

Module 4: Materials for Engineering Applications

Engineering Polymers: Introduction, molecular weight of polymers - number average and weight average molecular weight, numerical problems. Synthesis, properties and engineering applications of chlorinated polyvinyl chloride (CPVC), Synthesis, properties and engineering applications of polymethyl methacrylate (PMMA). Structure-properties relationship of polymers (Crystallinity, Strength, Elasticity and chemical resistivity]. Glass transition temperature (T_g), factor affecting T_g and its significance.

Polymer Composites: Introduction, fiber-reinforced polymers (FRPs); Kevlar – Synthesis, properties and industrial applications. Carbon-fiber - Preparation from Polyacrylonitrile (PAN), properties and industrial applications.

3D Printing materials: Introduction, synthesis, properties and applications of polylactic acid (PLA) resin.

Polymers

Introduction

Polymers are high-molecular-weight compounds obtained by the repeated union of simple molecules. (Monomers). Ex: Starch, Polyvinyl chloride, Polyethylene, Nylon 6, 6 and etc.

Classification of polymers.

Polymers are classified into two types as follows:

- i) Natural polymers: These are the polymers obtained naturally by plants and animals.
Ex: Silk, wool, natural rubber, protein, starch, cellulose, etc.
- ii) Synthetic Polymers: These are artificially prepared polymers also known as manmade polymers.
Ex: PVC, Nylon 6.6, Polythene, Phenol, Formaldehyde, Resin etc.,

Terms used:

Monomers: These are simple molecules, which combine with each other to form polymers. These are the building blocks of Polymer.

Polymerization: The process of linking monomers to form polymers with or without the elimination of by-products is called polymerization.

Degree of Polymerization (n): The total number of monomers present in a single chain of polymer is called the degree of polymerization.

Functionality: The total number of bonding sites or functional groups present in a monomer is called the functionality of the monomer

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Condensation Polymerization:- the process in which the monomers undergo intermolecular condensation reactions to form a polymer with the elimination of simple molecules like water, HCl, ammonia, phenol etc.



Free-radical polymerization is a method of polymerization that is a chain reaction started with the introduction of an initiator leading to the formation of free radicals and successive addition of these free-radical to form polymers. Free radical polymerization consists of 3 fundamental steps.

Initiation involves the formation of radicals followed by the radical's reaction with a monomer,

Propagation is the rapid and progressive addition of monomers to the growing polymer chain without a change of the active center.

Termination is the destruction of the growth active center, usually by *combination* or *coupling* of the radicals of two growing polymer chains or by *disproportionation*.

Number Average Molecular weight [Mn]: The number average molecular weight is the total weight of the sample divided by the number of molecules in the sample.



Where

- n_1, n_2, n_3 are the number of molecules having masses
- M_1, M_2, M_3 respectively. The above equation may also be written as,

Where

- n_i = masses of simple monomer molecules.
- M_i = number of monomer molecules.

Weight Average Molecular weight [Mw]: It gives representation to various molecular species in proportion to their average weight in the given material.

$$\overline{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \dots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots} \quad \longrightarrow \quad \overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

Where

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The polymer has the following molar mass distribution: 10 molecules with mass 5000, 20 molecules with mass 2500, 30 molecules with mass 1000, 40 molecules with mass 500 and 50 molecules with mass 100. Calculate the weight-average and number-average molecular masses of the polymer.

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$\overline{M}_n = \frac{1600 \times 10^2}{150}$$

$$\overline{M}_n = 1067$$

n_i	m_i	Simplified m_i	m_i^2	$n_i m_i$	$n_i m_i^2$
10	5000	50×10^2	2500×10^4	500×10^2	25000×10^4
20	2500	25×10^2	625×10^4	500×10^2	12500×10^4
30	1000	10×10^2	100×10^4	300×10^2	3000×10^4
40	500	5×10^2	25×10^4	200×10^2	2000×10^4
50	100	1×10^2	1×10^4	100×10^2	50×10^4
150				1600×10^2	42550×10^4

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$$\overline{M}_w = \frac{42550 \times 10^4}{1600 \times 10^2}$$

$$\overline{M}_w = 2659$$

The polymer containing 1000 polymeric chains has a following molar mass distribution 10% molecules with mass 50000, 20% molecules with mass 25000, 30% molecules with mass 10000, and 40% molecules with mass 5000. Calculate the weight average and number average molecular mass of the polymer.

