primarily used to separate dissolved solutes from water. Reverse osmosis is most commonly known for its use in drinking water purification, particularly for removing salt and other effluent materials from water molecules.



In this process, due to the presence of a membrane, large molecules of the solute are not able to cross through it and they remain on the pressurized side. The pure solvent, on the other hand, is allowed to pass through the membrane. When this happens the molecules of the solute start becoming concentrated on one side while the other side of the membrane becomes dilute. Furthermore, the levels of solutions also change to some degree.

In essence, reverse osmosis takes place when the solvent passes through the membrane against the concentration gradient. It basically moves from a higher concentration to a lower concentration.

Generally, RO membranes are in the form of flat sheets and hollow fine fibers. The semi-permeable membranes used for the RO process are typically made of a thin polyamide layer (<200 nm) deposited on top of a polysulfone porous layer (about 50 microns) on top of a non-woven fabric support sheet. Pore size is about 0.0001 microns, which excludes most dissolved contaminants while allowing water molecules to pass through.

Differences between types of filter membranes

Particular	**Microfiltration**	**Ultrafiltration**	**Nanofiltration**	**Reverse Osmosis**
Pore size	0.1 to 10 micrometers	of 0.01 to 0.1µm	0.1 to 10nm	<0.001 micrometers
Typical solution treatment	Solution with solid particles	Solution with colloids/macro molecules	small molecules, polyvalent ions	Ions, low molecular weight species, salts
Applied pressure for the process	0.2-5 bar	1-10 bar	5-10 bar	10-150 bar

Filter Membranes advantages, disadvantages and application

Type of Filter membranes	Advantages	Disadvantages	Application
Microfiltration	Simple operation and good stability	Cannot remove dissolved salts and small organic molecules	Drinking water pretreatment, primary filtration during water treatment
Ultrafiltration	High efficient removal of macromolecules and colloids	Limited separation on dissolved salts and small organic molecules	Industrial waste water treatment
Nanofiltration	Low energy consumption, High water production rate, Significant effect on improving quality	Poor selectivity for monovalent ions and membrane is easily get contaminated	Drinking water softening, organic matter removal
Reverse Osmosis	High water quality, suitable for high purification requirements	High energy consumption large amount of wastewater	Sea water desalination, pure water preparation, industrial wastewater treatment

POLYMERIC BIOMATERIALS

Polymers have very long chain molecules which are formed by covalent bonding along the backbone chain. The long chains are held together either by secondary bonding forces such as van der Waals and hydrogen bonds or primary covalent bonding forces through crosslinks between chains. The long chains are very flexible and can be tangled easily.

Polymer is a large molecule, or macromolecule, composed of many repeated subunits. Due to their broad range of properties, both synthetic and natural polymers play essential and widespread roles in everyday life. Polymers range from synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins fundamental to biological structure and function. Natural and synthetic polymers are created via the polymerization of many small molecules, known as monomers. Polymers have assumed an important role in medical applications. The unique properties of polymers are:

1. Flexibility

2- Resistance to biochemical attack

3- Good biocompatibility

4- Lightweight

5- Available in a wide variety of compositions with adequate physical and mechanical properties

6- Can be easily manufactured into products with the desired shape.

Thus, due to these features, polymers will find a broad range of applications in the medical field. One of the types of polymer is polymeric biomaterial. These are the materials used in medical applications that are composed of polymers, which are long chains of repeating molecular units. These biomaterials play a critical role in various medical devices and applications due to their versatility, biocompatibility, and ability to tailor their physical and chemical properties for specific uses.

Types of polymeric biomaterial

(a) **Synthetic polymeric biomaterial**:

Synthetic polymeric biomaterials are man-made materials created from polymers specifically engineered for use in medical and biological applications.

Examples

Polyvinylchloride (PVC): PVC is an amorphous, rigid polymer due to the presence of chloride with a Tg of 75~105°C. It is used in blood, solution storage bags, and surgical packaging. PVC tubing is commonly used in dialysis devices, catheters, and cannulae.

Polyethylene: Polyethylene (PE) is used in Pharmaceutical bottles, nonwoven fabric, catheters, pouches, flexible containers, and orthopedic implants

Polypropylene: It is used in Disposable syringes, blood oxygenator membranes, sutures, nonwoven fabric, and artificial vascular grafts

(b) **Natural Polymeric biomaterial**:

Natural polymeric biomaterials are materials derived from natural sources that are used in medical and biological applications. These materials are composed of polymers, which are large molecules made up of repeating structural units. Natural polymeric biomaterials are favored for their biocompatibility, biodegradability, and ability to interact with biological systems more naturally than synthetic polymers.

Examples

Collagen: It is a major component of our skin and bones, and is a popular choice for wound dressings, drug delivery, and tissue engineering.

Chitosan: This originates from shellfish and can form hydrogels, which are three-dimensional networks that hold a lot of water. These are useful for wound healing, drug delivery, and cell encapsulation.

Hyaluronic Acid: A naturally occurring sugar in our bodies, hyaluronic acid is used for dermal fillers, osteoarthritis treatment, and eye surgery due to its ability to lubricate and support tissues

Overall, natural polymeric biomaterials offer a biocompatible and often biodegradable solution for various medical applications. Their natural origin makes them a valuable tool in regenerative medicine and tissue engineering**.**

Emerging Application - 3D Printing

- 3D printing polymers are a key material in additive manufacturing. Polymers are long chains of molecules, and in 3D printing, they are typically used in filament form or as resin. These materials are chosen for their versatility, ease of use, and ability to be shaped into complex structures. PolyJet 3D printing is an additive manufacturing technology that uses a UV-curable liquid photopolymer, which produces high-resolution layers that enable the creation of complex and highly detailed 3D models. PolyJet can produce full-color, flexible 3D printed materials, simulating the over-molding process in manufacturing. It creates realistic multi-material prototypes and models with full-color elements, labels, and true-to-life textures in a single operation. Polylactic Acid, or PLA, is beloved in the 3D printing community. Acrylonitrile Butadiene Styrene (ABS) is a stalwart in the world of 3D printing. Thermoplastic Polyurethane, or TPU, is renowned for its elasticity and impact resistance, opening up a world of possibilities for 3D printing flexible, durable items. Nylon, or Polyamide, is a staple in industries requiring high strength, durability, and resistance to wear and chemicals. Polycarbonate stands as a beacon of strength and clarity in the filament family, revered for its impact resistance and exceptional durability.

SELF-HEALING POLYMERIC MATERIALS

Self-healing materials are artificial or synthetically created substances that have the built-in ability to automatically repair damages to themselves without any external diagnosis of the problem or human intervention.

The self-healing method has various applications in structural, electronic, medical, and aerospace products. This approach is very significant in situations where repairing or inspection is difficult, hazardous, and costly.

The most common types of self-healing materials are polymers or elastomers. The basic method used to describe the extent of healing in polymeric systems is healing efficiency. It is expressed as a percentage and signifies the extent to which a self-healing material recovers its properties after damage. It's typically calculated by comparing a key property of the healed material (e.g., tensile strength, electrical conductivity) to the same property of the undamaged material .

Applications of Self-Healing Materials

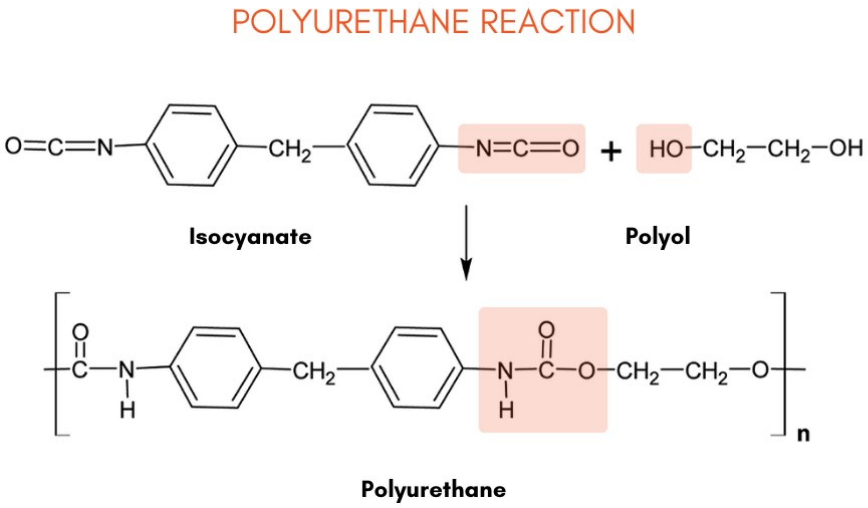
- The practical application of self-healing materials is apparent in various consumer products and industries. An example is self-healing protective coating materials in electronic devices and automobiles. These coating materials possess autonomous repair capabilities, effectively addressing surface damage
- Self-healing materials significantly enhance the durability and lifespan of smartphones and tablets, preserving their initial appearances and ensuring sustained electrical performance over extended periods.
- Aerospace applications also gain advantages from self-healing materials: they maintain essential functions by repairing severe damage from bird strikes or abrasion during flight. This not only enhances safety but also reduces maintenance expenses for aerospace structures.
- It is used in biofield as hydrogels and biocompatible substances, finds a wide range of applications in drug delivery systems, tissue engineering, and implantable medical devices.

