

(3)

POLYMERS

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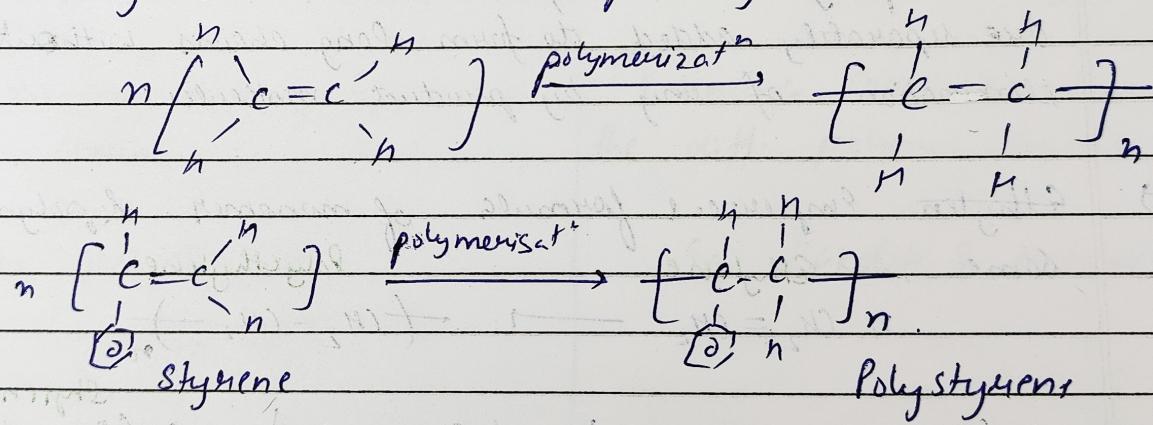
- A polymer is a high molar mass molecular compound made up of many repeating chemical units (Monomers).
- no. of pt. repeating units in chain formed in copolymer → degree of polymerization

Polymerisation → The process by which monomers are transformed into polymers is called polymerization

→ LDPE → more transparent, flexible, waxy
e.g. sandwich bag, squeeze bottle

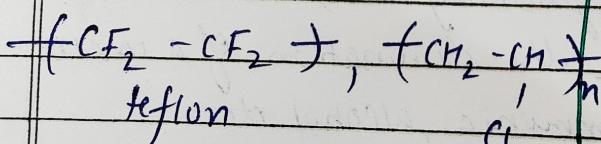
HDPE → more opaque, rigid, non-waxy
e.g. milk jug, grocery bag.

→ **Monomers** → Polymers are macromolecules formed by linking small molecules repeatedly called monomers.



Homopolymer

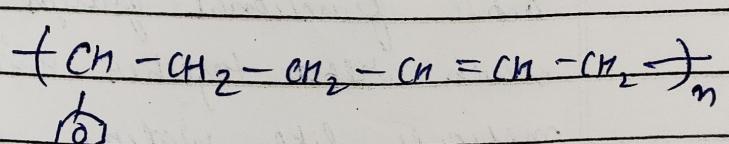
Polymers that are made up of one type of monomers.



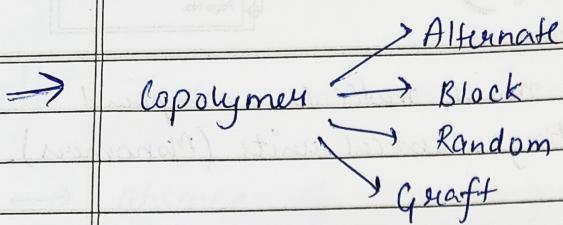
PVC

Copolymer

Not polymers that are made up of two or more type of monomers.



Styrene-Butadiene rubber



#

Polymers :-

1. Based on origin:

A. Natural

e.g. protein, nucleic acid.

B. Synthetic e.g. nylon, polycarbonate etc.

2. Based on polymerization rxn:

Addition

Condensation

must be instigated by application of heat,

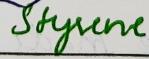
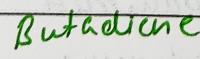
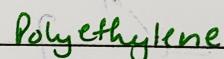
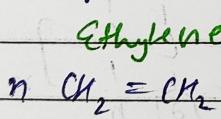
light, press for breaking down the = bond.

#

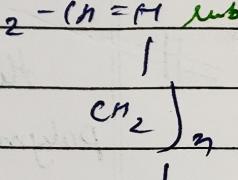
Addition polymers →

→ Addition polymers are formed when monomer units are separately added to form long chains without elimination of any by-product molecules.

