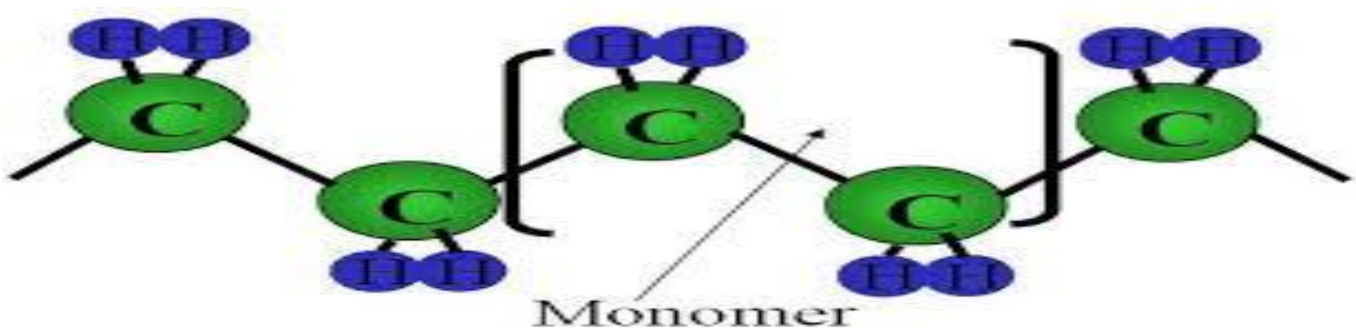
SOMAIYA VIDYAVIHAR UNIVERSITY
K J Somaiya College of Engineering

Polymers

Dr. Jitendra Satam

- A polymers are macromolecule with high molecular mass compound ranging from 5000 to one million
- Formed by combination of one or more low molecular weight compounds. The smallest unit from which polymer is obtained is called monomer.
- The process by which polymers are obtained is called polymerization
- For e.g. polyethylene is obtained by repeating ethylene unit as a result of polymerization.



CLASSIFICATION OF POLYMER

- Based on structure
  - Linear
  - Cyclic
  - Branched
  - Network
- Based on molecular forces
  - Thermoplastic
  - Thermosetting
  - Elastomers
  - Fibers
- Based on source
  - Natural
  - Synthetic
    - Addition
    - Condensation

Classification based on source

- **Naturally occurring Polymers:** These occur in plants and animals and are very essential for life e.g. starch, cellulose, amino acids, etc.

- **Synthetic polymers:** These polymers are prepared in laboratory they are man made polymers e.g. plastics, synthetic rubbers, etc.

- **Semi synthetic polymers:** These are derived from naturally occurring polymers by chemical modification. e.g. vulcanized rubber, Cuprammonium silk and Cuprammonium rayon, etc.

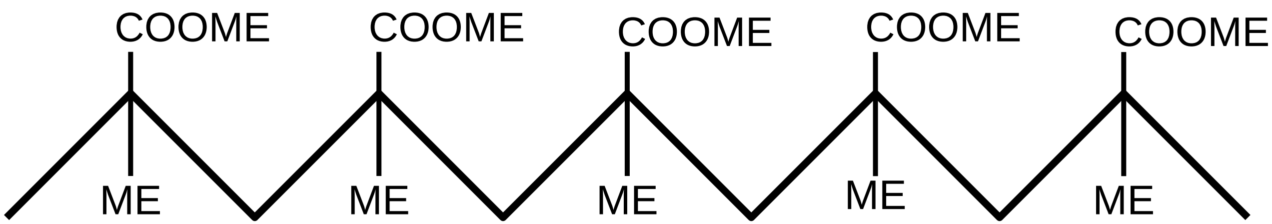
Classification based on Molecular forces

Polymers are classified into four categories based on magnitude of intermolecular forces

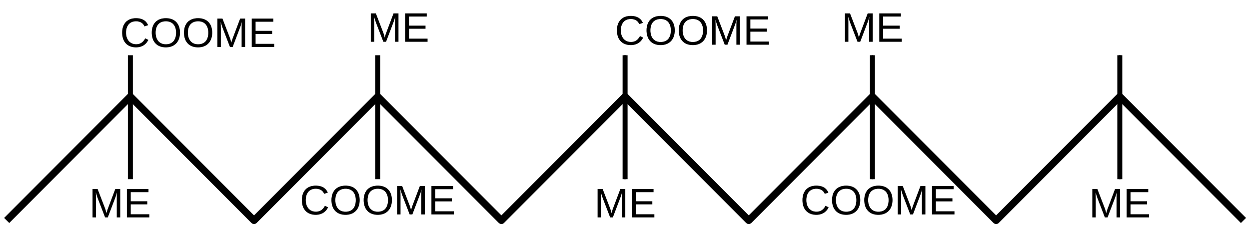
- Elastomers: In these polymers, chain are held by weakest intermolecular forces which permits the polymers to be stretched. The polymer regains its original position when forces are released.
- Fibers: In these polymers the inter molecular forces are strong due to hydrogen bonding, cross linking, cyclic structure
- Thermoplastics: These are polymers for which inter molecular forces between elastomers and fibers. Due to this they can be easily molded by heating.
- Thermosetting polymers: Thermosetting polymers undergo chemical changes and cross linking on heating and become permanently hard and infusible.

Classification based on Tacticity

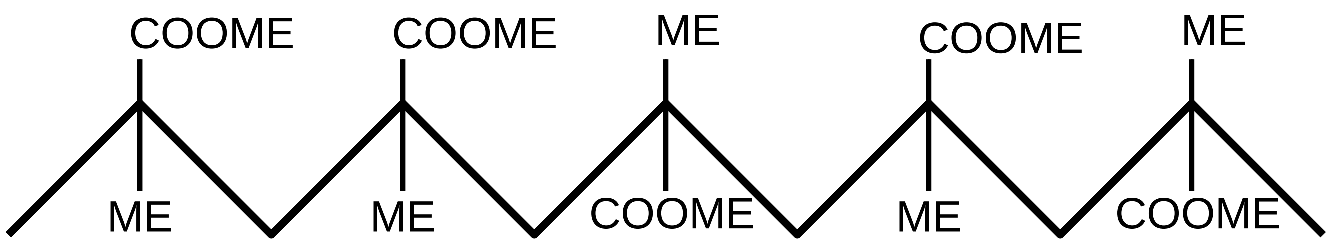
- Isotactic polymers: In isotactic, all the functional group lie on the same side of chain



- Syndiotactic polymers: In syndiotatactic, functional group arrangement is alternate