Self-healing material example

Polyurethane

Polyurethane self-healing materials are used in various applications due to their ability to recover from damage while offering durability and flexibility.

Polyurethane is a type of polymer that is prepared by an addition reaction between diisocyanate and diol or triol. Polyurethanes (PU) are widely used in the automotive industry. Polyurethanes can be used as protective coatings to protect car surfaces from scratches, abrasion, and corrosion. These coatings provide a durable and resistant barrier, helping to maintain the aesthetic appearance and durability of car parts.



NANOMATERIAL

Nanoscience and nanotechnology deal with objects that have dimensions in the range from 1 nm to about 100 nm. Nano-materials are materials which have at least one of their dimension in the nanometer (1 nm= 10–9 m) range. The physical and chemical properties of nano-materials differ significantly from those of their bulk counterparts. The new properties are the result of an increase in the ratio of surface area to volume. This will change the surface effects such as those that give rise to catalysis, adsorption, adhesion and photonic effects. The reason for this is that the electrons in nanomaterials are confined within such a small volume that quantum effects now dominate optical and electronic behavior. Nano-fibers, nano-wires, nano-scale particles, Nano-channels and nano-tubes are some of the important nanostructures.

Classification

(a) Based on origin

(i) Natural nanomaterials (ii) Artificial nanomaterials

Natural nanomaterials are those which are obtained naturally. Examples:- Carbon-nanotubes and fibers. Artificial nanomaterials are those that are synthesized artificially Examples/Ag nanoparticles and polymeric nanocomposites.

(b) Based on dimension

This classification is based on the number of dimensions that are not confined to the nanoscale range (<100nm). They may be amorphous or crystalline, single crystalline or polycrystalline, made up of one or more elements, metallic, ceramics or polymers.

(i) *Zero-dimensional:* Materials wherein all the dimensions are within the nanoscale range are called zero-dimensional nanomaterial. Eg: quantum dots.

(ii) *1 dimensional:* Here two dimensions are at the nanoscale range, another dimension is not. This leads to needle-like nanomaterials. Eg: nanotubes, nanorods, nanowires.

(iii) *2 dimensional:* Here one dimension is at the nanoscale range, the other two dimensions are not. They exhibit plate-like shapes. Eg: nanocoatings, nanofilms

(iv) *3 dimensional:* These materials are not confined to the nanoscale in any dimension. These are characterized by having three arbitrarily dimensions above 100 nm. They are also known as bulk nanomaterials. 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nano wires/ nanotubes as well as multilayers. Eg: Nanocrystalline materials, nanospheres.

There are other types of classifications based on their field of application, shapes, properties, structures, manufacturing process and morphologies.

Preparation of nanomaterials:

Nanomaterials can be synthesized by two different approaches. They are "Bottom-up" and "Top-down methods". Top-down methods start with micro – or macro scale materials, which are then broken down chemically or physically to nanoparticles. Methods that are used include ball milling, chemical etching, electrospinning and the vaporization of metals using plasmas. They are slow, not cheap, and not suitable for large-scale production. Bottom-up methods involve the assembly of very small units (atoms, molecules or small nanoparticles) to create larger nanomaterials and systems. The fabrication is much less expensive.

"Bottom-up" Approach:

Physical vapor deposition

PVD processes are atomistic deposition processes in which material is vaporized to form a solid or liquid source in the form of atoms or molecules, transported as vapor through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses. The material to be deposited is placed in an energetic, entropic environment so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to thousands of nanometers. The substrates can range in size from very small to very large, in shape from flat to complex geometries. The source-substrate geometry influences the ultimate film uniformity. Two principal methods for optimizing film uniformity over large areas involve varying the geometric location of the source and interposing static as well as rotating shutters between evaporation sources and substrates. The chemical purity of evaporated films depends on the nature and level of impurities that **(1)** are initially present in the source, **(2)** contaminate the source from the heater, crucible, or support materials, and **(3)** originate from the residual gases present in the vacuum system. Typical PVD deposition rates are 10-100 Å/s.

Fig. PVD: Process flow diagram

Vacuum evaporation is one of the important methods for depositing thin films using PVD technique.

Vacuum deposition: This method is used to form thin films of substances that can be vaporized without destroying their chemical identities. Eg. Optical lenses are coated with inorganic materials such as MgF_2, Al_2O_3 and SiO_2. During evaporation, a target consisting of the material to be deposited is bombarded by a high energy source such as a beam of electrons or ions in a high vacuum chamber with a pressure of 10^{-5} torr or less. This dislodges atoms from the surface of the target, 'vaporizing' them. Vaporized atoms from the target move in a straight path to the substrate to be coated. Finally, the metal atoms get deposited on the substrate surface mounted at an appreciable distance away from the evaporation source. Uniformity is obtained by rotating the substrate to be coated.

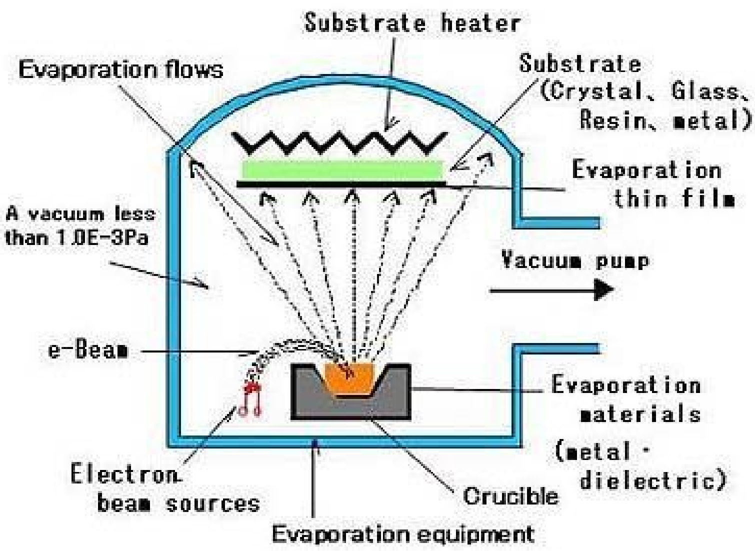


Fig. Schematic diagram of vacuum deposition

The vacuum environment may serve the following purposes by providing low pressure plasma environment, a means for controlling gas and vapor composition and a means for mass flow control into the processing chamber. And reducing the particle density of undesirable atoms and molecules (contaminants) so that the mean free path for collision is long

Advantages:

- PVD coatings are harder and more corrosion resistant than coatings applied by the electroplating process.
- Most coatings have high temperature and good impact strength, excellent abrasion resistance

- More environmentally friendly than traditional coating processes such as electroplating and painting.

- It is possible to change the target material without disturbing the system so that multilayer films can be formed.

Disadvantages:

- It is extremely difficult to coat undercuts and similar surface features
- High capital cost
- Some processes operate at high vacuums and temperatures, require skilled operators
- Processes involving a large amount of heat requires appropriate cooling systems
- The rate of coating deposition is usually quite slow

Chemical Vapor Deposition (CVD)

In this method, the surface is coated with a volatile, stable chemical compound at a temperature below the melting point of the surface. It involves the dissociation and /or chemical reactions of gaseous reactants in an activated (heat, light, plasma) environment, followed by the formation of a stable solid product. The deposition involves homogenous gas phase reactions, which occur in the gas phase, and/or heterogeneous chemical reactions which occur on/near the vicinity of a heated substrate leading to the formation of powders or films, respectively. It has been used to produce ultrafine powders and thin films.