→ Ethylene Empirical formula of monomer & polymer are same.



Styrene-butadiene

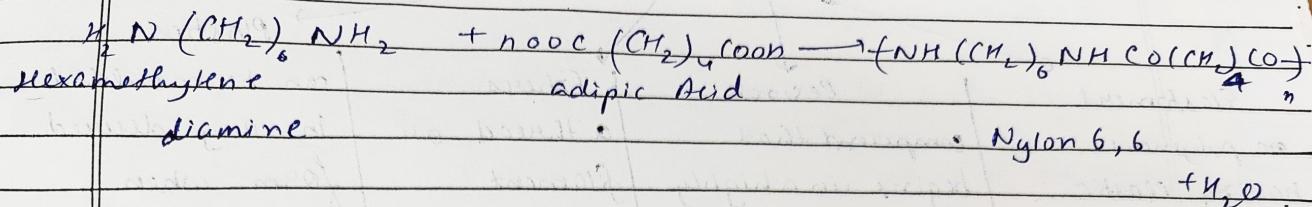


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Condensation polymers:

formed when the monomers containing active functional groups (generally two) which react together with the elimination of a small molecule like water, ammonia, alcohol etc.

E.g. : Nylon - 66 , Bakelite .



3. Based on thermal Behaviour :-

Thermoplastic

- polymers that turns to liquid when heated & freezes to a very glassy state when cooled efficiently.

- high - molecular weight

- no-cross linking b/w chains.

- Eg. polyethylene,
polystyrene

- chain slide past each other due to weak intermolecular forces.

- stretchy & low melting point,

Thermosetting

- When heated in a mould forms an insoluble hard mass which is infusible.

- low molecular weight.

- Extensive crosslinks b/w the diff. polymer chains

Eg: Bakelite & Melamine

- Strong intermolecular forces holds chain firmly in place.

- cannot be stretched,
are rigid & have
high melting point.

4. Polymeric Based on Applications:

Elastomers	Resins	Fibers	Plastics
polymers having elastic properties e.g. Rubber	compound that begins in a highly viscous state & hardens with treatment e.g. epoxy resin	a thread or filament from which a vegetable tissue or textile is formed e.g. Nylon	can be moulded in any desired form when subjected to heat & pressure in the presence of catalyst. e.g. PVC

Tacticity: the orientation of monomeric units in a polymer molecule. It affects physical properties of a polymers

group on same side of chain \rightarrow Isotactic

group alternate from side to side \rightarrow Syndiotactic

group disposed at random \rightarrow Atactic

Functionality The no. of bonding site in a monomer

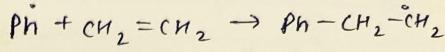
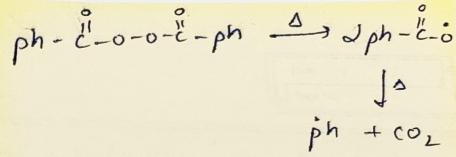
ADDITION POLYMERISATION

MECHANISM

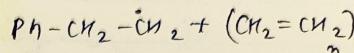
① Free Radical Polymerisation.

(i) Initiation Step:

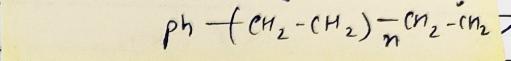
→ Homolytic dissociation of free radicals. (Ran2c)



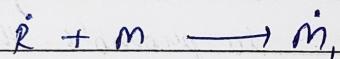
tert-butyl peroxide



Azobisisobutyronitrile

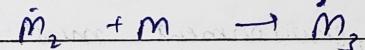
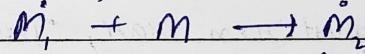


→ 2nd step involves the rxn of this radical with monomer unit.



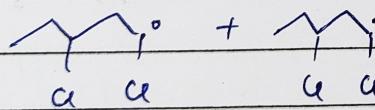
(ii) propagation step:

consists of growth of $\dot{\text{M}}$, free radical by successive rxn of large no.s of monomers molecules.