- <u>Atactic polymers</u>: In atactic, functional group arrangement is random



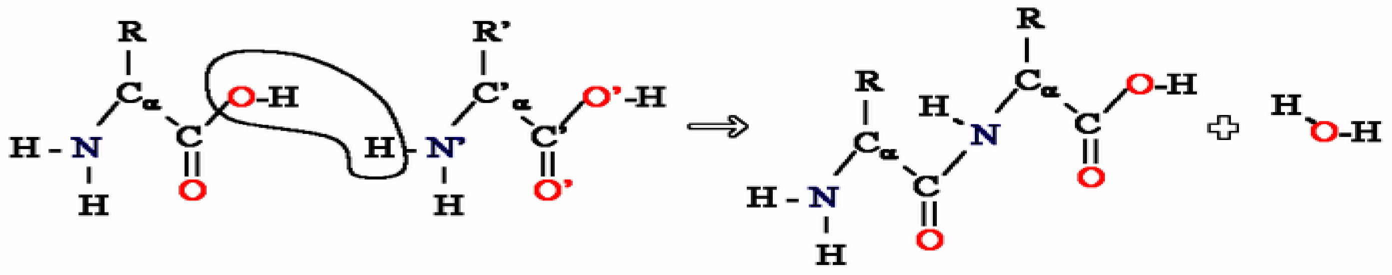
Every other carbon in the chain is a stereo-center

Classification based on Polymerization method

- Addition Polymerization: A polymer formed by direct repeated addition of monomers is called addition polymerization. In this types of polymers monomers are unsaturated compounds or derivatives of alkenes.

Fig 1: The polymerisation of ethene in to poly(ethene)

- Condensation Polymerization: Condensation polymerization involves condensation of two different monomers which are normally bi functional group. During the process there is loss of small molecule such as water



Plastics

- Plastic is a substance that can be easily moulded into a desired shape by the effect of mechanical force & heat.
- In the manufacturing of plastic raw materials like coal, petroleum, cellulose, salt, sulphur, limestone, air, water etc. are used.

Plastics as engineering materials:-

- Low fabrication cost, low thermal & electrical conductivities, high resistance to corrosion, Plastics are resistant to chemicals & solvents
- Plastics reduce noise & vibrations in machines
- Plastics are bad conductors of heat are useful for making handles used for hot objects, most plastics are inflammable.
- Plastics are electrical insulators & find large scale use in the electrical industry.
- Plastics are clear & transparent so they can be given beautiful colors.

Compounding of plastics

The process of mechanical mixing of various additives with polymers (resin) to impart some special properties to the plastics.

The additives gets incorporated with resins to give homogeneous mixture.

The principle **Additives / Ingredients** used in compounding are:

- Resin or Binder
- Fillers or extenders
- Plasticizers
- Pigments or Dyes
- Activators, catalysts or accelerators
- Lubricants
- Stabilizers

Fabrication (Molding) of Plastics

Giving any desired shape to the plastics (granules or powders) by using mould under the application of heat and pressure. A proper method is to be selected depending on the shape and type of resin used. Methods involves partial melting of resinous mass by heating.

In case of **thermo-plasts** molten resin is introduced in die/mould and desired shape could be achieved by compression and further cooling.

In case of **thermo-sets** partially polymerized mass or raw materials are introduced in the die/mould, which further cured at high temperature in the mould itself to achieve desired shape.

Note:

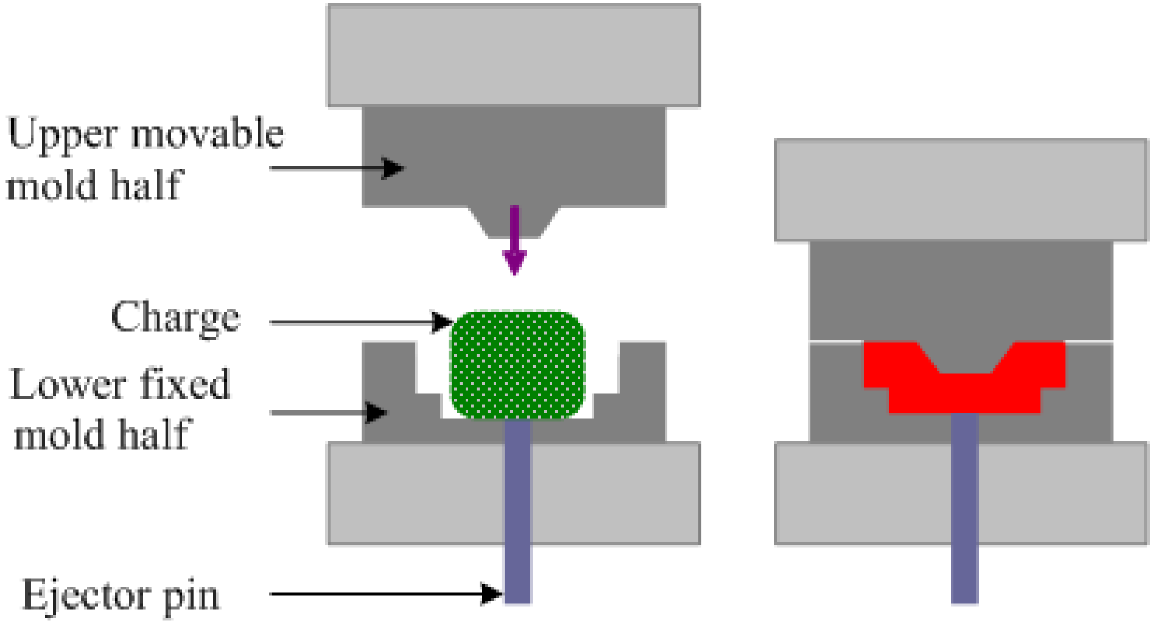
- In case of thermoplasts, curing is done at room temperature (low temperature), while in case of thermosets, curing is done at high temperature to obtain desired cross-linking

Four important types of fabrication Methods

- Compression Molding : (Suitable for Thermosets / Thermoplasts)
- Injection Molding : (Suitable for Thermoplasts)
- Transfer Molding : (Suitable for Thermosets)
- Extrusion Molding : (Suitable for Thermoplasts)