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$\overline{M}_n = \frac{15000 \times 10^3}{1000}$$

$$\overline{M}_n = 15000$$

$n_i \%$	n_i	m_i	Simplified m_i	m_i^2	$n_i m_i$	$n_i m_i^2$
10%	100	50000	50×10^3	2500×10^6	5000×10^3	250000×10^6
20%	200	25000	25×10^3	625×10^6	5000×10^3	125000×10^6
30%	300	10000	10×10^3	100×10^6	3000×10^3	30000×10^6
40%	400	5000	5×10^3	25×10^6	2000×10^3	10000×10^6
	1000				15000×10^3	415000×10^6

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$$\overline{M}_w = \frac{415000 \times 10^6}{15000 \times 10^3}$$

$$\overline{M}_w = 27667$$

A sample of polymer contains 30% molecules with molecular mass 20,000, 40% with molecular mass 30,000 and 30% with molecular mass 60,000. What is the number average molecular mass of the polymer?

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$\overline{M}_n = \frac{360 \times 10^4}{100}$$

$$\overline{M}_n = 36000$$

$n_i m_i$	n_i	m_i	Simplified m_i	m_i^2	$n_i m_i^2$
60×10^4	30	20000	2×10^4	4×10^8	120×10^8
120×10^4	40	30000	3×10^4	9×10^8	360×10^8
180×10^4	30	60000	6×10^4	36×10^8	1080×10^8
360×10^4	100	110000	11×10^4	49×10^8	1560×10^8

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$$\overline{M}_w = \frac{1560 \times 10^8}{360 \times 10^4}$$

$$\overline{M}_w = 4.33 \times 10^4$$

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Using the following data calculate the number average and weight average molecular mass of the polymer

n_i	Molecular mass Range
0.02	8,000-16,000
0.1	16,000-24,000
0.2	24,000-32,000
0.3	32,000-40,000
0.27	40,000-48,000
0.11	48,000-56,000

n_i	Molecular mass Range	Mean M_i	Simplified m_i	m_i^2	$n_i m_i$	$n_i m_i^2$
0.02	8,000-16,000	12,000	12×10^3	144×10^6	0.24×10^3	2.88×10^6
0.1	16,000-24,000	20,000	20×10^3	400×10^6	2×10^3	14.4×10^6
0.2	24,000-32,000	28,000	28×10^3	784×10^6	5.6×10^3	156.8×10^6
0.3	32,000-40,000	36,000	36×10^3	1296×10^6	10.8×10^3	388.8×10^6
0.27	40,000-48,000	44,000	44×10^3	1936×10^6	11.88×10^3	522.7×10^6
0.11	48,000-56,000	52,000	52×10^3	2704×10^6	5.72×10^3	297.4×10^6
			53×10^3	7264×10^6	60×10^3	1383×10^6

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$$\overline{M}_w = \frac{1383 \times 10^6}{60 \times 10^3}$$

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$\overline{M}_n = \frac{60 \times 10^6}{1}$$

$$\overline{M}_n = 60 \times 10^6$$

$$\overline{M}_w = 23.05 \times 10^3$$

Structure and the Property Relation of a Polymer

Tensile strength: A polymer should have more tensile strength it depends on

a. **Molecular weight of the polymer:** Low molecular weight polymers are soft gummy, & less resistant to heat. But high molecular weights of the polymers are tough & resistant to heat.

b. **Structure of the polymer:** Cross linked & branched polymers are stronger than linear less branched polymers.

Crystallinity: A polymer with a high degree of crystallinity has a higher melting point, greater tensile strength & resistance to heat. The degree of crystallinity depends on

a. **Structure of polymers:** Linear polymers without bulky groups & hydrogen bonding are more crystalline than branched & polymers with bulky groups.

Ex: HDPE High-density polyethene has a higher degree of crystallinity than polyvinylacetate.

b. **Configuration of the polymer:** Isotactic Polymers are more crystalline than atactic polymers.

Ex: Isotactic polyvinyl chloride is more crystalline than Atactic polyvinyl Chloride (random arrangements of groups)

c. It also depends on polar groups & hydrogen bonding. For polymers with polar groups & hydrogen bonding, they exhibit a high degree of crystallinity.

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Elasticity: A polymer should exhibit good elasticity. Elasticity is due to the uncoiling & recoiling of the molecular chain under the application of force. It should not break on prolonged stretching. The elasticity of a polymer can be improved.