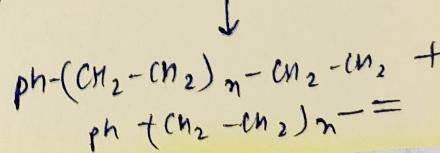
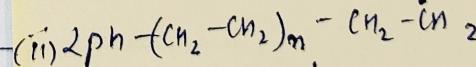
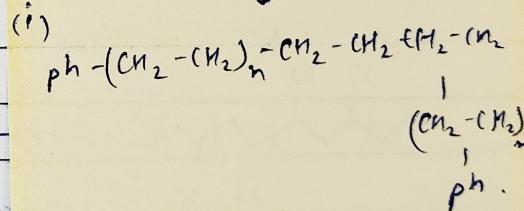
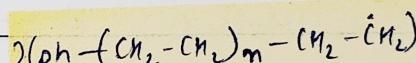
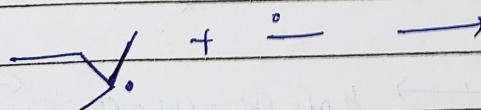


(iii) Terminal steps

a) by coupling



b) by disproportionation



②

JONIC CHAIN POLYMERISATION

- free Radical Rxn → non-specific

→ ionic polymerization procedures & catalysts depend on nature of substituent (R) on vinyl (ethenyl) monomer.

Cationic Initiation

- limited to polymerization of monomers where the R group is e⁻ donating
 - helps stabilize the delocalization of the +ve charge through p orbitals of the double bond.

Anionic Initiation

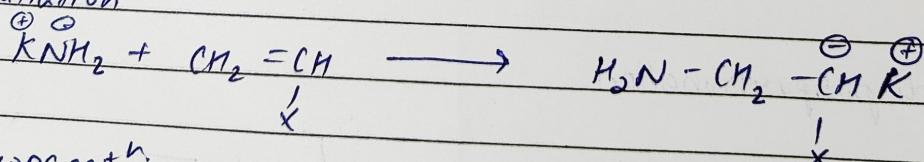
- requires the R group to be e⁻ withdrawing in order to promote the formation of stable carbocation.

- Using catalyst, highest Mn salt, Termination is just disproportionation, environment must be pure.

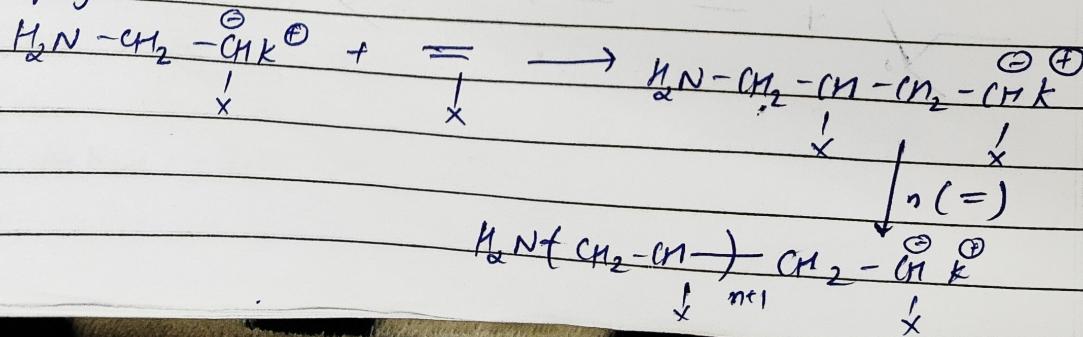
- $\rightarrow R \rightarrow$ Acrylonitrile,
 vinyl chloride etc.
 \rightarrow Catalyst + kNH_2 , n -Butyl
 & organometallic reagents.
 $\rightarrow R \rightarrow$ e.g propylene
 \rightarrow Catalysts with e- acceptor
 properties e.g $AlCl_3$, $SnCl_4$,
 $TiCl_4$, BF_3 .

Anionic Polymerisation

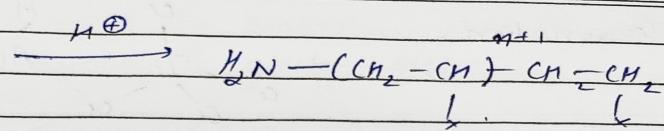
→ Initiation



→ propagation

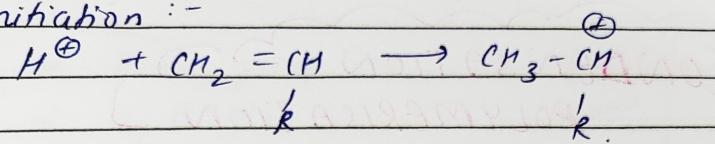


→ Termination:

