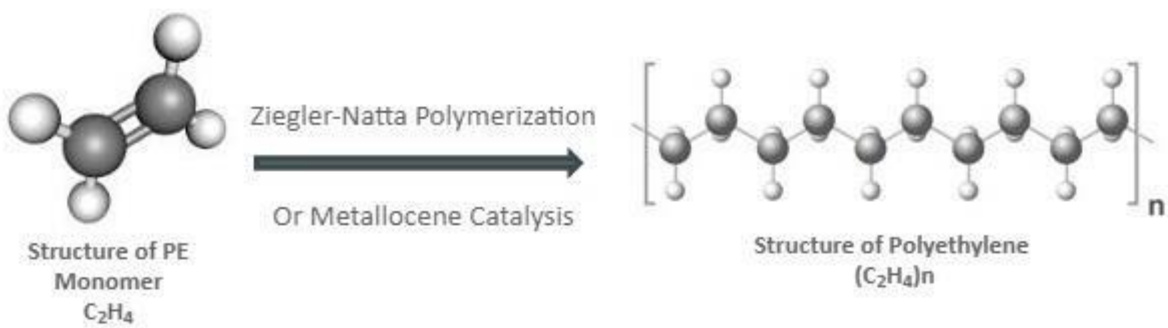
19CH103 ENGINEERING CHEMISTRY

UNIT-4 HIGH POLYMERS

POLYETHYLENE

Polyethylene is made by addition or radical polymerization of ethylene (olefin) monomers. (Chemical formula of Ethene - C_2H_4). Ziegler-Natta and Metallocene catalysts are used to carry out polymerization of polyethylene.



Common Types of Polyethylene (PE)

PE belongs to polyolefin family of polymers and is classified by its density and branching. The most common types of polyethylene are:

- Branched Versions
    - Low-density polyethylene (LDPE)
    - Linear low-density polyethylene (LLDPE)

- Linear Versions
    - High-density polyethylene (HDPE)
    - Ultra-high-molecular-weight polyethylene (UHMWPE)
- Cross-linked polyethylene (PEX or XLPE)

In addition PE is also available in other types such as: (not discussed in detail in this guide)

- Medium-density polyethylene (MDPE)
- Very-low-density polyethylene (VLDPE)
- High-molecular-weight polyethylene (HMWPE)
- Ultra-low-molecular-weight polyethylene (ULMWPE)
- Chlorinated polyethylene (CPE)

Some of the polyethylene suppliers include: Borealis, Celanese Corporation, Dow Chemicals, ExxonMobil Chemical, LyondellBasell, NOVA Chemicals, SABIC. See all Polyethylene Suppliers

Properties of High Density Polyethylene

1. HDPE Melting point: 120-140°C
2. Density of HDPE: 0.93 to 0.97 g/cm^3
3. High Density Polyethylene Chemical resistance:
    - Excellent resistance to most solvents
    - Very good resistance to alcohols, dilute acids and alkalis
    - Moderate resistance to oils and greases
    - Poor resistance to hydrocarbons (aliphatic, aromatic, halogenated)
4. Continuous temperature: -50°C to +60°C, Relatively stiff material with useful temperature capabilities
5. Higher tensile strength compared to other forms of polyethylene
6. Low cost polymer with good processability
7. Good low temperature resistance
8. Excellent electrical insulating properties
9. Very low water absorption

10. FDA compliant

Disadvantages of HDPE

- Susceptible to stress cracking
- Lower **stiffness** than polypropylene
- High mold shrinkage
- Poor UV- and low heat resistance
- High-frequency welding and joining impossible

However, weathering resistance of HDPE can be improved by the addition of carbon black orUV absorbing additives. Carbon black also helps to reinforce the material.

Applications of High Density Polyethylene (HDPE)

Excellent combination of properties makes HDPE an ideal material in diverse applications across industries. It can be engineered according to the end use requirements.

Some of the major uses of high density polyethylene include:

HDPE in Packaging and Consumer Good Applications

1. **Packaging Applications** – High Density Polyethylene is used in several packaging applications including crates, trays, bottles for milk and fruit juices, caps for food packaging, jerry cans, drums, industrial bulk containers etc. In such applications HDPE provides the end product a reasonable impact strength.