- a. By introducing cross-linkages at suitable positions.
- b. Avoiding side groups such as aromatic and cyclic structures.
- c. By introducing more nonpolar groups on the chain, so that the chain does not separate on stretching.
- d. By introducing internal plasticisers during polymerisation.

Chemical. Resistance: The Polymer should have more resistance to chemical attack and should not become soft, swell, or lose its strength. The chemical resistivity of a polymer depends mainly on.

a. Presence of polar & non-polar groups in the polymer chain: Presence of polar groups, such as $-OH$, $-COOH$, is less resistant to chemical attack. But non-polar groups such as $-CH_3$, $-C_6H_5$, $NHCO$, etc., are not usually attacked by chemicals. Ex: PVC, ABS, PS, etc., have high chemical resistance.

b. Degree of crystallinity & Molecular mass: Chemical resistance increases with an increase in degree of crystallinity because crystalline regions make the penetration of chemicals or solvents more difficult. The higher the degree of crystallinity, the higher the chemical resistance.

Glass Transition Temperature: The temperature at which a polymer transforms from a hard glassy state to a soft rubbery state is called the glass transition temperature.

Significance of Tg:

It is used as a measure for evaluating the flexibility of a polymer and the type of response the polymeric material would exhibit to

Tg is very useful in choosing the right processing temperature for fabrication (moulding, calendaring and extrusion)

Tg is very useful in determining the coefficient of thermal expansion, heat resistant, refractive index, electrical property, etc.,

Factors affecting glass transition temperature

1. **Chain Flexibility:** Linear polymer chains have a high degree of rotational freedom, i.e., greater chain flexibility and a low Tg. Aromatic or cyclic groups on the backbone of carbon

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atoms hinder rotational freedom, i.e., chain flexibility decreases and T_g increases. Crystalline polymers are more rigid, stiffer and more resistant to solvents.

2. **Cross-linking and branching:** A small amount of branching will tend to lower T_g , and a high density of branching reduces chain mobility and elevates the T_g . The cross-linking brings the polymer chains closer together, lowers free volume, and restricts molecular motion, hence raising T_g .
3. **Intermolecular forces:** The presence of a large number of polar groups in the molecules leads to strong intermolecular cohesive forces like the hydrogen and van der Waals forces of attraction, which restrict the segmental motion. As a result, T_g increases.
4. **Molecular mass:** The Higher the molecular mass, the more the restriction on molecular freedom. However, T_g is not significantly affected by molecular masses if the degree of polymerisation is above 250 °C.
5. **Stereo regularity of the polymer:** A syndiotactic polymer has a higher T_g than an atactic polymer, which in turn has a higher T_g than its isotactic stereoisomer.

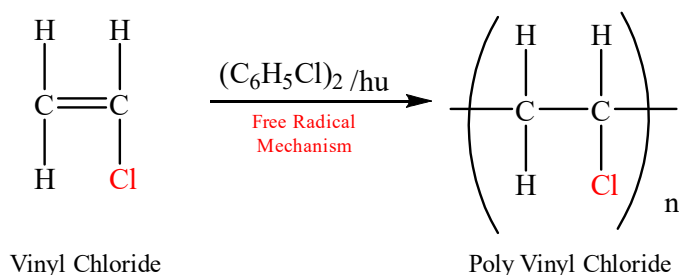
Synthesis of Chloro PolyVinyl Chloride (CPVC)

Chlorinated Polyvinyl Chloride (CPVC) is a thermoplastic made by adding chlorine to PVC, giving it superior heat, fire, and chemical resistance, making it ideal for hot/cold water plumbing, fire sprinklers, and industrial chemical handling where regular PVC falls short. It's more ductile, stronger under pressure, and offers a longer service life than PVC, making it suitable for replacing metal pipes in corrosive environments.

Chlorinated polyvinyl chloride (CPVC) is a thermoplastic produced by chlorination of polyvinyl chloride (PVC) resin. This involves two steps.

Preparation of Polyvinyl Chloride

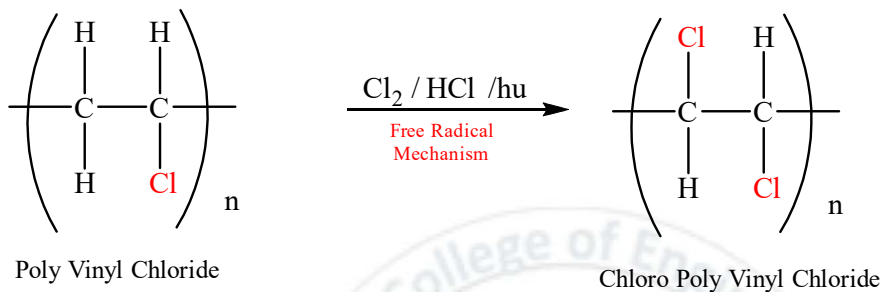
Poly Vinyl Chloride is obtained by the free radical reaction by exposing Vinyl chloride to sunlight in presence of Initiators like benzoyl peroxide.