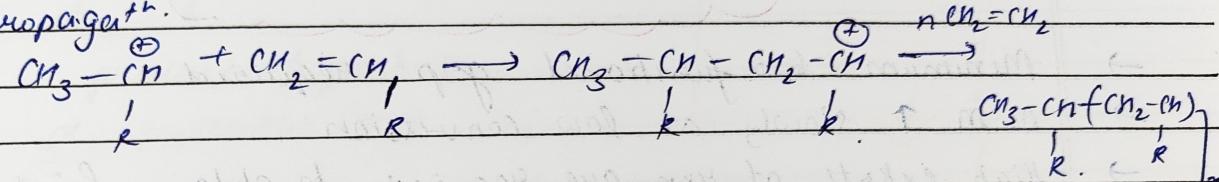


Cationic Polymerization:

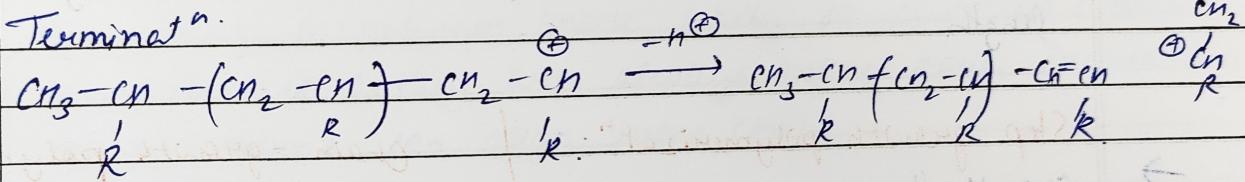
Initiation:-



Propagation:-



Termination:

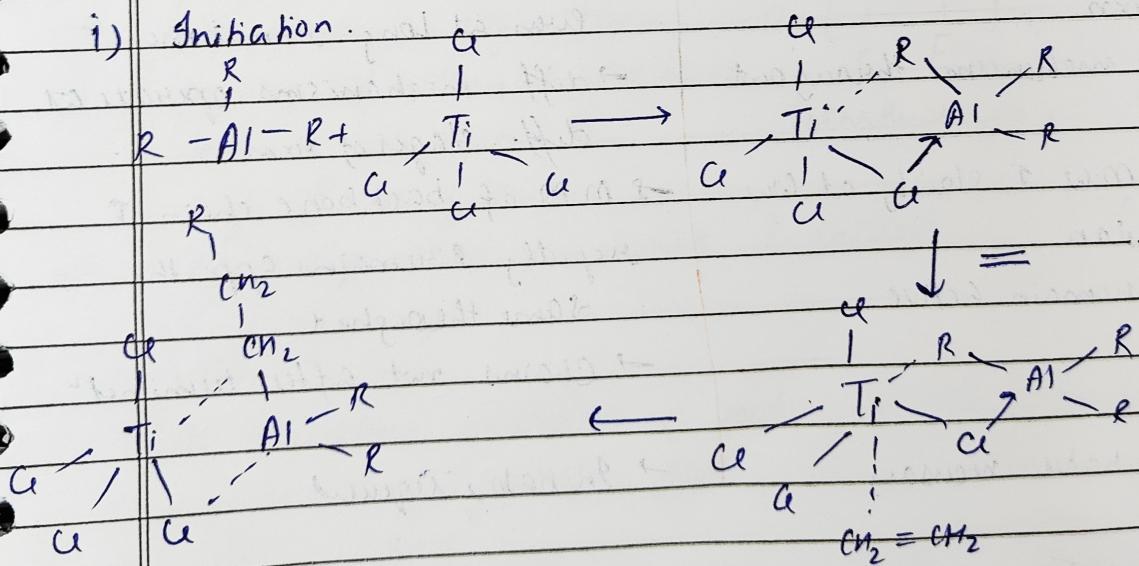


(i)

Coordination polymerisation :-

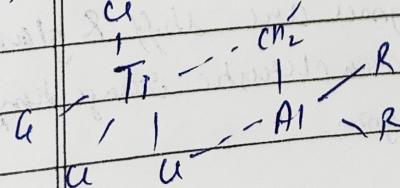
(Ziegler-Natta) ($TiCl_4 + R_3Al$) Stereospecific polymer

i) Initiation:

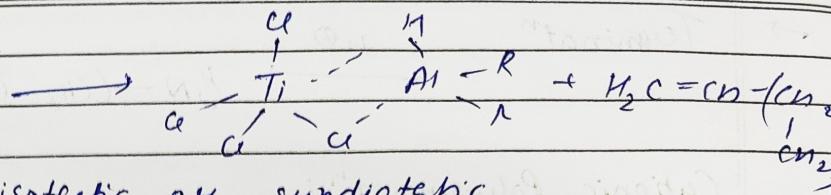


(ii)

Propagation:



(iii) Termination.