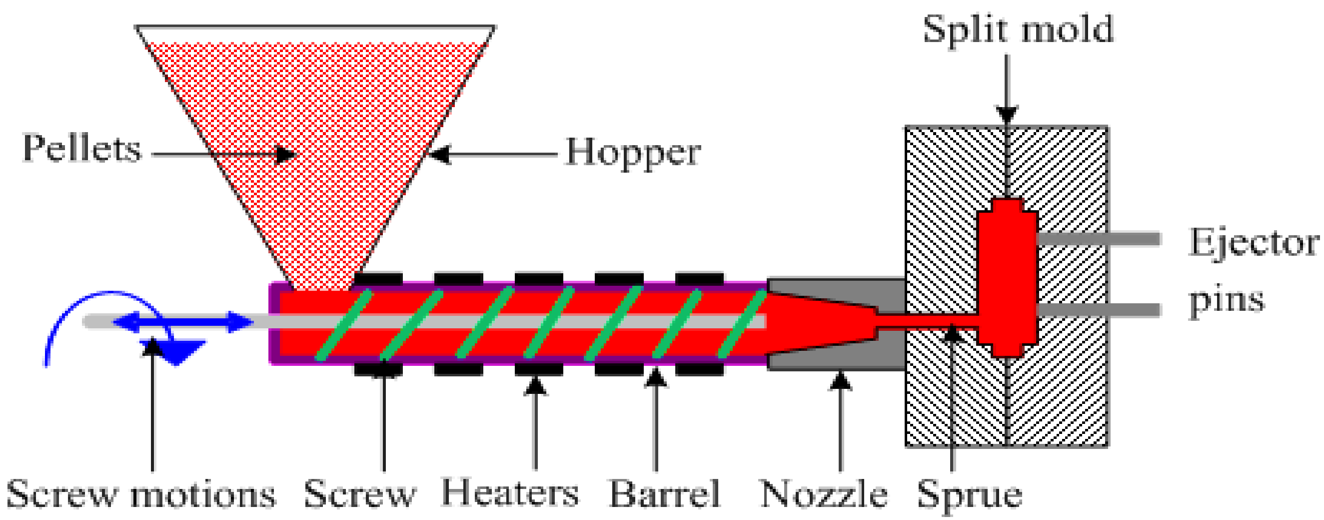
Compression Molding

1. Common and oldest method for molding thermosetting / thermoplastic materials
2. Compression of raw materials or soften resinous mass is done in the mould/die under heat and pressure
3. Predetermined quantity of raw materials is introduced carefully in the mould, further compressed by hydraulic pressure (2000 to 10000 psi)
4. Molten or soften resinous mass gets filled in the cavity of mould.
5. Curing is done by heating (Thermosetting) or by cooling (Thermoplastics)
6. Finally moulded article is separated from the mould by opening the mould apart.
7. **Applications** : Electric switch boxes, Ash trays, cabinets for radio, television, computers etc.



Injection Molding

- Especially used for thermoplastic materials
- Powder or granular resin is heated in a cylinder and injected at a controlled rate in a mould
- Piston plunger or screw is used to force the material in mould.
- Pressure upto 1758 kg/cm^2 (125 psi) is used
- Once the article is formed mould is cooled and half mould is opened to remove the finished article.
- Disadvantage of the method is formation of air bubbles or cavities in the articles
- **Applications:** Smaller but large volume articles such as, pen caps, bottle caps, cups, containers, mechanical parts



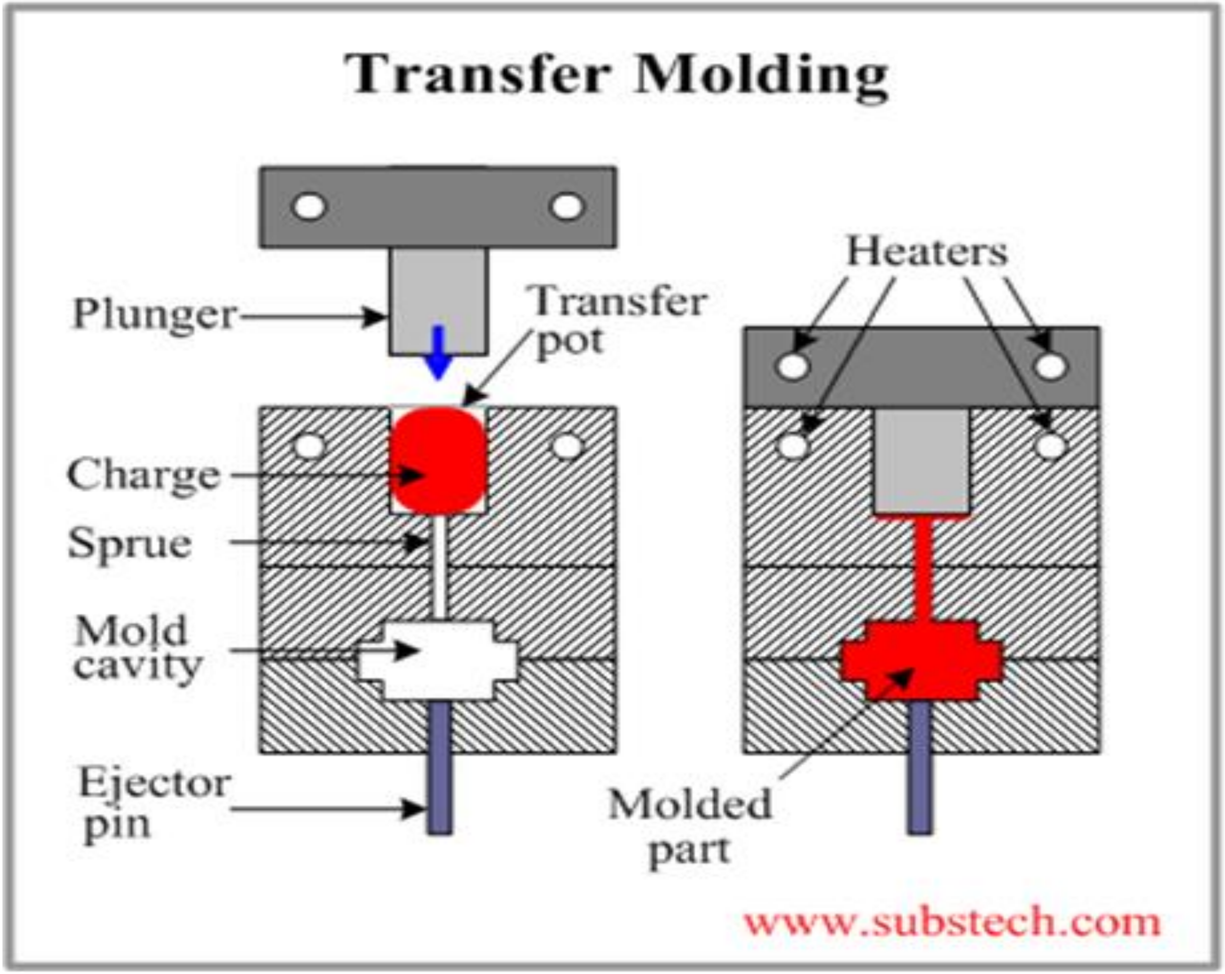
Transfer Molding

- The method combines features of both Compression Molding (hydraulic pressing of molding materials - thermosets) and Injection Molding (ram-plunger and filling the mold through a sprue).
- The method is used especially for molding thermosetting resins (thermosets)
- Products with relatively intricate designs could be fabricated with this method
- Powdered raw materials are heated at certain low temperature to soften and then introduced through an orifice or sprue in the mould
- Then it is cured in the mould at high temperature for certain time
- Finally the moulded article is removed by separation of mould