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Chlorination of Polyvinyl Chloride

It is made by reacting Suspension or Mass PVC, with chlorine in presence of UV light (Chlorination), hence called as Chlorinated PVC. Chlorination of PVC should be controlled and limited to between 50% and 65%, above which the PVC becomes fragile.



Properties of CPVC Compound

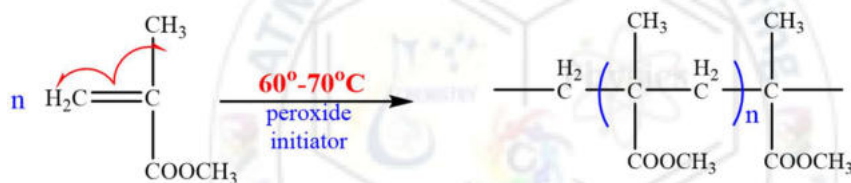
- **Chemical Resistance:** CPVC compound exhibits excellent resistance to a wide range of corrosive chemicals, including acids, alkalis, salts, and various organic compounds. This makes it suitable for use in chemical processing, water treatment, and other corrosive environments.
- **Heat Resistance:** CPVC compound can withstand higher temperatures compared to standard PVC, making it suitable for hot water distribution systems, industrial piping, and applications where elevated temperatures are a concern.
- **Flame Retardancy:** CPVC compound is inherently flame retardant, with a high Limiting Oxygen Index (LOI), which reduces the risk of fire propagation. This property makes it ideal for use in fire sprinkler systems and other fire safety applications.

Applications of CPVC Compound

- **Plumbing Systems:** CPVC compound is widely used in residential, commercial, and industrial plumbing systems for both hot and cold water distribution. Thanks to its excellent chemical and heat resistance, it provides a reliable solution for transporting potable water and various fluids.
- **Chemical Processing:**
- In chemical processing industries, CPVC compound handles a broad range of aggressive substances, including acids, alkalis, and solvents. Manufacturers rely on CPVC pipelines to safely transport corrosive chemicals under demanding conditions.
- **Industrial Piping:**

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- Industrial facilities use CPVC compound to convey corrosive chemicals and manage process flows. Its resistance to high temperatures and harsh substances makes it ideal for wastewater treatment, pharmaceutical manufacturing, and other industrial applications.
- Fire Sprinkler Systems:**
- CPVC piping systems play a key role in fire protection thanks to their flame-retardant properties and thermal stability. Builders and safety engineers often choose CPVC as a cost-effective and reliable option for fire sprinkler installations.
- Polymethyl methacrylate PMMA (Plexi Glass)**
- Plexiglas is the trade name of polymethyl methacrylate. The monomer used to prepare plexiglass is methyl methacrylate. Plexiglass is prepared by the emulsion polymerisation method at 60 to 70 °c in the presence of a trace of H₂O₂ or Acetyl peroxide as an initiator.



Properties	Applications
Plexiglass is a white transparent thermoplastic	It is used in the preparation of aircraft windows.
It has high optical clarity.	Attractive signboards.
It is resistant to chemical action.	Manufacturing transparent moulded articles & tubes
It has good impact strength.	Lenses for automobiles, artificial eyes,

Polymer composite

Composites are materials that consist of two or more chemically and physically distinct phases separated by a distinct interface. The different systems are judiciously combined to achieve a system with more useful structural or functional properties than any of the constituents alone.

A polymer matrix composite (PMC) is a composite material composed of a variety of short or continuous fibres bound together by an organic polymer matrix. PMCs are designed to transfer loads between fibres of a matrix.

Fibre-reinforced polymer composites

Fibre-reinforced plastic is a composite material made of a polymer matrix reinforced with fibres.