→ They can be isotactic or syndiotactic

CONDENSATION POLYMERISATION

- Minimum two functional grp required
- M.M ↑ slowly at low conversion
- High extnts of rxn are required to obtain high chain length

Step growth polymeriztⁿ.

growth throughout matrix

- Rapid loss of monomer early in rxn.
- Same mechanism throughout
- Avg. M.W ↑ slowly at low conversion
- Ends remains active
- No initiator necessary

chain-growth polymerzⁿ.
growth by addition of monomer only at one end of chain.

- Some monomer remains even at long rxn times.
- diff mechanisms operate at diff. stages of rxn.
- M.M of backbone chain ↑ rapidly & remains app. the same throughout
- Chains not after terminatⁿ
- Initiator required

Glass Transition temp. (T_g):

- At low temp., all amorphous polymers are stiff & glassy.
- On warming, polymers soften in a characteristic range temp. known as glass-rubber Transition region.

→ The temp. at which the amorphous phase of polymer is converted b/w rubbery & glassy states.

Brittle, hard & glassy $< T_g <$ flexible, soft & rubbery.

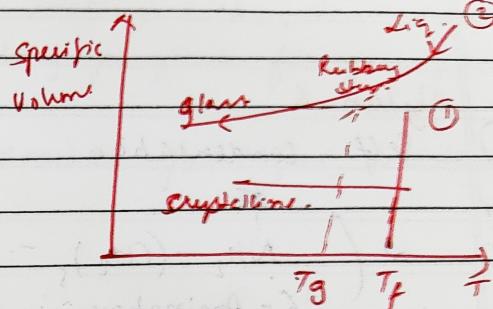
$T_g \propto$ bulky group.

\propto H-bonds

\propto 1

presence of plasticizer

\propto molecular mass



→ Alternating co-polymer more likely to crystallize than random ones as they are always more easily crystallized as the chains can align more easily.

Teflon or Fluon (PTFE)

Properties:

→ extreme tough, high softening point, high chemical resistance towards all chemicals, high S, waxy tough.

→ can be punched, machined & drilled.

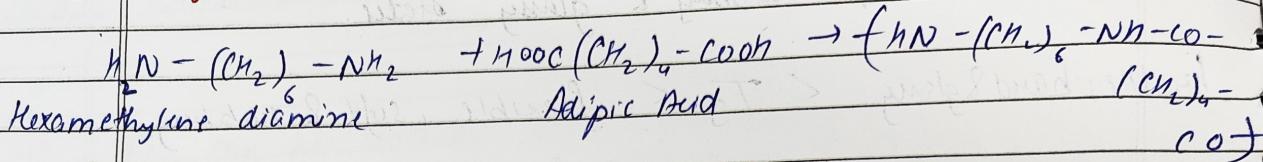
Uses:

- As insulating material (motors, cables, wires)
- for making gaskets, packing etc
- for coating
- In non-lubricating bearing & non-sticking stop-cock

Nylon: (Polyamides) Nylons are used mostly for making fibres, belong to polyamides.

①

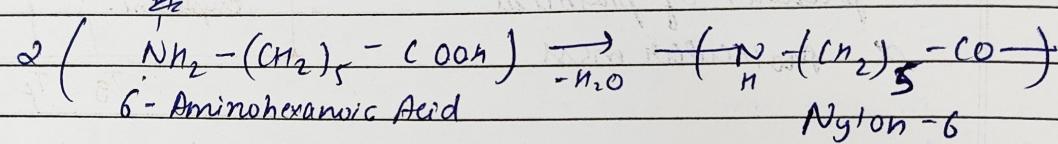
Nylon 6:6



②

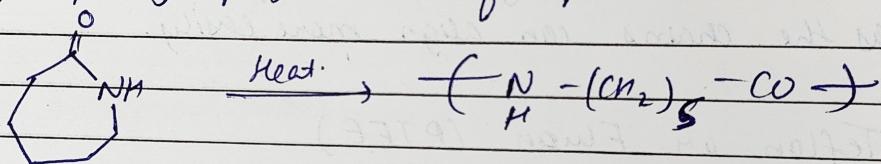
Nylon 6

① Self Condensation:



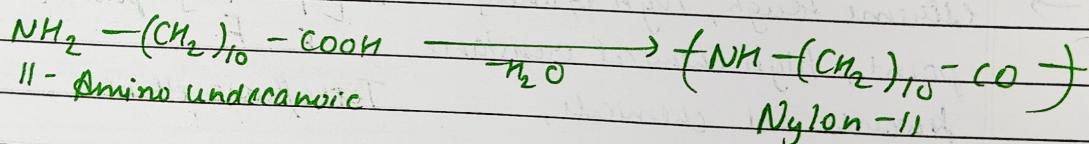
①

Ring opening polymerisation of Caprolactum



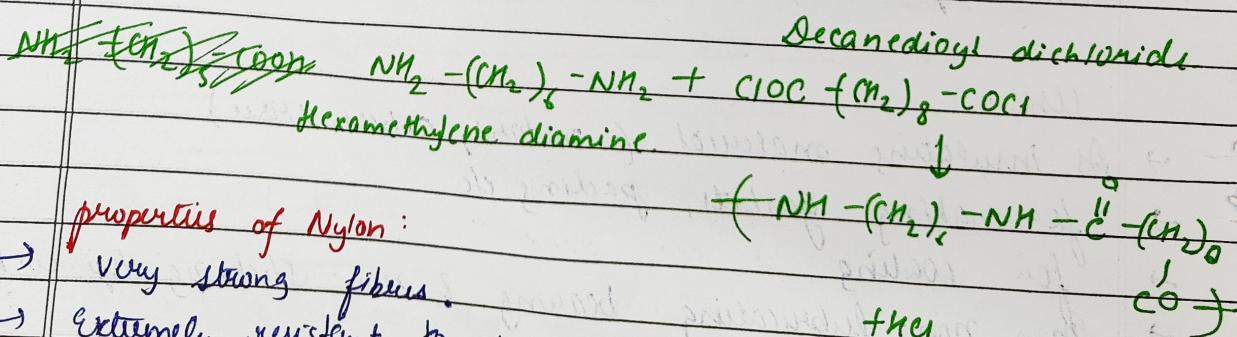
(3)

Nylon II



4

Nylon 6:10



Properties of Nylon:

→ Very strong fibers.

→ Extremely resistant to abrasion & flexing
→ Specific gravity is 1.14.

→ Specific gravity is 1.14 very light.
→ absorb little water.

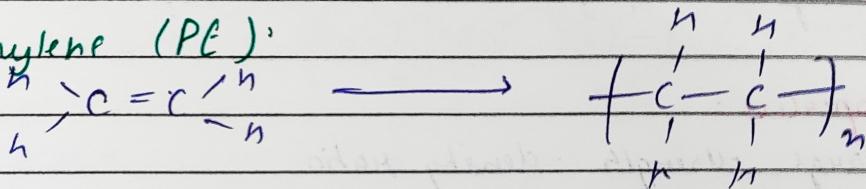
→ absorb little water even, dry fast & simple in laundering.

- Excellent in elasticity & resistant to temperature.
- Resistant to chemicals & oil.

Uses:

- Nylon 6·6 → fibers use in making socks, denims, carpets
- Nylon 6 & nylon 11 → moulding purposes for gears, bearing etc.
- They are used for making filaments for ropes, bristles for brushes etc.

Polyethylene (PE):



Properties:

- ① rigid, waxy, white translucent, non polar material.
- ② exhibit considerable chemical resistance to strong acids, alkalis & salt solns at room temp.
- ③ good insulator of electricity.
- ④ swollen & permeable to most oils & solvents.

LDPE:

- It is a linear polymer with branching.
- Manufactured under (1000 - 3000 atm) & 80 - 350°C using initiators as Benzoyl peroxide.

Properties:

- density range $0.910 - 0.925 \text{ g/cm}^3$
- not reactive at room temp.
- can withstand temp. of 80°C continuously & 95°C for a short time.
- has more branching than HDPE.
- flexible & tough.
- $f \downarrow$ as less tightly packed & less crystalline.

Uses :-

- most common in plastic bags.
- dispensing bottles, wash bottles, tubing etc.
- parts of computer hardware
- parts that require flexibility, for which it serves very well.
- corrosion-resistant work surfaces.