In general, the CVD equipment consists of three main components:

(a) *Chemical vapor precursor supply system:* to generate vapor and deliver to the reactor.

(b) *CVD reactor component*: consists of a reaction chamber equipped with a load-lock for the transport and placement of the substrate into the chamber, a substrate holder, and a heating system with temperature control. The main function is to heat the substrate to the deposition temperature.

(c) *Effluent gas handling system*: This component consists of a neutralizing part for the downstream gases, and /or a vacuum system to provide the required reduced pressure for the CVD process.

Process principles and deposition mechanism: CVD process involves the following key steps:

1. Generation of active gaseous reactant species

2. Transport of these gaseous species into the reaction chamber.

3. Gaseous reactants undergo gas phase reactions forming intermediate species.

   (a) At a high temperature above the decomposition temperatures of intermediate species inside the reactor, homogeneous gas phase reaction can occur where the intermediate species undergo subsequent decomposition and/or chemical reaction.

   (b) At temperatures below the dissociation of the intermediate phase, diffusion/convection of the intermediate species across the heated substrate surface occur. These intermediate species subsequently undergo steps (4-7)

4. Adsorption of gaseous reactants on to the heated substrate and the heterogeneous reaction occurs at the gas-solid interface (i.e. heated substrate) which produces the deposit and by-product species.

5. The deposits will diffuse along the heated substrate surface forming the crystallization center and growth of the film takes place.

6. Gaseous by-products are removed from the boundary layer through diffusion or convection.

7. The unreacted gaseous precursors and by-products will be transported away from the deposition chamber.

Examples: Titanium tetrabromide is evaporated and the gaseous $TiBr_4$ is mixed with hydrogen. The mixture is then passed over a substrate heated to about 1300 °C, such as silica or alumina.

The metal halide undergoes reaction with hydrogen to form a thin film of titanium metal

$$TiBr_4(g) + 2H_2(g) \longrightarrow Ti(s) + 4HBr(g)$$

Films of silicon are formed by decomposing $SiCl_4$ in the presence of H2 at 1200 °C.

$$SiCl_4(g) + 2H_2(g) \longrightarrow Si(s) + 4HCl(g)$$

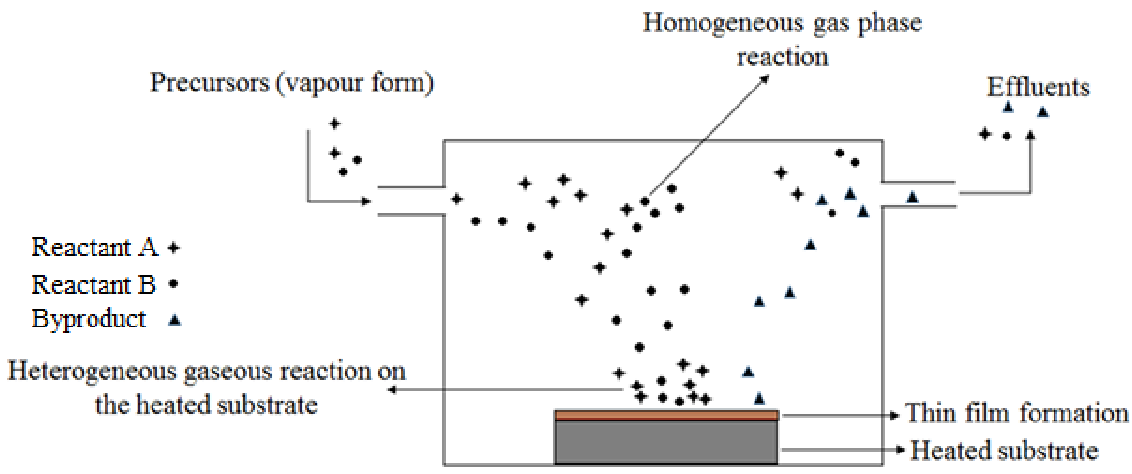


Fig. Schematic diagram of simplified CVD reactor

Advantages

- Capable of producing highly dense and pure materials without carbon or oxygen impurities.
- Produces uniform films with good reproducibility and adhesion at reasonably high deposition rates.
- Has good throwing power and hence can be used to uniformly coat complex shaped components and deposit films.
- Able to control crystal structure, surface morphology and orientation of the products by controlling the process parameters.
- Deposition rate can be adjusted readily. The low deposition rate is favored for the growth of epitaxial thin films for microelectronic applications. The deposition of thick protective coatings is favored by a high deposition rate.
- Reasonable processing cost using the CVD technique.

- The flexibility of using a wide range of chemical precursors such as nitrides, borides, organometallics which enable the deposition of a large spectrum of materials including metal carbides, nitrides, oxides and sulfides.

Drawbacks

- Chemical and safety hazards caused by the use of toxic, corrosive, flammable and/or explosive precursor gases.

- Difficult to deposit multicomponent materials with well-controlled stoichiometry using multisource precursors because different precursors have different vaporization rates.

- The use of more sophisticated reactor and /or vacuum system by CVD variants such as low pressure or ultrahigh vacuum CVD, plasma-assisted CVD and photo-assisted CVD tends to increase the cost of fabrication.

Applications:

- Production of high-quality optical fibers suitable for long distance applications.

- Diamond thin films: They are used as heat sinks for microelectronics and optoelectronics, sensors, microwave devices, coatings for IR windows in nuclear detectors, UV imaging, cold cathodes. The potential applications of diamond films involve speaker diaphragms which are coated with thin films of diamond to provide improved acoustic properties.

Comparison between PVD & CVD

Features	**PVD**	**CVD**
Mechanism of deposition	Thermal energy	Chemical reaction
Deposition rate	High	Moderate
Deposited species	Atoms & ions	Precursor molecules dissociate into atoms
Energy of deposited species	Low (0.1-0.5 eV)	Low; can be high with plasma-assisted CVD
Throwing power	Poor	Good

Sol-gel method

The sol-gel process is a wet-chemical technique used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for the preparation of gel by either discrete particles or network polymers. The process usually consists of five steps:

1. *Preparation of a precursor solution*: The desired colloidal particles are dispersed in a liquid to form a sol. Typical precursors are metal alkoxides, which undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.
2. *Deposition of the sol onto a substrate*: The sol solution is coated on a substrate by spraying, dipping or spinning.

3. *Formation of gel*: The particles in the solid state are polymerized through the removal of the stabilizing components. This can be done either by heating the sol at a low temperature or allowing it to stand for a certain duration. This results in the formation of a gel.
4. *Drying process*: Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification.
5. *Heat Treatment:* After drying, a thermal treatment, or firing process, is often necessary to favor further poly-condensation reaction and enhance mechanical properties, structural stability of the gel.

The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used as a means of producing very thin films of metal oxides for various purposes. Examples include gallium-based nano-materials, Dye-doped gel Glasses, Glass dispersed liquid crystals, Synthesis of glass-metal nano-composite, Metal-silica and Metal oxide-silica nanocomposites.

"Top Down" Approach

Ball Milling

In this process, small balls are allowed to rotate around the inside of a drum and drop with gravity force on to a solid enclosed in the drum. The significant advantage of this method is that it can be readily implemented commercially. The grinding of ceramics can reduce them to a fine powder with each particle having nanoscale dimensions. It is difficult to avoid contamination of the nanoparticles by the materials used in the abrasion process and the particle sizes are not uniform. Polymers cannot be reduced to nanoparticles by grinding because of their molecular structure and their impact resistance. Ball milling can be used to make a variety of new carbon types, including carbon nanotubes. It is useful for preparing other types of nanotubes, such as boron nitride nanotubes and a wide range of elemental and oxide powders. For example, iron with grain sizes of 13-30 nm can be formed. Ball milling is the preferred method for preparing metal oxides.

To successfully prepare metal oxides, it is important to keep the crystallites from reacting and to understand the kinetic energy transferred during crushing. However, a by-product can sometimes be useful. In the production of nanocrystalline Zirconia (ZrO2), zirconium chloride is treated with magnesium oxide during milling to form zirconia and magnesium chloride:

$$ZrCl_4 + 2MgO \rightarrow ZrO_2 + 2MgCl_2$$

The by-product, magnesium chloride, acts to prevent the individual nanocrystallites of zirconia agglomerating. It is washed out at the end of the process.