The fibres are usually glass, carbon, or aramid; other fibres, such as paper or wood, or asbestos

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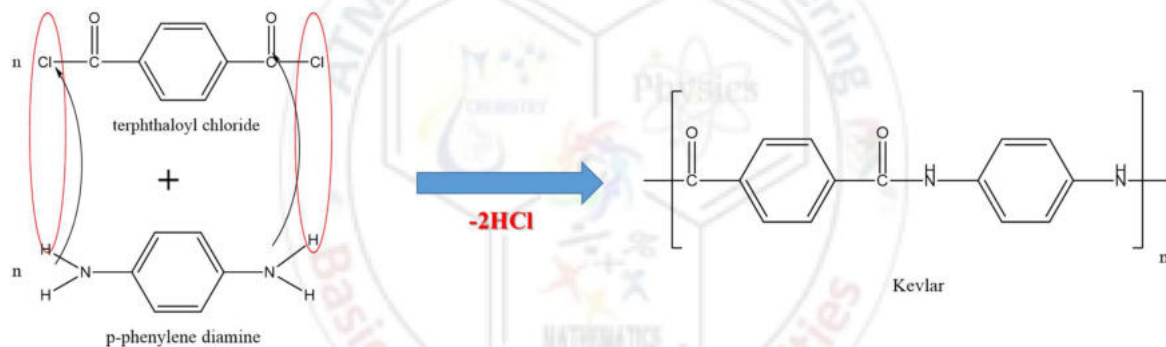
have sometimes been used. The fibres provide strength and stiffness to the composite and generally bear most of the applied loads. The matrix bonds and protects the fibres and transfers stress from fibre to fibre through shear stress. FRPC is of three types. Glass Fibre, Carbon Fibre and Aramid Fibre.

Kevlar fibers:

Kevlar is a type of aramid fiber, and is heat-resistant and strong synthetic fiber. Kevlar has many applications, ranging from bicycle tyres and racing sails to bulletproof vests, all due to its high tensile strength-to-weight ratio; by this measure, it is five times stronger than steel.

Synthesis:

Kevlar is synthesised in solution from the monomers of 1,4-benzene dicarbonyl chloride & 1,4-phenylenediamine in a condensation reaction, yielding hydrochloric acid as a byproduct.



Properties

- Low density
- High strength
- Good impact resistance
- Good abrasion resistance
- Good chemical resistance
- Good resistance to thermal degradation
- Compressive strength similar to E-glass fibres
- Some grades of aramid fibre can degrade when exposed to ultraviolet light

Applications of Kevlar fibre:

- Ballistic protective applications such as bulletproof vests
- Protective apparel such as gloves, motorcycle protective clothing and hunting gaiters, chaps and pants.

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- Sails for sailboats, yachts etc
- Belts and hosing for industrial and automotive applications
- Aircraft body parts
- Boat hulls
- Fibre optic and electromechanical cables
- Friction linings such as clutch plates and brake pads
- Gaskets for high temperature and pressure applications
- Adhesives and sealants

Carbon fiber

Carbon fiber is a material consisting of thin, strong crystalline filaments of carbon, essentially carbon atoms bonded together in long chains. Carbon fiber is a material made from thin filaments of carbon atoms bonded together in a crystalline structure, which results in an exceptional strength-to-weight ratio.

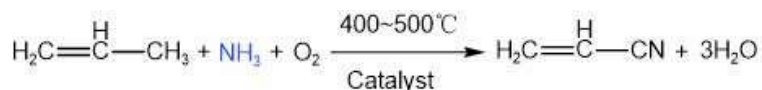
Synthesis:

Most of the carbon fiber fabrication processes involve the following essential steps:

1. A fiberization procedure to make a precursor fiber. This generally involves wet-, dry-, or melt-spinning, followed by some drawing or stretching.
2. A stabilisation treatment that prevents the fibre from melting in the subsequent high-temperature treatments.
3. A thermal treatment called carbonisation that removes most non-carbon elements.
4. An optional thermal treatment called graphitization that improves the properties of carbon fiber obtained in step 3.
5. Polyacrylonitrile (PAN) is the most used precursor for carbon fibre due to its superior strength and stability, and higher carbon yield.

Synthesis of polyacrylonitrile:

This method involves the reaction of propylene in the presence of ammonia, air, and water, using bismuth molybdate and uranium oxyantimonate as catalysts, in a fluidized bed at 450 °C.