HDPE :

- linear polymer with little or no branching
- low pressure (1000 - 3000 atm) & below 100°C using ZNC

Properties :

- large strength-density ratio
- mass density range → 0.941 to 0.97 g/cm³
- It has little branching giving it stronger intermolecular forces & tensile strength than LDPE.
- Hard, more opaque & withstand high temp (120°C for short period, to 110°C continuously).

Uses :

- 3D filament, Banners, Bottle caps, food storage containers, folding chair & tables.

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P-F resins (Phenol-formaldehyde)

- made by condensation polymerisation & are thermosetting.
- two imp. commercial PF resins

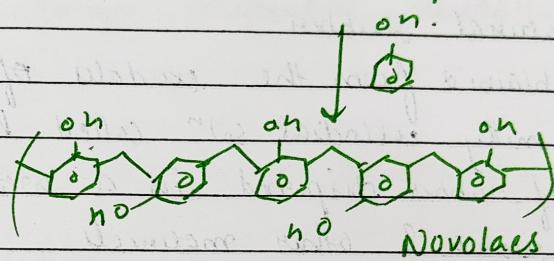
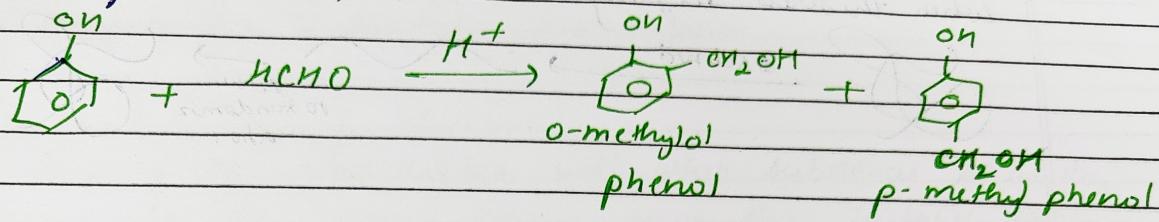
→ Novolacs & Resole.

- nature of product formed depends largely on molar ratio of phenol to formaldehyde & also on nature of catalyst.

- phenol ring has 3 potential reactive sites
formaldehyde has 2 reactive sites

(1) Novolacs :

P/F ratio > 1
 catalyst \rightarrow acid, \therefore

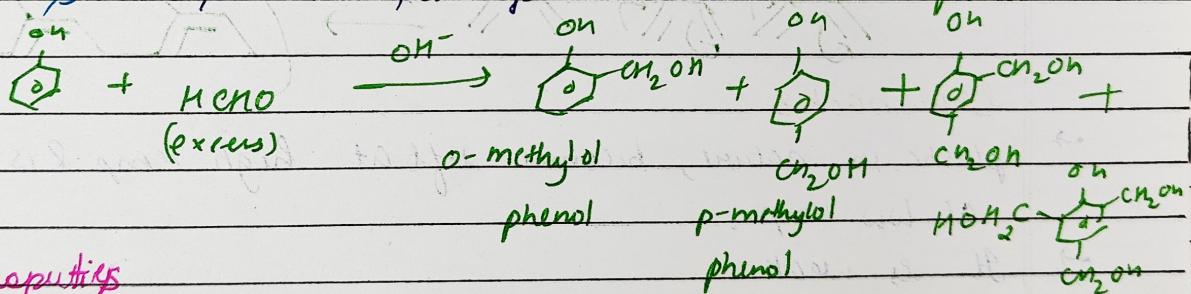


\rightarrow soluble & fusible.

\rightarrow 5-6 phenol rings per molecule are linked through methylene bridges.

(2) Resins :

$P/F < 1$, catalyst \rightarrow base.



Properties

\rightarrow rigid, hard, scratch-resistant, infusible, water resistant, insoluble solid.

\rightarrow attacked by alkalis.

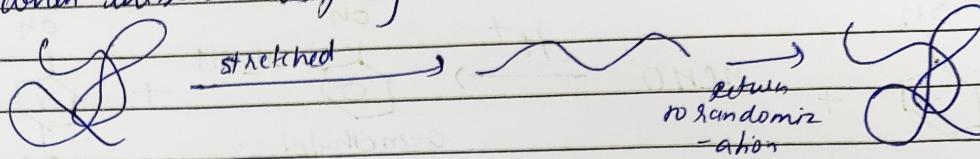
\rightarrow resistant to non-oxidizing acids, salts & many organic solvents.