PROPERTIES OF NANOMATERIALS

1. **Surface properties**: When a bulk material is subdivided into materials on the nanoscale, the total volume remains the same but the collective surface area is increased. This results in an increase in surface-to-volume ratio at the nanoscale as compared to bulk materials. The molecules or atoms at the surface of a nanomaterial possess high surface energy with high reactivity and have a greater tendency to agglomerate. Thus, nanomaterials have a profound effect on reactions that occur at the surface such as catalysis reactions and detection reactions.
2. **Electrical properties**: In bulk metals, the valence and conduction bands overlap, while in metal nanoparticles there is a gap between these bands. The gap observed in metal nanoparticles can be similar in size to that seen in semiconductors (< 2 eV) or even insulators (> 2 eV). This results in a metal becoming a semiconductor. For example, carbon nanotubes can be used as conductors or semiconductors depending on their nanostructure.
3. **Optical properties**: Nanomaterials have peculiar optical properties as a result of the way light interacts with their nanostructure. Eg: In Semiconductor nanocrystals, like

quantum dots, can even have their light emission tuned by size and shape. These properties make nanomaterials useful for solar cells, displays, and bioimaging.

4. **Mechanical properties**: Mechanical properties of nanomaterials may reach the theoretical strength, which is one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is simply due to the reduced probability of defects. Carbon nanotubes are 100 times stronger and six times lighter than steel.

APPLICATION OF NANOMATERIALS

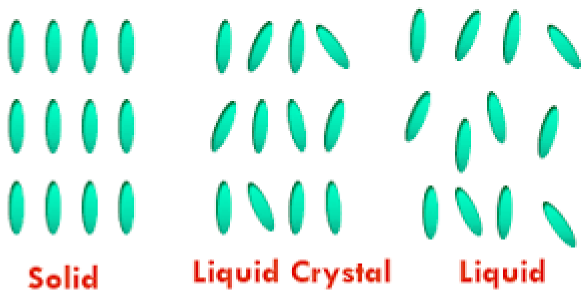
Nanomaterials have revolutionized various engineering fields due to their unique properties. Here are some prominent examples:

- **Nanostructured Materials:** Nanostructured materials with tailored grain sizes and porosity can offer superior mechanical properties like strength, ductility, and wear resistance. These are used in aerospace, automotive, and sporting goods applications.
- **Nanoelectronics:** Miniaturization of electronic components using nanomaterials allows for the development of high-density integrated circuits, leading to faster and more efficient devices.
- **Nanophononics:** Nanomaterials enable the manipulation of light at the nanoscale for applications like solar cells, LEDs, and optical fibers with enhanced light-guiding properties.
- **Nanomedicine:** Nanoparticles are used for drug delivery, targeted therapeutics, imaging, and tissue engineering. Their controlled release properties and ability to target specific cells hold immense potential for personalized medicine.

Introduction to Liquid Crystals:

Liquid Crystals (LC) possess the properties of both conventional liquids and solid crystals. In a crystalline state, the molecules (or atoms) have a definite position and orientation in space in a regular repeated manner in a rigid arrangement and are immobile. They tend to orient in a preferred direction with fixed positions in their lattice i.e., the molecules in solids have a positional and orientational order. On the other hand, the molecules in liquid state neither occupy a specific position nor oriented in a particular manner. The molecules are somewhat free to move randomly and collide with each other, abruptly changing their positions i.e., the liquids do not have positional or orientational order. A liquid crystal (LC) is a state of matter between solids and liquids with both the properties. Normally when a low molar mass solid melts, it forms an ordinary liquid and is isotropic. Organic or inorganic substances which are geometrically anisotropic i.e., long and relatively narrow molecular shape exhibit this intermediate state of order between solids and isotropic liquids. They undergo more than a single transition while passing from solid to liquid through different intermediate states on heating. These intermediate states with different molecular ordering are known as mesophases (also termed as LC phase), derived from a Greek word, *meso* meaning middle. In mesophases, the individual molecules orient with respect to each other, i.e., the molecules tend to remain oriented in a particular direction, called orientational order. The direction of preferred orientation in a mesophase (LC phase) is called the director ($\bar{n}$). In mesophases, the individual molecules also exhibit some regular position with respect to each other, called positional order.

The molecular arrangement in solid, liquid crystal (meso phase) and liquid states can be shown as below.



Since the molecules are in constant motion, in a mesophase they spend more time pointing at the director than in any other direction. The extent of orientational order can be described by taking an average. An average of 0° with respect to the director indicates perfect orientation and can be seen in solids. An average of greater than 45° indicates no orientational order and found in liquids. However, in mesophase (LC state), a smaller average angle with the director is observed which indicates orientational order. Possessing the unique property of orientational or positional order makes them more viable for various technical applications. Some of the mesophases are nematic, smectic, columnar, cubic, lamellar etc.

Display technology has become ubiquitous in our daily life, its widespread applications cover smart phones, tablets, desktop monitors, Televisions, data projectors and augmented reality/virtual reality devices. The LCD was invented in the late 1960s and early 1970s. Since the 2000s, LCDs have gradually displaced bulky and heavy cathode ray tubes (CRTs) and have become the dominant technology. However, an LCD is non-emissive and requires a backlight unit, which not only increases the panel thickness but also limits its flexibility.

Basic structure of LCDs:

The following fig.1 shows a cross section of a typical LCD. There are polarizing films on the outside of the top and bottom glass substrates. The glass substrates (inside of the top and bottom) are coated with a thin layer of indium-tin oxide (ITO), which acts as a transparent conducting film, and then coated with a thin film (polymer) which promotes the alignment of the LCs. In some displays the conducting film is coated only on one of the glass substrates. The LCs are between the glass substrates and completely sealed from the atmosphere. If the display is to use ambient light, there is a reflector behind one of the glass substrates. If the display is to use a light source, then there is a light source (often an LED) behind the display that provides illumination.

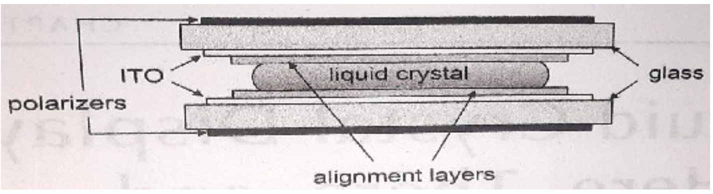


Fig.1: Various components of LCD

Working principle of LCDs:

Without the LC material between the polarizers, the crossed polarizers would block out the light, making the screen appear dark. With the LC material between the polarizers, by adjusting the voltage on the electrodes, the amount of twist by the LC material will vary and the amount of light is passing through. Displays have a reflector on the rear side in which the ambient light is used as a source of light.

Different types of LCDs (TN, IPS, VA):

The three main operating modes for LCDs are (1) the in-plane switching (IPS) mode, (2) the vertical-alignment (VA) mode, and (3) the twisted nematic (TN) mode, which is currently the most often used. While other operating modes do exist, their commercial viability has not yet been shown. The quest for higher-speed operation and improved viewing angles has led to the development of new and improved operating modes.

Twisted Nematic (TN) Displays:

Twisted Nematic (TN) Displays:

A Twisted Nematic (TN) display is the most common type of LCD technology, widely used in various devices like computer monitors, televisions, and handheld devices. The display is named "Twisted Nematic" because it utilizes a layer of nematic liquid crystals (molecules possessing orientational order but no positional order) that are naturally twisted in their resting state. The working principle of TNs is as follows

Basic Structure

- **Liquid Crystal Layer**: The core of a TN display is a thin layer of liquid crystals sandwiched between two indium tin oxide coated glass substrates. This coating is essential to apply an electric field across the liquid crystal layer.
- **Polarizers**: Two polarizing filters which are perpendicular to each other are placed on either side of the ITO coated glass substrates
- **Alignment of Liquid Crystals**: The inner surfaces of the glass substrates are coated with a special alignment layer, usually made of polyimide. The alignment layer is then rubbed in a specific direction using a process called "rubbing process". The rubbing process orients the liquid crystal molecules in contact with the alignment layer. The direction of rubbing on one glass substrate is perpendicular (at 90 degrees) to the direction of rubbing on the other substrate. This perpendicular alignment creates the twisted structure of the liquid crystals, where the molecules gradually twist from one orientation at one substrate to the perpendicular orientation at the other substrate. Therefore, the alignment layers cause the director of the LC between the glass substrates to rotate by 90° in going from one glass surface to another.