Processing of PAN carbon fibre

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- **Spinning:** PAN polymer is dissolved and extruded through spinnerets into a chemical bath (wet spinning) to form fine filaments, which are stretched and washed to align molecules.
- **Stabilization (Oxidation):** Fibers are heated in air (200-300°C) to convert thermoplastic PAN into a non-plastic, ladder-like structure, preventing melting during later high-heat steps. Color changes from white to black.
- **Carbonization:** Fibers are heated to 1,000-3,000°C in an inert (oxygen-free) atmosphere (like nitrogen) to remove remaining non-carbon atoms (N, H, O) and form crystalline carbon structures.
- **Graphitization (Optional):** For ultra-high modulus fibers, heating to 1500-3000°C further orders the carbon crystallites.
- **Surface Treatment:** The fiber surface is slightly oxidized or etched to improve bonding with resins.
- **Sizing:** A protective coating (sizing) is applied to protect fibers and enhance composite performance, followed by winding onto bobbins.

Properties of Carbon Fibre

- **High Strength-to-Weight Ratio:** Stronger than steel but much lighter, offering superior specific strength.
- **High Stiffness & Modulus:** Very rigid and resistant to bending.
- **Low Thermal Expansion:** Maintains shape and size under temperature changes.
- **Corrosion & Chemical Resistance:** Doesn't rust and resists many chemicals.
- **Fatigue Resistance:** Durable under repeated stress.
- **Electrical & Thermal Conductivity:** Can conduct electricity and heat, useful for electronics.
- **X-ray Permeable:** Allows X-rays to pass through.

Applications of Carbon Fibre

- **Aerospace:** Aircraft structures, satellite components (due to lightness and stability).
- **Automotive & Motorsports:** Car bodies, chassis, high-performance vehicle parts (lightweighting).
- **Sports Equipment:** Bicycle frames, tennis rackets, golf clubs, fishing rods (strength & lightweight).
- **Civil Engineering:** Reinforcement for concrete, bridge components (strength, corrosion resistance).

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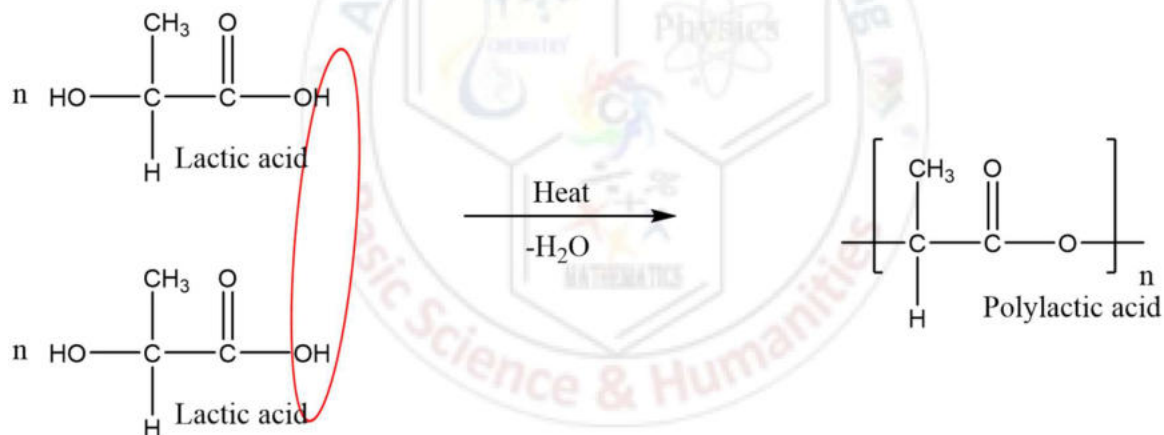
- **Military & Defense:** Armor, drones, structural components.
- **Electronics:** Heat sinks, electromagnetic interference (EMI) shielding.
- **Renewable Energy:** Wind turbine blades (stiffness, strength).

Polylactic acid, (PLA):

PLA are a biodegradable polymer, it has become a popular material due to it being economically produced from renewable resources. The monomer is typically made from fermented plant starch such as corn, cassava, sugarcane or sugar beet pulp. Its low melting point, high strength, low thermal expansion, good layer adhesion, and high heat resistance when annealed make it an ideal material for 3D Printing

Synthesis of PLA

The direct condensation of lactic acid monomers can also be used to produce PLA. This process needs to be carried out at less than 200 °C



Properties

- It is an amorphous glossy polymer
- Lactic acid is a colourless or yellow syrupy liquid
- It has a melting point range from 130-180 °C
- non-toxic
- capable of maintaining good mechanical integrity until degraded
- The high surface energy of PLA results in good printability, making it widely used in 3D printing

Applications

- They are used as parts of the medical device
- They are used to replace tissues
- They are used in Tooth reconstruction
- Used to deliver drugs to body parts
- Packaging and materials