2. **Consumer Goods** – Low cost and easy processability make HDPE a material of choice in several household/ consumer goods like garbage containers, housewares, ice boxes, toys etc.

POLY VINYL CHLORIDE

Polyvinyl Chloride (PVC or Vinyl) is an economical and versatile thermoplastic polymer widely used in building and construction industry to produce door and window profiles, pipes (drinking and wastewater), wire and cable insulation, medical devices etc. It is the world's third largest thermoplastic material by volume after **polyethylene** and **polypropylene**.

It is a white, brittle solid available in powder form or granules. Thanks to its versatile properties such as lightweight, durable, low cost and easy processability, PVC is now replacing traditional building materials like wood, metal, concrete, rubber, ceramics, etc. in several applications.

This plastic database is available to all, free of charge. You can filter down your options by property (mechanical, electrical…), applications, conversion mode and many more dimensions.

PVC was first made in 1872 by German chemist Eugen Baumann. The polymer appeared as a white solid inside flasks of the newly discovered vinyl chloride gas that had been left exposed to sunlight.

Polyvinyl Chloride is available in two broad categories:

- **Plasticized or Flexible PVC or PVC-U** (Density: 1.1-1.35 g/cm^3): Addition of compatible plasticizers to PVC lowers the crystallinity and by acting like lubricants, yields a much clearer and flexible plastic.

- **Unplasticized or Rigid PVC or PVC-P** (Density: 1.3-1.45 g/cm^3): It is a stiff and cost effective plastic material with high resistance to impact, water, weather, chemicals and corrosive environments.

Strengths	**Limitations**
Rigid PVC	
• Low cost & high stiffness • Intrinsic flame retardant • FDA compliant & also suitable for transparent applications • Better chemical resistance than plasticized PVC • Good electrical insulation & vapor	• Difficult to melt process • Limited solvent stress cracking resistance • Becomes brittle at 5°C (when not modified with impact modifiers and/or processing aids) • Low continuous service temperature of 50°C

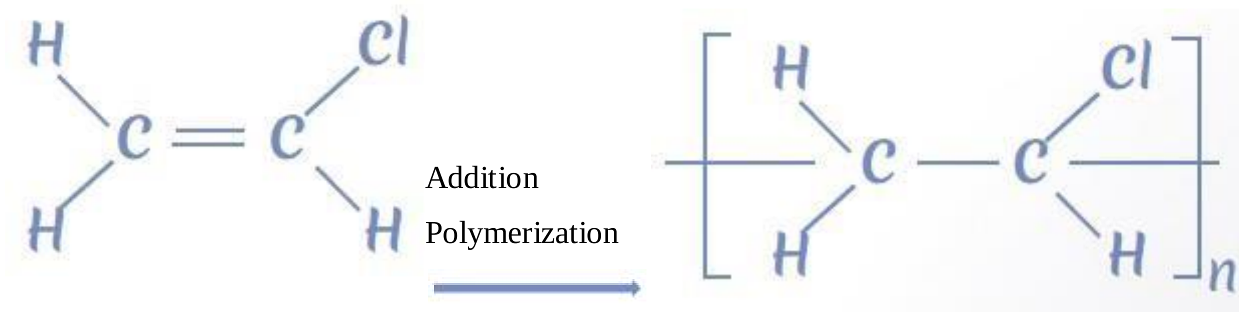
barrier properties • Good dimensional stability at room temperature	
Flexible PVC	
• Low cost, flexible & high impact strength • Good resistance to UV, acids, alkalis, oils and many corrosive inorganic chemicals • Good electrical insulation properties • Non-flammable & versatile performance profile • Easier to process than rigid PVC	• Properties can change with time, due to plasticizer migration • Attacked by ketones; some grades swollen or attacked by chlorinated and aromatic hydrocarbons, esters, some aromatic ethers and amines, and nitro-compounds • Tends to degrade at high temperatures • Non suitable for food contact with some plasticizers • Lower chemical resistance than rigid PVC

» Compare properties of Flexible PVC Vs. Rigid PVC in detail

PVC Manufacturing Process

In 1872, E. Bauman exposed vinyl chloride sealed in a tube to sunlight and produced a white solid called PVC. By World War I, Germany was producing a number of flexible and rigid PVC products which were used as a **replacement for corrosion-resistant metals**.