Advantages:

- Articles with intricate shapes could be designed
- Aerospace and automobile parts, car body, helmets
- The articles produced are blister free
- Fine wires and glass fibers can be inserted in the mould
- Even thick pieces can be cured completely and uniformly

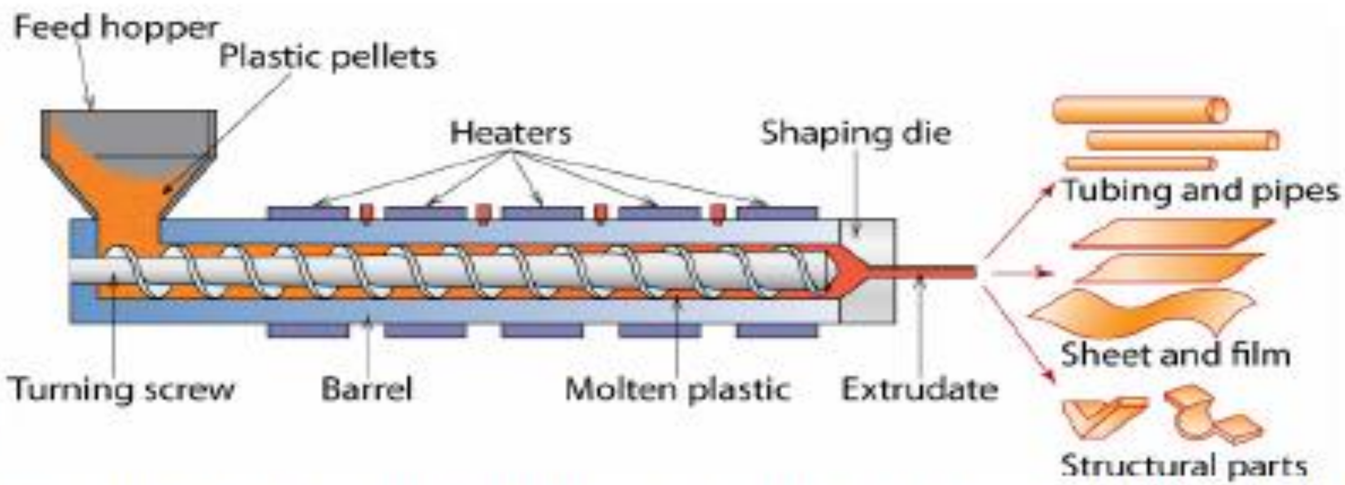
Transfer Molding



Extrusion Molding (Horizontal)

- The method is used for the manufacturing of continuous type of thermoplastic articles with constant cross-section. **Eg. Tubes, rods, strips, insulated electric cables**
- Dry powder or granules of thermoplastic materials are introduced through hopper and further melted by heating.
- There are two types of extrusion moulding:
  1. Vertical extruder moulding
  2. Horizontal extruder moulding
- Molten mass is pushed through the orifice of the die by using screw
- Once the article leaves the orifice, it is allowed to pass through water for solidification
- Proper temperature control of heating chamber and the speed of the screw are the major factors behind successful operation

Extrusion Molding (Horizontal)



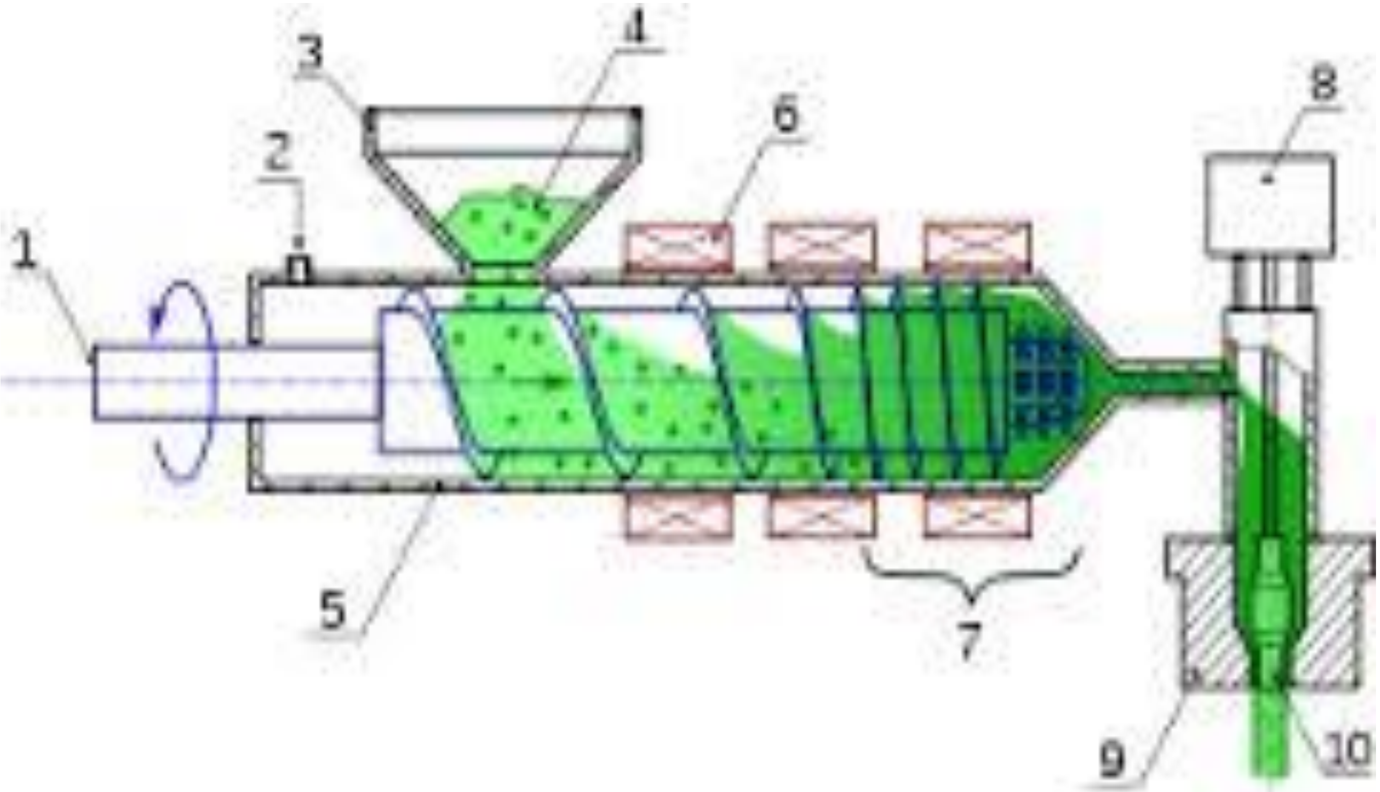
Extrusion

- This process makes parts of constant cross section like pipes and rods. liquid polymer goes through a die to produce a final shape. It involves four steps:

  1. Pellets of the polymer are mixed with colouring and additives.
  2. The material is heated to its proper plasticity.
  3. The material is forced through a die.
  4. The material is cooled.