Light Passage and Polarization

- **Polarized Light**: When unpolarised light enters the display, it first passes through the rear polarizer, becoming linearly polarized.
- **Twisting the Light**: As the polarized light passes through the twisted liquid crystal layer, the orientation of the light's polarization is rotated by 90 degrees, following the twist of the liquid crystals and passes through the second polarizer making the display appear bright.

Voltage Application

- **Electro-Optical Effect**: When a voltage is applied across the liquid crystal layer through the electrodes, the electric field causes the liquid crystals to align themselves perpendicular to the substrates, effectively untwisting the helical structure.
- **Control of Light**: The degree of untwisting depends on the magnitude of the applied voltage. A fully untwisted configuration will not rotate the polarization of the light which blocks the light making the display appear dark.

Image Formation

- **Pixel Control**: By varying the voltage applied to different pixels, the amount of light passing through each pixel can be controlled. This modulation of light intensity across an array of pixels forms the images on the display.
- **Colour Filters**: For colour displays, each pixel is usually divided into subpixels with red, green, and blue colour filters. By controlling the light passing through these subpixels, a full range of colours can be produced.

The entire process explained above is depicted in fig. 2

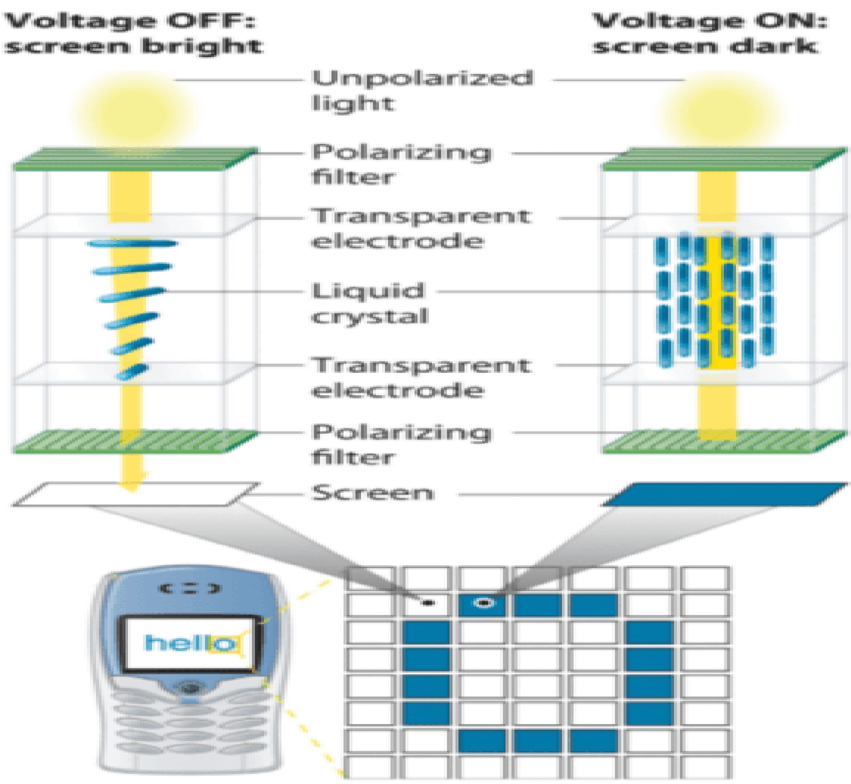


Fig. 2: OFF and ON states of TN LCD

The described LCD produces black numbers, letters, or figures on a silver background using ambient light. Due to minimal current flow between the ITO electrodes, this type of display consumes very little power, making it ideal for battery-powered applications. This type of display is called a passive display, as it does not generate its own light.

To function as an active display, a diffuse light source can be placed behind the display. The light passes through the display once, forming black characters on a bright background. While this increases power consumption significantly due to the backlight, it allows the display to function even in low ambient light conditions.

TN displays are a cost-effective choice for many applications, especially those requiring fast response times, such as gaming. However, their limitations in viewing angles, colour accuracy, contrast, and uniformity can make them less suitable for tasks that demand high image quality and consistency. For users who prioritize these aspects, IPS or VA panels may be better alternatives despite their higher cost.

Applications of Twisted Nematic Displays:

- **Computer Monitors:** TN displays are widely used in budget-friendly computer monitors due to their fast response times and low cost.
- **Gaming Monitors:** Many gaming monitors use TN technology because of its quick response time and low input lag, essential for a smooth gaming experience.
- **Laptops:** TN panels are commonly found in laptops, especially in the lower and mid-range segments, due to their cost-effectiveness and adequate performance for general computing tasks.
- **Televisions:** Some budget televisions use TN technology, although they are less common compared to IPS and VA panels.

Advantages of Twisted Nematic Displays (TN Displays):

- **Fast Response Time:** TN displays have quick response times, making them suitable for applications where fast-moving images are essential, such as gaming monitors and fast-paced video playback.
- **Low Cost:** TN technology is relatively inexpensive to manufacture, making TN displays more affordable than other types of LCDs.

- **High Brightness:** TN panels can achieve high brightness levels, which enhances visibility in well-lit environments.

- **Energy Efficiency:** TN displays consume less power compared to other display technologies, making them energy-efficient.

Disadvantages of Twisted Nematic Displays:

- **Poor Viewing Angles:** TN displays suffer from limited viewing angles, with color and contrast distortion occurring when viewed from angles other than the direct front.

- **Inferior Color Reproduction:** TN panels generally have lower color accuracy and color gamut compared to other types of displays like IPS (In-Plane Switching) and OLED (Organic Light Emitting Diode).

- **Low Contrast Ratios:** The contrast ratio of TN displays is usually lower, resulting in less vibrant images compared to VA (Vertical Alignment) or OLED displays.

- **Color Shift:** TN displays can exhibit color shifting when viewed from different angles, leading to inconsistent color representation.

Vertically Aligned nematic (VAN) displays:

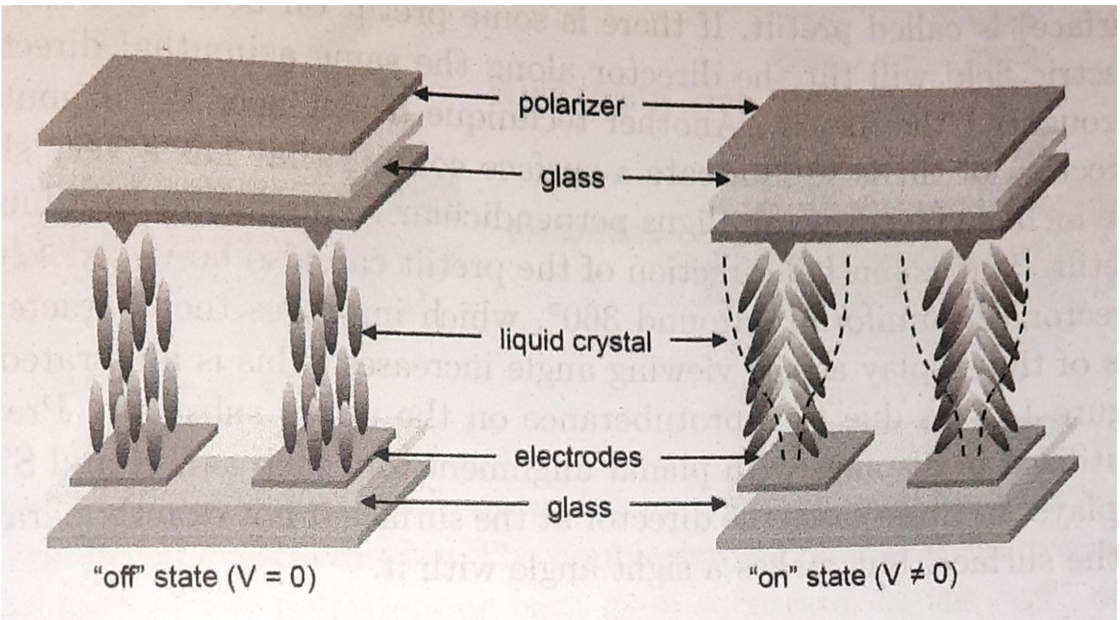


Fig. 3: OFF and ON states of VAN LCDs

Vertically Aligned Nematic (VAN) displays, also known as Vertical Alignment (VA) displays, have a distinct structure that allows for superior contrast ratios and better viewing angles compared to Twisted Nematic (TN) displays. Here is a detailed explanation of the basic structure and working principles of VAN displays:

Basic Structure of VAN Displays

Glass Substrates:

- **Top and Bottom Glass Substrates**: Like all LCDs, VA displays consist of two glass substrates (plates) that encase the liquid crystal layer.
- **Transparent Electrodes**: Both substrates are coated with transparent conductive electrodes made of indium tin oxide (ITO). These electrodes are used to apply an electric field across the liquid crystal layer.