Vinyl chloride monomer (VCM) is produced from the chlorination of ethylene and pyrolysis of the resulting ethylene dichloride (EDC) in a cracking unit. PVC (glass transition temperature: 70-80°C) is produced by polymerization of vinyl chloride monomer (VCM).



Molecular Formula of Vinyl Chloride
C_2H_3Cl

Molecular Formula of Polyvinyl Chloride
$(C_2H_3Cl)_n$

The popular methods used to manufacture PVC commercially are: **Suspension PVC (S-PVC) Process** and **Bulk or Emulsion (E-PVC) Process**

Suspension Polymerization accounts for 80% of PVC production worldwide

Suspension PVC (S-PVC) Process

In pressure-tight reactor, the monomer is introduced with polymerization initiator and other additives. The content of the reaction vessel are mixed continuously to maintain suspension and ensure uniform particle size of PVC resin.

Typical suspension polymerized PVC has a mean particle size of 100-150 µm with a range of 50-250 µm.

S-PVC grades are formulated to meet an extensive range of requirements such as, high plasticizer absorption for flexible products, or high bulk density and good powder flow required for rigid extrusion

Bulk or Emulsion (E-PVC) Process

In this process, surfactants (soaps) are used to disperse the vinyl chloride monomer in water. The monomer is trapped inside soap micelles are protected by the soap and polymerization takes place using water soluble initiators.

The primary particles are solid, smooth surfaced spheres which are clustered into irregular shaped aggregates with a typical mean particle size of 40-50 µm with a range of 0.1-100 µm.

E-PVC resins are used in a wide range of specialty applications such as coating, dipping or spreading

Suspension PVC (S-PVC) Process	Bulk or Emulsion (E-PVC) Process
• Lower flexible PVC formula costs • PVC particles obtained are mixed with plasticizers & can be extruded in pellets which are further usedfor processing via extrusion, calendering, injection molding... • Processing equipment is typically very expensive	• Higher flexible PVC formulacosts • PVC powder obtained is mixed with plasticizers to produce a paste which is further used for coatings, dipping, spraying... • Processing Equipment may or may not be very expensive

Chlorinated PVC (CPVC)

CPVC is manufactured by chlorination of PVC polymer thereby raising the chlorine content from 56% to around 66%.

Chlorination of PVC reduces the forces of attraction between the molecular chains. CPVC is also essentially amorphous. Both of these factors allow CPVC to be stretched more easily and to a greater extent than PVC above its Tg. Pipe (436), moldings (376) and sheet are formulated for high temperature use based on CPVC or blends of CPVC and PVC.

Key Properties of PVC Polymer

1. **Electrical Properties**: PVC is a good insulation material, thanks to its good dielectric strength
2. **Durability**: PVC is resistant to weathering, chemical rotting, corrosion, shock and abrasion. It is therefore the preferred choice for many long-life and outdoor products
3. **Flame Retardancy**: Because of its high chlorine content, PVC products are self- extinguishing. Its oxidation index is ≥45. Antimony trioxide has been used extensively, usually in combination with phosphate ester plasticizers, giving excellent fire performance and mechanical properties.

4. **Cost/Performance Ratio**: PVC has good physical as well as mechanical properties and henc provides excellent cost-performance advantages. It has long life span and need low maintenance

5. **Mechanical Properties**: PVC is abrasion-resistant, lightweight and tough

6. **Chemical Resistance**: PVC is resistant to all inorganic chemicals. It has very good resistance against diluted acids, diluted alkalis and aliphatic hydrocarbons. Attacked by ketones; some grades swollen or attacked by chlorinated and aromatic hydrocarbons, esters, some aromatic ethers and amines, and nitro- compounds

PVC resin obtained from polymerization is extremely unstable due to low thermal stability & high melt viscosity. It needs to be modified before processing into finished products. Its properties can be enhanced/modified by adding several additives such as heat stabilizers, UV stabilizers, plasticizers, impact modifiers, fillers, flame retardants, pigments, etc. It shows a wide spectrum of properties ranging from the extremely rigid to very flexible.