- An extruder has a hopper to feed the polymer and additives, a barrel with a continuous feed screw, a heating element, and a die holder. An adapter at the end of an extruder blowing air through an orifice into the hot polymer extruded through a ring die produces plastic bags and films.

Extrusion Molding (Vertical)



	Condensation polymerisation		Addition polymerisation
(1)	It is also known as step growth polymerisation	(1)	It is also known as chain growth polymerization
(2)	It takes place in monomers having reactive functional groups	(2)	It takes place only in monomers having multiple bonds.
(3)	It takes place with elimination of simple molecule like H_2O,NH_3,HCl etc.,	(3)	It takes place without elimination of simple molecule.
(4)	Repeat units of monomers are different	(4)	Repeat units & monomers are same.
(5)	The polymer is formed in gradual steps	(5)	Reaction is fast and polymer is formed at once.
(6)	The molecular mass of polymer increases throughout the reaction	(6)	There is very little change in the molecular mass throughout the reaction
(7)	Product obtained may be thermosetting/thermoplastic	(7)	Product obtained are thermoplastic
(8)	E.g.:- Bakelite, polyester ,polyamides etc.,	(8)	E.g:-Polyethylene, PVC, poly styrene.

Conducting Polymers

- Generally polymers are insulators because of the absence of free electrons.
- But they can be made conductive in certain cases by the process called doping.
- Two conditions for the polymer to become conducting are:
  1. Polymers should possess conjugated double bonds
  2. Polymer structure has to be disturbed either by adding or removing electrons by the process of doping.
- There are 3 major classes of conducting polymers
  1. Intrinsically conducting polymers
  2. Doped conducting polymers
  3. Extrinsically conducting polymers

1. Intrinsically conducting polymers

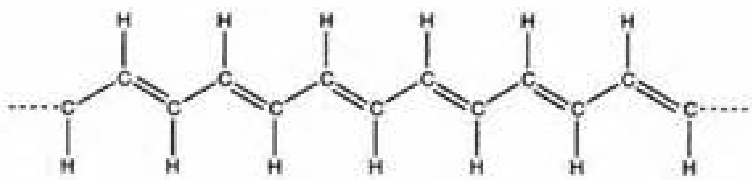
- **This** belong to a class of organic materials consist of Conjugated pi-electrons in the backbone of their macromolecules which is responsible for high electrical conductivity.
- In an electric field, conjugated pi-electrons of the polymer gets excited and can be transported through the solid polymer.
- Overlapping of orbitals of conjugated pi-electrons over the entire backbone of the polymer results in the formation of valence bands and conduction bands. This induces conductivity in the presence of electric field.

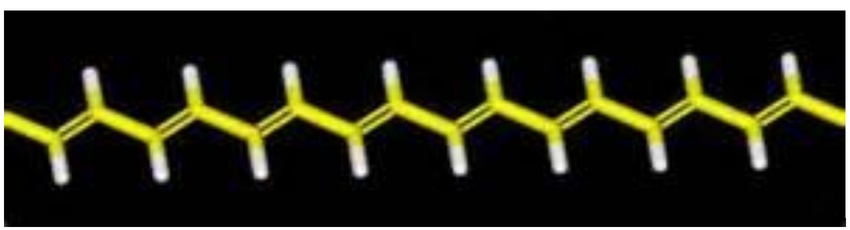
For example:

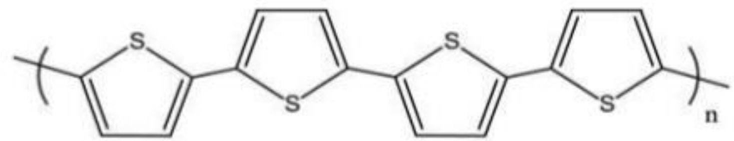
Poly-acetylene, poly-aniline, poly-pyrolle and poly-thiophene etc.

Few Common Conducting Polymers

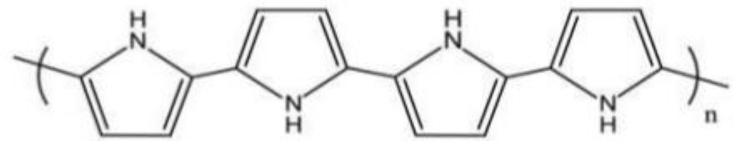
Polyacetylene



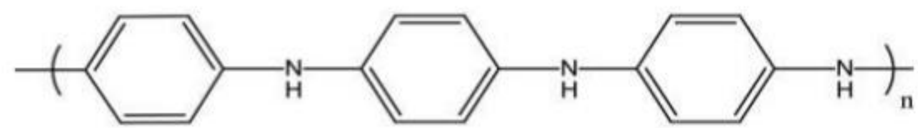




polythiophene



polypyrrole



polyaniline

- Due to their high electrical properties, ICPs are intensively investigated for application in electronics, microelectronics, optoelectronics mainly for areas in aerospace and automobile industries.
- Among the most promising applications of the ICPs are corrosion protection, solid-state charge storage devices, electromagnetic screens, antistatic coatings and gas separation coatings.
- However, poor mechanical properties, environmental sensitivity, moderate stability of electrical properties with temperature significantly limit the industrial applicability of ICPs.

2. (DCP) Doped conducting polymer

- While the addition of a donor or an acceptor molecule to the polymer is called "doping", the reaction that takes place is actually a redox reaction.
- The first step is the formation of a cation (or anion), which is called a soliton or a polaron.

$$Pn \Leftrightarrow [Pn + A -] \text{ (reduction - oxidation)}$$

- As synthesized conductive polymers exhibit very low conductivities. It is not until an electron is removed from the valence band (p-doping) or added to the conduction band (n-doping, which is far less common) does a conducting polymer become highly conductive.
- Doping (p or n) generates charge carriers which move in an electric field. Positive charges (holes) and negative charges (electrons) move to opposite electrodes. This movement of charge is what is actually responsible for electrical conductivity.