Alignment Layers:

- **Vertical Alignment Layers**: The inner surfaces of the glass substrates are coated with vertical alignment layers. These layers ensure that the liquid crystals are aligned perpendicular to the glass surfaces when no voltage is applied.
- **Pre-Tilt Alignment**: Some VA displays use a slight pre-tilt angle to improve viewing angles and response times. The alignment layers are treated to induce this pre-tilt.

Liquid Crystal Layer:

Vertically Aligned Liquid Crystals: The liquid crystal molecules are naturally aligned perpendicular to the glass substrates in their resting state. This vertical alignment blocks light passage, creating a dark state.

Polarizers:

- **Front and Rear Polarizers**: Polarizing filters are placed on the outer sides of the glass substrates. The orientation of these polarizers is crucial for controlling light transmission.
- **Crossed Polarizers**: Typically, the polarizers are oriented perpendicularly to each other to enhance light modulation.

Working Principle of VAN Displays (As shown in Fig 3)

- **No Voltage Applied (Off State)**:

In the absence of an electric field, the liquid crystals are vertically aligned, blocking light transmission. The crossed polarizers also block light, resulting in a dark state.

- **Voltage Applied (On State)**:

When a voltage is applied, the electric field causes the liquid crystals to tilt away from their vertical alignment.

The degree of tilt depends on the strength of the applied voltage. This tilting allows light to pass through the liquid crystal layer and reach the second polarizer.

The second polarizer then controls the amount of light that exits the display, creating different shades of gray or color.

- **Light Modulation**:

By controlling the voltage applied to each pixel, the display modulates the light passing through, producing various levels of brightness and colors.

For color displays, each pixel is typically divided into red, green, and blue subpixels with corresponding color filters.

Applications of VAN

- **Televisions**: VA panels are widely used in LCD TVs due to their high contrast ratios and good color reproduction.
- **Monitors**: VA displays are popular for general-purpose monitors and professional monitors where high contrast and color performance are important.
- **Mobile Devices**: Some high-end smartphones and tablets use VA panels for better viewing angles and color quality.

Advantages and Disadvantages

Advantages:

- Better viewing angles compared to TN panels.
- Higher contrast ratios and deeper blacks.
- Good color reproduction.

Disadvantages:

- Slower response times compared to TN panels.
- Potential for motion blur and ghosting in fast-moving scenes.

- More expensive than TN panels but generally cheaper than IPS panels.

In-plane switching (IPS) Nematic Displays:

In-Plane Switching (IPS) is a type of liquid crystal display (LCD) technology that was developed to overcome the limitations of Twisted Nematic (TN) and Vertically Aligned Nematic (VA) displays, particularly in terms of viewing angles and color reproduction. Here's a detailed explanation of the basic structure and working principles of IPS displays:

Basic Structure of IPS Displays

Glass Substrates:

- **Top and Bottom Glass Substrates**: Similar to other LCD types, IPS displays have two glass substrates that sandwich the liquid crystal layer.
- **Transparent Electrodes**: These substrates are coated with transparent conductive electrodes, typically made of indium tin oxide (ITO), which are used to apply an electric field across the liquid crystal layer.

Alignment Layers:

Horizontal Alignment: The inner surfaces of the glass substrates are coated with alignment layers that ensure the liquid crystals lie parallel to the glass substrates. This horizontal alignment is crucial for the operation of IPS displays.

Liquid Crystal Layer:

In-Plane Aligned Liquid Crystals: The liquid crystal molecules are aligned parallel to the substrates. When no voltage is applied, the molecules remain in this horizontal alignment, and light can pass through without much alteration.

Polarizers:

- **Front and Rear Polarizers**: Polarizing filters are placed on the outer sides of the glass substrates. The polarizers are typically aligned perpendicularly to each other.
- **Light Control**: The orientation of these polarizers is essential for controlling light transmission through the display.

Working Principle of IPS Displays (As shown in Fig. 4)

- **No Voltage Applied (Off State)**:

In the absence of an electric field, the liquid crystals are aligned in-plane, parallel to the glass substrates. Light passes through the first polarizer, the liquid crystal layer, and is blocked by the second polarizer due to their perpendicular alignment, resulting in a dark state.

- **Voltage Applied (On State)**:

When a voltage is applied, the liquid crystals rotate within the plane of the substrates. This reorientation of the liquid crystals affects the polarization of the light passing through them.

The reoriented light can now pass through the second polarizer, allowing it to exit the display and form the image.

- **Light Modulation**:

By precisely controlling the voltage applied to each pixel, the display can modulate the alignment of the liquid crystals, thereby controlling the amount of light passing through and creating different shades and colors.

For colour displays, each pixel is divided into red, green, and blue subpixels, with corresponding colour filters.

Advantages of IPS Displays

- **Wide Viewing Angles**:
- **Better Colour Reproduction**: IPS displays offer more accurate and consistent colour reproduction due to the uniform alignment of liquid crystals. This makes them ideal for tasks requiring precise colour accuracy, such as photo and video editing.
- **Improved Contrast and Brightness**: Although VA panels typically have higher contrast ratios, IPS panels still offer good contrast and brightness levels. The uniform light transmission and reduced colour shift contribute to better overall image quality.
- **Stable Response Times**: IPS displays generally provide stable response times that are sufficient for most applications, including gaming and video playback. Advances in IPS technology have also improved their performance in high-speed scenarios.

Disadvantages of IPS Displays

Cost: IPS panels are generally more expensive to manufacture compared to other types

of LCD panels like TN (Twisted Nematic). This higher cost is often passed on to consumers.

Response Time: While IPS panels have improved over the years, they typically have slower response times compared to TN panels. This can result in motion blur or ghosting, which is particularly noticeable in fast-paced gaming or high-motion video content.

Power Consumption: IPS panels tend to consume more power than TN panels. This is because the backlight has to be stronger to ensure uniform brightness and color accuracy, which can reduce battery life in portable devices like laptops and smartphones.

Glow Effect: IPS panels can exhibit a phenomenon known as "IPS glow." This is a glowing effect that appears around the edges of the screen when viewing dark content, especially from off-center angles**.**

Applications:

- **Televisions - Home Entertainment**: IPS technology is used in high-end televisions to deliver vibrant colors and wide viewing angles, enhancing the viewing experience for multiple viewers in a room. The ability of IPS panels to maintain image quality from various angles makes them ideal for family or group viewing.
- **Smartphones and Tablets**: Many smartphones and tablets use IPS displays to offer better color accuracy and more consistent image quality. The wide viewing angles of IPS screens improve the user experience when devices are viewed from different angles, such as when sharing content with others.
- **High-Performance Laptops**: IPS panels are used in high-performance and professional laptops where accurate color reproduction and wide viewing angles are important for tasks such as content creation, design, and media consumption.
- **Medical Monitors** : IPS displays are used in medical imaging and diagnostic monitors because of their high color accuracy and consistency. Accurate color representation is crucial for interpreting medical images and diagnostics.
- **Vehicle Dashboards and Infotainment Systems**: IPS panels are increasingly used in automotive displays for dashboards and infotainment systems, providing clear, consistent, and colorful displays that are easy to read from different angles inside the vehicle.