Selection of these additives to enhance polymer properties is dependent on end application requirement. For example:

1. **Plasticizers** (Phthalates, Adipates, Trimellitate, etc.) are used as softening agents to enhance rheological as well mechanical performance (toughness, strength) of vinyl products by raising the temperature. Factors that affect the selection of plasticizers for vinyl polymer are:

- Polymer Compatibility
- Low Volatility
- Cost

Flexible PVC Pipe

Explore more about **plasticizers for polymers**, various chemical types, regulatory updates & more to select right additive for your application

2. PVC has a very low thermal stability and stabilizers help prevent degradation of polymer during processing or exposure to light. When subjected to heat, vinyl compounds initiate a self-accelerating dehydrochlorination reaction and these stabilizers neutralize the HCl produced enhancing the life of polymer. Factors to be considered while selecting **heat stabilizer** are:

- Technical requirements
- Regulatory Approval
- Cost

3. Fillers are added in PVC compounds for a variety of reasons. Today, a **filler can be a true performance additive** by delivering value in new and interesting ways at the lowest possible formulation cost. They help to:

   - Increase stiffness and strength
   - Improve impact performance
   - Add color, opacity and conductivity
   - And more..

   Calcium carbonate, titanium dioxide, calcined clay, glass, talc etc. are common types of fillers used in PVC.

4. External **lubricants** are used to assist smooth passage of PVC melt through processing equipments. while internal lubricants reduce melt viscosity, prevent overheating and ensure good color of product

5. **Other additives** like processing aids, impact modifiers, are added to enhance mechanical as well as surface properties of PVC

PVC Blend with Other Thermoplastics

PVC/Polyester Blends – These blends combine superior physical properties of polyesters with the excellent processing characteristics of PVC. Benefits include abrasion resistance, tensile properties and tear resistance.

PVC/PU Blends – These blends offer increased abrasion and chemical resistance. Some TPUs are biocompatible and when blended with PVC results in valuable products for PVC industry

PVC/NBR Blends – Flexible **PVC modified with NBR** are melt processable yet possess good elasticity/recovery characteristics

PVC/polyolefin rubber alloys - They have potential utility in many applications where conventional **flexible vinyl compounds** do not meet certain end-use performance requirements.

Limitations of Polyvinyl Chloride

- Poor heat stability
- Properties can change with time, due to plasticizer migration
- Flexible PVC has lower chemical resistance than rigid PVC
- Rigid PVC has low continuous service temperature of 50°C

Application of PVC Resin

Commercially, PVC is one of the most important thermoplastics in the world today. **Rigid (unplasticized) PVC** is one of the most widely used plastic materials. Main Applications of both types of PV (rigid and flexible) include:

Application	Rigid PVC	Flexible PVC
Construction	Window Frames, Pipes, House Siding, Ports, Roofing	Waterproof Membranes, Cable Insulations, Roof Lining, Greenhouses
Domestic	Curtain Rails, Drawer Sides, Laminates, Audio and Videotape Cases, Records	Flooring, Wall Coverings, Shower Curtains, Leather Cloth, Hosepipes
Packaging	Bottles, Blister Packs, Transparent Packs and Punnets	Cling Film
Transport	Car Seat Backs	Under Seal, Roof Linings,Leather Cloth Upholstery, Wiring Insulation, Window Seals, Decorative Trim
Medical	-	Oxygen Tents, Bags And Tubing For Blood Transfusions, Drips

		and Dialysis Liquids
Clothing	Safety Equipment	Waterproofs for Fishermen and Emergency Services, Life-Jackets, Shoes, Wellington Boots, Aprons and Baby Pants
Electrical	Insulation pipes, Jacketing, Electricity Distribution Boxes, Switches, Transparent Distributor BoxHousings, Plug Housings & Battery Terminals	Cable & Wire insulation, plugs, cable jackets, sockets, Sable Heads and Distributors
Others	Floppy-Disk Covers, Credit Cards, Traffic Signs	Conveyor Belts, Inflatables, Sports Goods, Toys, Garden Hoses

Processing of Vinyl Plastic

Some of the main processes include extrusion, calendering, injection molding, stretch blow molding, etc.