(DCP) Doped conducting polymer

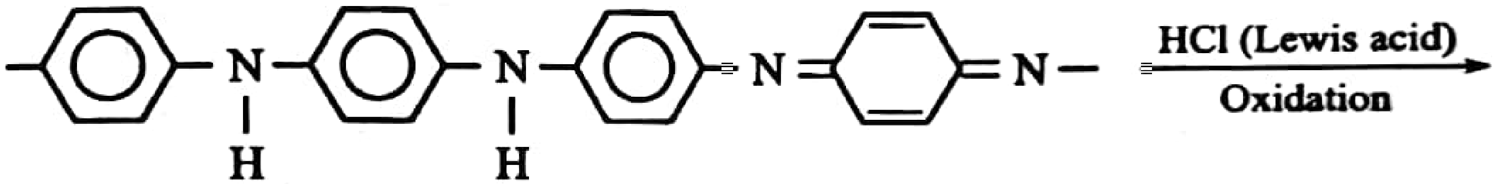
- This is obtained by exposing a polymer to a charge transfer agent in a gas phase or in solution.
- Conductivity of ICPs can be increased by creating positive or negative charges on the polymer backbone by oxidation or reduction by the process of doping.

p-doping involves treating intrinsically conducting polymer with a Lewis acid thereby oxidation takes place and positive charges on the polymer backbone are created. Some common P-dopants are I_2, Br_2, AsF_5, PF_6 etc.

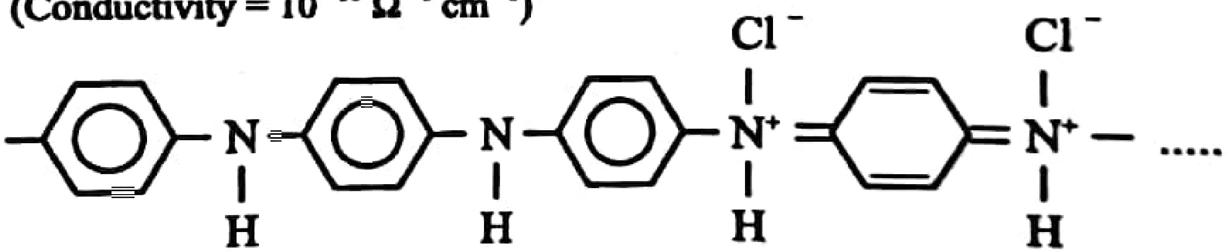
$$\underset{\text{Polyacetylene}}{(C_2H_2)_n} + 2FeCl_3 \longrightarrow (C_2H_2)_n^+ FeCl_4^- + FeCl_2$$

(Lewis acid)

$$2\,(C_2H_2)_n + 3\,I_2 \longrightarrow 2\,[\,(C_2H_2)_n^+\, I_3^-\,]$$



Emeroldine base (a polyaniline)
(Conductivity = $10^{-10}\ \Omega^{-1}\ cm^{-1}$)



Emeroldine hydrochloride (a salt known as *synthetic metal*)
(Conductivity = $10^{3}\ \Omega^{-1}\ cm^{-1}$)

n-doping involves treating intrinsically conducting polymer with a Lewis base thereby reduction takes place and negative charges on the polymer backbone are created. Some common N-dopants are Li, Na, Ca etc.

$$\ldots - CH = CH - CH = CH - \ldots + B \xrightarrow{\text{Reduction}} \ldots - CH = CH - \underset{\substack{| \\ B^{+}}}{\bar{C}H} = CH - \ldots$$

Polyacetylene (Lewis base)

$$\ldots - CH = CH - CH = CH - \ldots + C_{10}H_7NH_2 \xrightarrow{\text{Reduction}} \ldots - CH = CH - \underset{\substack{| \\ {}^{+}NH}}{\bar{C}H} = CH - \ldots + C_{10}H_8$$

Polyacetylene Naphthalamine (Lewis base) Naphthalene

3. Extrinsically Conducting Polymer

This type of conducting polymers possesses conductivity due to the presence of externally mixed conducting elements or compounds. These are of the following two types:

1. **Conductive element filled polymer:** Such polymers contains non-conducting polymers (behaving as binder) holds the conducting elements or compounds (behaving as conducting filler) such as carbon black, metals, metal oxides, etc. Such polymers possesses good bulk conductivity, low cost, light weight, mechanically tough and easily processable.
2. **Blended conducting polymer:** Such polymers are obtained by blending conventional polymers with conducting polymers either through physical or chemical process.