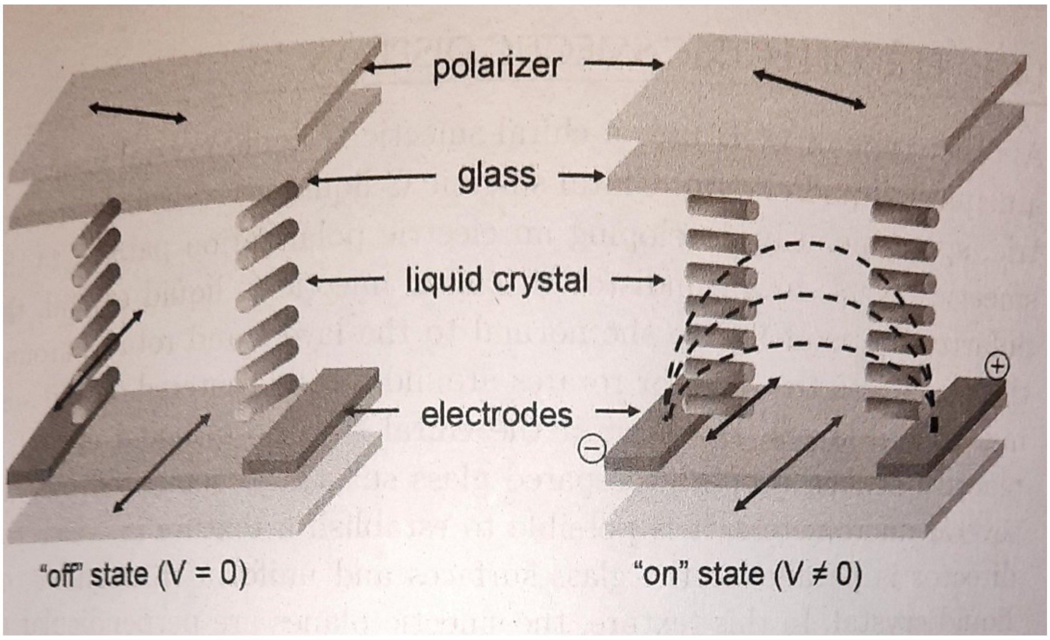


Fig. 4: OFF and ON states of IPS LCDs

In IPS displays, the liquid crystal molecules are aligned parallel to the glass substrates. This horizontal alignment allows light to pass through the liquid crystal layer with minimal distortion when the molecules are adjusted by an electric field. The consistent alignment helps maintain colour accuracy and brightness uniformity across a wide range of viewing angles. In VAN displays, the liquid crystal molecules are aligned perpendicular to the glass substrates when no voltage is applied, and they tilt when a voltage is applied. This vertical alignment can cause greater light scattering and variability in image quality when viewed from different angles, leading to some colour and contrast shifts.

Organic Light-Emitting Diode (OLED) Displays:

After 30 years of intensive material and device development and heavy investment in advanced manufacturing technologies, organic light-emitting diode (OLED) displays have grown rapidly, enabling foldable smart phones and rollable TVs. In the past few years, emissive OLED displays have gained momentum and have competed fiercely with LCDs in TVs and smartphones because of their superior unprecedented dark state, thin profile, and freeform factor. However, some critical issues such as burn-in and lifetime still need to be improved.

Recently, micro-LEDs (μLEDs) and mini-LEDs (mLEDs) have emerged as next generation displays. The micro-LEDs are attractive for transparent displays with high luminance whereas the mini-LEDs can serve either as a locally dimmable backlight for high dynamic range (HDR) LCDs or as emissive displays. Both μLEDs and mLEDs offer ultrahigh luminance and long lifetimes. These features are highly desirable for sunlight readable displays such as smartphones, public information displays, and vehicle displays. The largest challenges that remain are the mass transfer yield and defect repair, which will affect the cost.

To compare different displays, the following performances are important

(1) A HDR and a high ambient contrast ratio

(2) High resolution or a high-resolution density for virtual reality to minimize the screen-door effect.

(3) A wide colour gamut

(4) A wide viewing angle and an unnoticeable angular color shift

(5) A fast motion picture response time to suppress image blur

(6) Low power consumption, which is particularly important for battery-powered mobile displays

(7) A thin profile, freeform, and lightweight system

(8) Low cost.

Organic electroluminescence (EL) is the electrically driven light-emitting phenomenon from organic materials. An example of an organic compound used in OLEDs (Organic Light Emitting Diodes) is **Alq3** (tris(8-hydroxyquinolinato)aluminum). It's a widely used material in OLEDs for the emission layer. Alq3 is a small organic molecule that can emit light when an electric current is applied to it, and it is known for its efficiency in producing green light.

In addition to Alq3, polymers such as **PFO** (poly(9,9-dioctylfluorene)) are also used in OLEDs, especially for flexible displays, where they help create light-emitting layers. These organic materials are a key part of the technology that makes OLED displays bright, thin, and flexible.

Basic Structure of OLEDs

Organic Layers:

- **Emissive Layer:** Contains organic compounds that emit light when an electric current passes through them. These compounds are usually based on small organic molecules or polymers.

- **Conductive Layer:** Helps transport electrons and holes to the emissive layer. It usually consists of organic materials that conduct electrical charges.

Anode and Cathode:

- **Anode:** A transparent conductive layer (often made of indium tin oxide, ITO) that injects positive charges (holes) into the organic layers.
- **Cathode:** A layer that injects negative charges (electrons) into the organic layers. The cathode can be made of metals such as aluminum or lithium.

Substrates:

Glass or Flexible Plastic: The OLED layers are typically sandwiched between a glass or plastic substrate (on the bottom) and an encapsulating layer (on the top). Flexible substrates allow for bendable or rollable OLED displays.

Encapsulation:

Protective Layer: Encapsulation protects the organic materials from moisture and oxygen, which can degrade the performance of the OLED.

The structure and typical materials used in bilayer OLED is given in the following fig. 5.

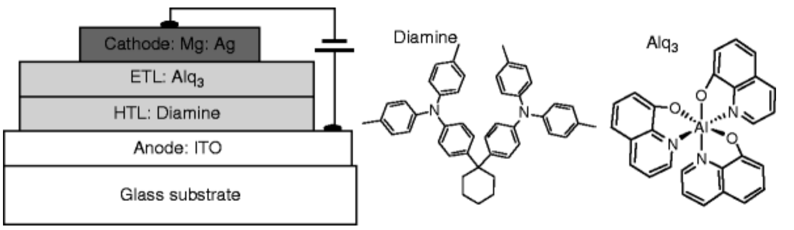


Fig. 5: Structure and materials used in bilayer OLED

Working Principle of OLEDs

Charge Injection:

When a voltage is applied across the OLED, the anode injects holes into the conductive layer, and the cathode injects electrons into the emissive layer.

Charge Transport:

The holes and electrons move towards each other through the conductive and emissive layers.

Recombination and Light Emission:

When an electron and a hole meet in the emissive layer, they form an exciton (a bound state of the electron and hole). The exciton quickly recombines, releasing energy in the form of a photon. This process is known as electroluminescence.

Colour Generation:

The colour of the emitted light depends on the specific organic compounds used in the emissive layer. Different materials emit different colors (red, green, blue), and combining these can produce a full-colour display.

Advantages of OLEDs:

OLEDs are superior to LCDs in many ways.

- The biggest advantage is that OLEDs are much thinner (around 0.2–0.3mm or about 8 thousandths of an inch, compared to LCDs, which are typically at least 10 times thicker) and consequently lighter and much more flexible.
- OLEDs produce truer colors (and a true black) through a much bigger viewing angle (unlike LCDs, where the colors darken and disappear if you look to one side).
- OLEDs are brighter and need no backlight, so they consume much less energy than LCDs (that translates into longer battery life in portable devices such as cellphones and MP3 players).
- LCDs are relatively slow to refresh (often a problem when it comes to fast-moving pictures such as sports on TV or computer games), OLEDs respond up to 200 times faster.
- Being much simpler, OLEDs should eventually be cheaper to make than LCDs (though being newer and less well-adopted, the technology is currently much more expensive).

Drawbacks of OLEDs:

- OLED displays don't last as long: degradation of the organic molecules meant that early versions of OLEDs tended to wear out around four times faster than conventional LCDs or LED displays.
- Organic molecules in OLEDs are very sensitive to water. Though that shouldn't be a problem for domestic products such as TV sets and home computers, it might present more of a challenge in portable products such as cellphones.