The intimate mixing of the PVC resin with its associated additives is necessary prior to converting into a thermoplastic melt. **Thermal stabilization is required for processing rigid PVC**, otherwise material may decompose during processing. Also, spray, blush & peel are very common molding defects associated with rigid PVC…Learn systematic methods **to solve routine molding issues**!

PVC is sensitive to the thermal history and the window of processing temperatures is quite small. Drying before processing is highly recommended, moisture rate should be lower than 0.3%.

Drying before processing is highly recommended for plasticized PVC, moisture rate should be lower than 0.3%.

Plasticized PVC	**Rigid PVC**
Injection Molding	
• Melt temperature: 170 and 210°C • Mold temperatures: 20 to 60°C • Mold shrinkage: 1 and 2.5% • Material Injection Pressure: Up to 150 MPa • Packing Pressure: Up to 100 MPa	• Melt temperature: 170 and 210°C. • Mold temperatures:20 to 60°C • Mold shrinkage: 0.2 and 0.5%. • Recommended Screw with an L/D ratio of 15 to 18
Extrusion	
• Extrusion temperatures are 10-20°C below injection molding temperatures in order to avoid premature thermal degradation.	

PVC has largely been overlooked as being suitable for **3D printing**, and the new developments are opening the way for PVC into the growing world of additive manufacturing. For example, Chemson Pacific Pty Ltd, a Vinyl Council of Australia member, demonstrated a world-first for 3DVinyl™ **PVC material by 3D printing** a giant flower vase using a pellet-fed 3D-printer.

PVC material can be bonded using different joining techniques to fabricate PVC into the finished article. All welding techniques involve the application or generation of heat to soften the material whilst pressure is applied simultaneously. **Bonding techniques**, involving adhesives, are also common.

TEFLON:

Teflon is a plastic like substance which is produced by polymerizing tetrafluoroethylene ($CF_2 = CF_2$).

Polytetrafluroethylene (PTFE):

Polytetrafluroethylene is also known as Teflon. It is a synthetic fluoropolymer of tetrafluoroethylene. it is a polymer which have numerous applications.

The IUPAC name of Teflon is:

Poly (1, 1, 2, 2-tetrafluoroethylene).

FORMATION OF POLYTETRAFLUROETHYLENE or TEFLON or PTFE:

It is formed when chloroform is treated with the hydrofluoric acid and antimony trifluoride .

Reactions:

$$CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow[-HCl\ (b.pt.\ -76^oC)]{800^oC} CF_2 = CF_2$$

when polymerused tetrafluoroethylene forms a material which plasic like on appearance and is called *Teflon.*

$$nCF_2 = CF_2 \longrightarrow (-CF_2 - CF_2 -)_n$$

(Tetrafluoroethylene) (Teflon)

PROPERTIES OF TEFLON OR (PTFE):

• Teflon is one of the chemically inert substance. And It is not affected by strong acids which are chemically harmfull and even after by boiling aqua- regia.

- it has the property to be stable at high temperatures

• It is a thermoplastic polymer, that appears as a white solid at room temperature, having a density of about 2200 kg/m3. It has a melting point of 600 K (327 °C; 620 °F).

• It bears mechanical properties such at the degrade gradually at temperatures above 194 K (−79 °C; −110°F).

• PTFE mainly consist of carrbon-fluorine bonds and it also gains the properties from the bonds created only. alkali metals and most highly reactive fluorinating agents are the only chemicals that can affect its property.

• It has a coefficient of friction that is 0.05 to 0.10 which is the third-lowest of any known solidmaterial. It has one of the profecien tdielectric properties.

APPLICATIONS AND ITS USES:

• PTFE is usually used to coat in the non-stick frying pans as it has the ability to resist hightemperatures.

• IT is mostly used as a film interface patch for sports and medical applications, havinga pressure-sensitive adhesive backing. It is installed in one of the high friction areas of footwear, in soles, ankle-foot orthosis.

- It is widely used in medical synthesis,test and many more medicines.