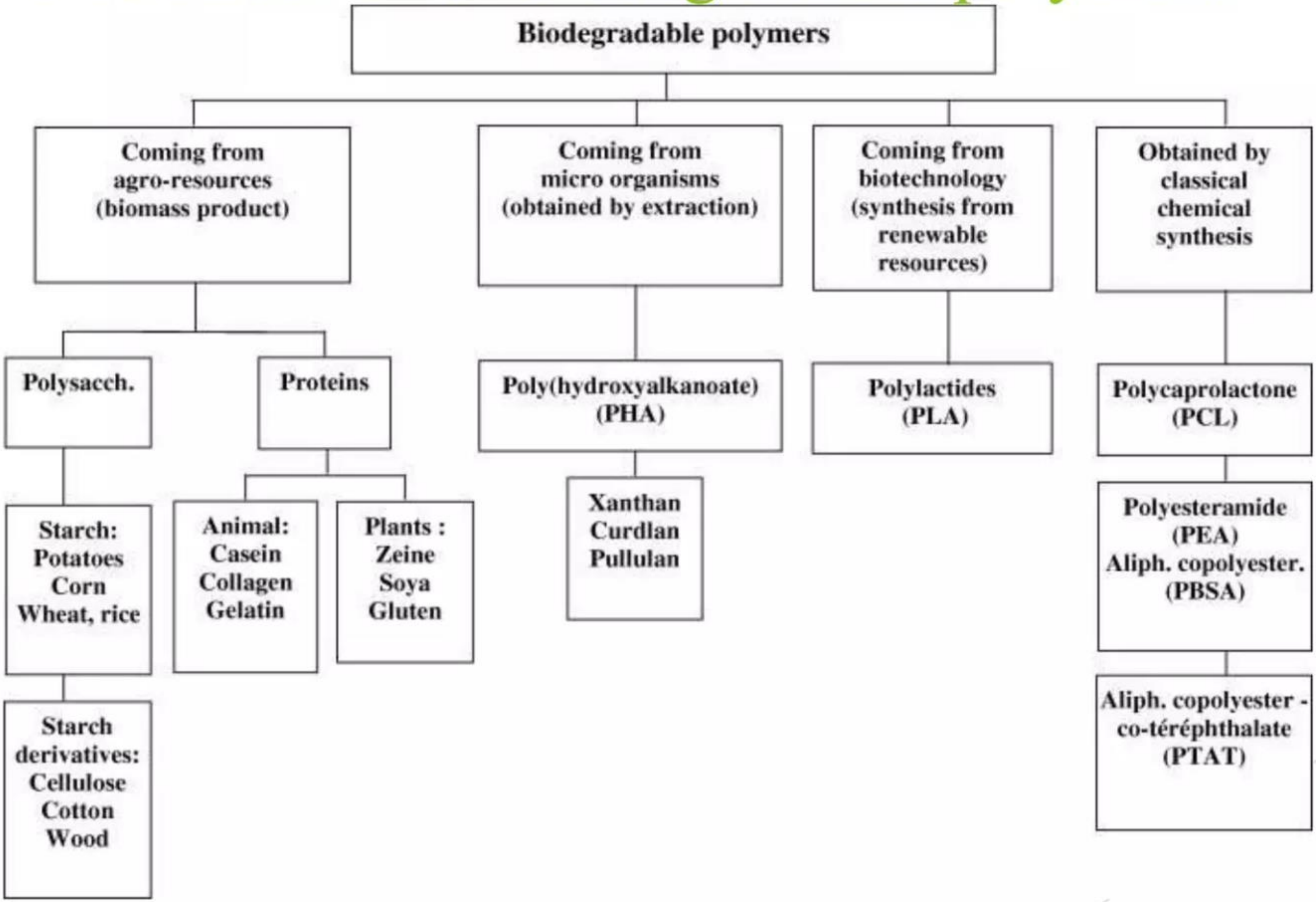
Applications of conducting polymers

- In rechargeable light weight batteries
- In optical display devices
- In aircrafts and aerospace components
- In diodes and transistors
- In solar cells

BIODEGRADBALE POLYMER

Biodegradable Polymer

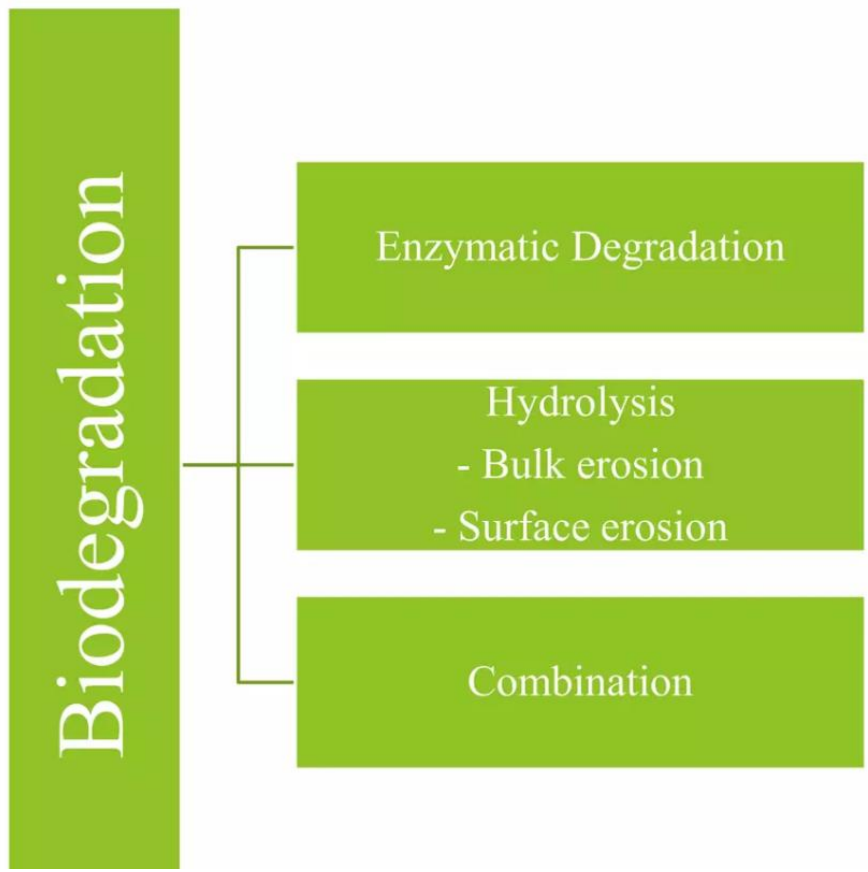
- Biodegradable polymers are polymers in which monomers are joined to one another by functional group linkage and has unstable link in backbone.
- They are broken down to biologically accepted molecules that are metabolized and removed from the body via normal metabolic pathway.


Biodegradable polymers
Coming from agro-resources (biomass product)
Coming from micro organisms (obtained by extraction)
Coming from biotechnology (synthesis from renewable resources)
Obtained by classical chemical synthesis
Polysacch.
Proteins
Poly(hydroxyalkanoate) (PHA)
Polylactides (PLA)
Polycaprolactone (PCL)
Starch: Potatoes Corn Wheat, rice
Animal: Casein Collagen Gelatin
Plants : Zeine Soya Gluten
Xanthan Curdlan Pullulan
Polyesteramide (PEA) Aliph. copolyester. (PBSA)
Starch derivatives: Cellulose Cotton Wood
Aliph. copolyester - co-téréphthalate (PTAT)

Biodegradation

- It is process of converting polymer material into harmless, simple and gaseous products by the action of enzymes, micro-organism and water.
- The process of biodegradation is threefold: first an object undergoes bio-deterioration, which is the mechanical weakening of its structure; then follows bio-fragmentation, which is the breakdown of materials by microorganisms; and finally assimilation, which is the incorporation of the old material into new cells.

Mechanism of Biodegradable Polymers



Advantages of Biodegradable polymer

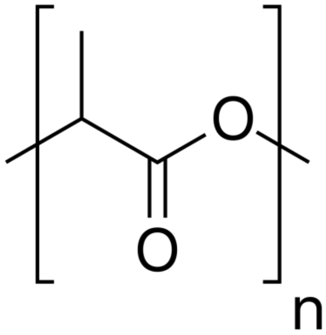
- **Biodegradable Plastics Produce Less Emissions**
- **Biodegradable Plastics = Less Waste**
- **Petroleum Will Eventually Run Out**
- Growing crops to create biodegradable plastics can theoretically last forever, if there is good farmland available.
- Combine this with renewable energy use and you have a winning combination for environmentally friendly production.
- **Biodegradable Plastics Can Decompose Quickly**
- Over the cycle of their decomposition, traditional plastics can release pollutants such as methane or bisphenol-A (BPA) (other than that phthalates such as BBP, DBP and DIBP), which can harm both the environment and human health. Bio-polymers don’t contain these chemicals and so when they biodegrade, our environment and our health aren’t affected.