- OLED displays can suffer from burn-in, where static images left on the screen for prolonged periods can cause permanent ghost images.

Applications of OLEDs

1. Televisions:
    - High-end OLED TVs offer superior picture quality with deep blacks, vibrant colors, and excellent contrast ratios.
2. Smartphones and Tablets:
    - Many flagship smartphones and tablets use OLED screens for their superior display quality and thinner form factor.
3. Wearable Devices:
    - OLEDs are used in smartwatches and fitness trackers for their flexibility, lightweight nature, and vibrant displays.
4. Monitors:
    - Professional-grade monitors for photo and video editing leverage OLED technology for accurate color reproduction and high contrast.
5. Automotive Displays:
    - OLEDs are used in car dashboards and infotainment systems for their flexibility and superior display quality.
6. Virtual Reality (VR) and Augmented Reality (AR):
    - OLEDs are preferred in VR and AR devices for their fast response times and high resolution, enhancing the immersive experience.

MicroLEDs

MicroLEDs represent a cutting-edge display technology that offers significant improvements over traditional display types such as OLEDs and LCDs.

Basic Structure of MicroLEDs

MicroLED displays consist of microscopic light-emitting diodes (LEDs) that form individual pixels. Each pixel is composed of three sub-pixels (red, green, and blue) to produce a full range of colors. The components of MicroLED are:

MicroLED Chips:

- These are tiny LED chips that emit light when an electric current is applied. These chips are typically smaller than 100 micrometers each.
- Each sub-pixel (red, green, and blue) is a separate microLED.

Substrate: It is the base material on which the microLEDs are assembled. Common substrates include sapphire, silicon, or glass.

Backplane: Contains the driving circuitry that controls the current supplied to each microLED, allowing for precise control of brightness and color.

Interconnects: These are the electrical connections that link the microLEDs to the driving circuitry.

Encapsulation Layer: It protects the microLEDs from environmental factors such as moisture and dust.

Working Principle of MicroLEDs

Charge Injection: When a voltage is applied across the microLED, electrons and holes are injected into the p-n junction (the interface between the p-type and n-type semiconductor materials).

Recombination and Light Emission: The electrons and holes recombine at the p-n junction, releasing energy in the form of photons (light). This process is called electroluminescence. The color of the emitted light depends on the material composition of the microLED (e.g., InGaN for blue/green, AlGaInP for red).

Color Mixing: Each pixel consists of red, green, and blue microLEDs. By varying the intensity of each sub-pixel, a wide range of colors can be produced through additive color mixing.

Brightness Control: The brightness of each microLED is controlled by adjusting the current supplied to it. Higher current results in brighter light emission.

Advantages of MicroLEDs

- High Brightness and Efficiency: MicroLEDs can achieve very high brightness levels while maintaining energy efficiency. They are brighter than OLEDs and consume less power.
- Superior Color Accuracy and Range: MicroLEDs offer a wider color gamut and more accurate color reproduction due to the direct emission of light from individual LEDs.
- Fast Response Time: MicroLEDs have extremely fast response times, reducing motion blur and making them ideal for fast-moving content like gaming and sports.
- Long Lifespan: Unlike OLEDs, microLEDs are not prone to burn-in and have a longer operational lifespan since they do not degrade as quickly.
- High Contrast Ratio: MicroLEDs can achieve true black levels by turning off individual LEDs, resulting in an infinite contrast ratio.
- Scalability and Modularity: MicroLED displays can be made in various sizes and shapes, and modular panels can be combined to create larger displays without visible seams.

Disadvantages of MicroLEDs

- Manufacturing Complexity: The process of fabricating and assembling millions of tiny microLEDs is highly complex and requires precise alignment and bonding techniques.
- Cost: Due to the sophisticated manufacturing process, microLED displays are currently more expensive to produce than OLED and LCD displays.
- Yield and Uniformity: Achieving high yield and uniformity in the production of microLEDs can be challenging, leading to higher costs and potential quality issues.
- Integration: Integrating microLEDs with existing backplane technologies and driver circuits requires advanced microfabrication techniques.

Applications of MicroLEDs

- Televisions: High-end TVs with superior brightness, color accuracy, and contrast ratios. Examples include Samsung's "The Wall."
- Wearables: Smartwatches and fitness trackers benefit from the high brightness and low power consumption of microLEDs.
- Augmented Reality (AR) and Virtual Reality (VR): MicroLEDs are ideal for AR and VR headsets due to their fast response times, high brightness, and compact size.

- Automotive Displays: Used in dashboards and infotainment systems for their brightness and durability.

Foldable Displays:

Foldable displays represent an innovative advancement in display technology, allowing screens to bend, fold, and flex without compromising functionality. This technology enables new form factors for electronic devices, enhancing portability and versatility.

Basic Structure of Foldable Displays

Foldable displays are primarily based on flexible OLED (Organic Light Emitting Diode) technology, although research is ongoing into flexible MicroLEDs and other display types. The structure includes:

- **Flexible Substrate**: A base layer made of materials such as polyimide, which is thin, durable, and bendable, replacing the rigid glass used in traditional displays.
- **Flexible OLED Layers:**

Organic Layers: These layers include the emissive layer, conductive layer, and other organic compounds that emit light when an electric current is applied.

Encapsulation Layers: Protect the organic materials from environmental factors like moisture and oxygen. Flexible encapsulation techniques, such as thin-film encapsulation, are used to maintain flexibility.

- **Thin-Film Transistor (TFT) Backplane**: Controls the pixels by switching them on and off. The backplane must be flexible and durable to withstand repeated bending.
- **Touch Sensor Layer:** Flexible touch sensors are integrated to enable touch functionality. These sensors are made from flexible materials like indium tin oxide (ITO) or silver nanowires.
- **Cover Layer**: The topmost layer that protects the display from scratches and damage. Flexible cover materials, such as ultra-thin glass or plastic, are used.

Working Principle of Foldable Displays

The working principle of foldable displays is like that of traditional OLED displays but adapted to flexible materials:

- **Charge Injection**: When voltage is applied, electrons and holes are injected into the emissive layer from the cathode and anode, respectively.
- **Recombination and Light Emission**: The electrons and holes recombine in the emissive layer, releasing energy in the form of photons, which is visible light.
- **Flexibility**: The flexible materials and components are engineered to withstand mechanical stress and maintain performance while bending or folding.

Advantages of Foldable Displays

- Portability and Versatility: Foldable displays allow devices to be more compact and portable. For instance, a tablet-sized screen can be folded into a smartphone-sized device.
- Innovative Form Factors: Enables new design possibilities for devices, such as foldable smartphones, rollable TVs, and flexible wearables.
- Enhanced User Experience: Larger screen real estate can be achieved in a compact form, providing a better viewing experience for multimedia and multitasking.
- Durability: Flexible displays can be more resistant to impact and drops compared to traditional glass-based screens.

Disadvantages of Foldable Displays

- Durability and Longevity: Ensuring that the display can withstand repeated bending without degrading in performance is a significant challenge. Wear and tear at the fold crease is a common issue.
- Manufacturing Complexity: Producing foldable displays involves complex manufacturing processes and stringent quality control to ensure flexibility and durability.
- Cost: The advanced materials and processes required to produce foldable displays make them more expensive than traditional displays.
- Creasing and Folding Marks: Visible creases or folding marks can appear at the fold points, which can affect the visual experience.
- Battery and Component Integration: Integrating flexible batteries and other components that can withstand bending is challenging, affecting the overall design and functionality.

Applications of Foldable Displays

- Smartphones: Foldable smartphones, such as the Samsung Galaxy Fold and Huawei Mate X, offer larger screens in a compact form factor.
- Tablets and Laptops: Devices that can switch between tablet and laptop modes, providing versatility for both productivity and entertainment.
- Wearables: Flexible displays for smartwatches and fitness trackers that conform to the wrist for better comfort and functionality.
- Televisions: Rollable TVs that can be rolled up when not in use, saving space and offering a sleek design.
- E-readers and Notebooks: Foldable e-readers and digital notebooks that offer a larger reading or writing surface in a portable form.
- Automotive Displays: Flexible displays in car interiors that can conform to the dashboard or other curved surfaces for enhanced aesthetics and functionality.