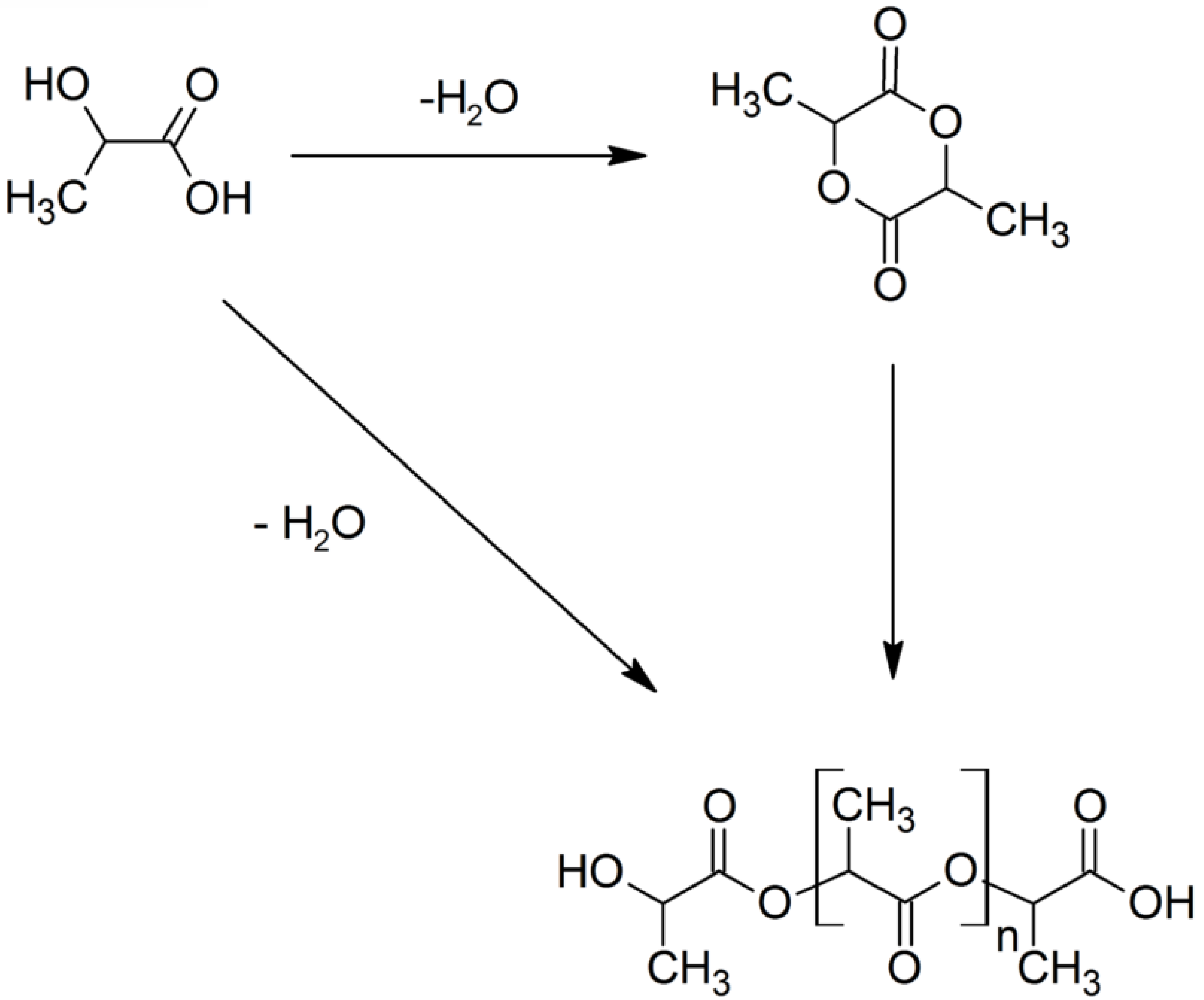
- Biodegradable products are usually seen as a key part of sustainable business practices.
- Application in agriculture: time controlled biodegradable olefin can be used in agriculture for mulching, netting , twine, etc.
- Biopolymer can be used as absorbable surgical implants, controlled release of drug, absorbable skin grafts and bone places to support the body recovery system.

Biodegradable polymers-Polylactic acid

Polylactic acid, also known as poly(lactic acid) or polylactide (abbreviation PLA) is a thermoplastic polyester with backbone formula (C3H4O2)n or [–C(CH3)HC(=O)O–]n, formally obtained by condensation of lactic acid C(CH3)(OH)HCOOH with loss of water (hence its name).

It can also be prepared by ring-opening polymerization of lactide [–C(CH3)HC(=O)O–]2, the cyclic dimer of the basic repeating unit.




HO
O
H3C
OH
-H2O
H3C
O
O
O
O
CH3
- H2O
HO
O
O
CH3
O
n
O
OH
CH3
CH3

Properties

- PLA polymers range from amorphous glassy polymer to semi-crystalline and highly crystalline polymer with a glass transition 60–65 °C, a melting temperature 130-180 °C, and a Young's modulus 2.7–16 GPa.
- Heat-resistant PLA can withstand temperatures of 110 °C. The basic mechanical properties of PLA are between those of polystyrene and PET.
- The melting temperature of PLLA can be increased by 40–50 °C and its heat deflection temperature can be increased from approximately 60 °C to up to 190 °C by physically blending the polymer with PDLA (poly-D-lactide).
- PDLA and PLLA form a highly regular stereocomplex with increased crystallinity. The temperature stability is maximised when a 1:1 blend is used, but even at lower concentrations of 3–10% of PDLA, there is still a substantial improvement.
- Biodegradation of PDLA is slower than for PLA due to the higher crystallinity of PDLA.
- Racemic PLA and pure PLLA have low glass transition temperatures, making them undesirable because of low strength and melting point. A stereocomplex of PDLA and PLLA has a higher glass transition temperature, lending it more mechanical strength.

Uses

- PLA is used in a large variety of consumer products such as disposable tableware, cutlery, housings for kitchen appliances and electronics such as laptops and handheld devices, and microwavable trays.
- It is used for compost bags, food packaging and loose-fill packaging material that is cast, injection molded, or spun.
- In the form of a film, it shrinks upon heating, allowing it to be used in shrink tunnels. In the form of fibers, it is used for monofilament fishing line and netting. In the form of nonwoven fabrics, it is used for upholstery, disposable garments, awnings, feminine hygiene products, and diapers.
- PLA has applications in engineering plastics, where the stereocomplex is blended with a rubber-like polymer such as ABS. Such blends have good form stability and visual transparency, making them useful in low-end packaging applications.

- PLA is used for automotive parts such as floor mats, panels, and covers. Its heat resistance and durability are inferior to the widely used polypropylene (PP), but its properties are improved by means such as capping of the end groups to reduce hydrolysis.
- In the form of fibers, PLA is used for monofilament fishing line and netting for vegetation and weed prevention. It is used for sandbags, planting pots, binding tape and ropes .
- PLA can degrade into innocuous lactic acid, so it is used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh. Depending on the exact type used, it breaks down inside the body within 6 months to 2 years. This gradual degradation is desirable for a support structure, because it gradually transfers the load to the body (e.g. to the bone) as that area heals. The strength characteristics of PLA and PLLA implants are well documented.