Uses :

- \rightarrow electrical insulators parts like switches, plugs, switch board
- \rightarrow In paint & varnish
- \rightarrow hydrogen exchanger resins in water softening

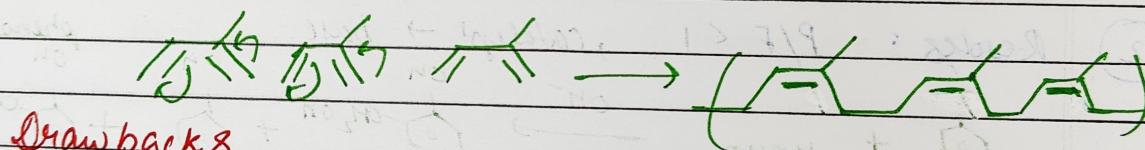
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Glastomers: long polymer which under stress undergoes elongation by several times & regains its original shape when the stress is fully released.



(1) natural rubber:

- obtained from the exudate of rubber trees in form of milky colloidal soln called latex containing 25-45% of rubber dispersed in a watery medium with small amounts of protein & other materials.
- latex is either processed either by
 - i) coagulation by acid or by heat & processed further
 - ii) mixed with compounding materials & precipitated directly from the soln



Drawbacks

- plastic in nature, becomes soft at high temp & is too brittle at low temp.
- It is weak
- Large water absorption capacity
- Little durability

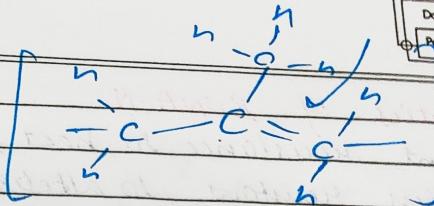
Vulcanization

Through this elasticity of rubber & plasticity by the formation of crosslinked M-network.

- It is done by heating the rubber with S under press.

S attacks this bond.

A type rubber contain 3-5% sulphur
but battery case rubber may contain as much as 30% Sulphur



Compounding of Rubber:

mixing of raw rubber with other substances so as to impart the product specific properties suitable for particular job.

① Softeners & plasticizers are added to give rubber greater tensile strength & adhesion.

② Vulcanizing Agents: S, SCl

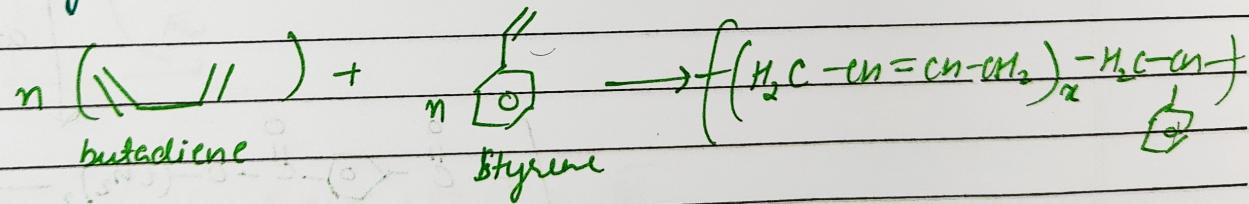
③ Accelerators: These materials drastically shorten the time required for vulcanization. e.g. 2-mercaptol

④ Antioxidants:

⑤ Reinforcing filler → gives strength & rigidity to rubber products.
e.g. CaCO_3

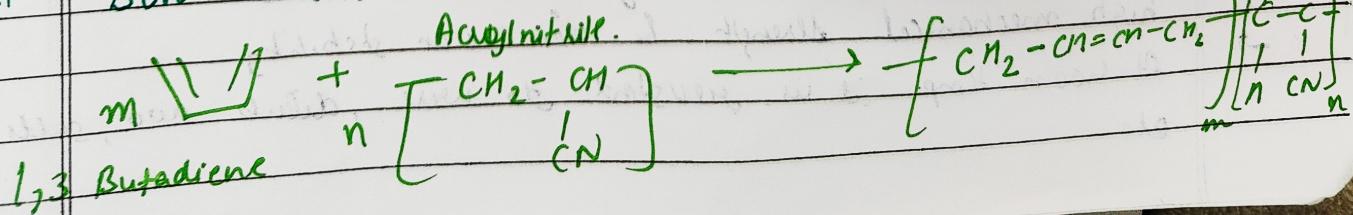
⑥ Colouring agents.

Styrene rubber (Buna S or SBR)



→ Styrene domains acts as anchors or junctions.
→ Butadiene provide flexible linkages.

BUNA-N (nitrile rubber)



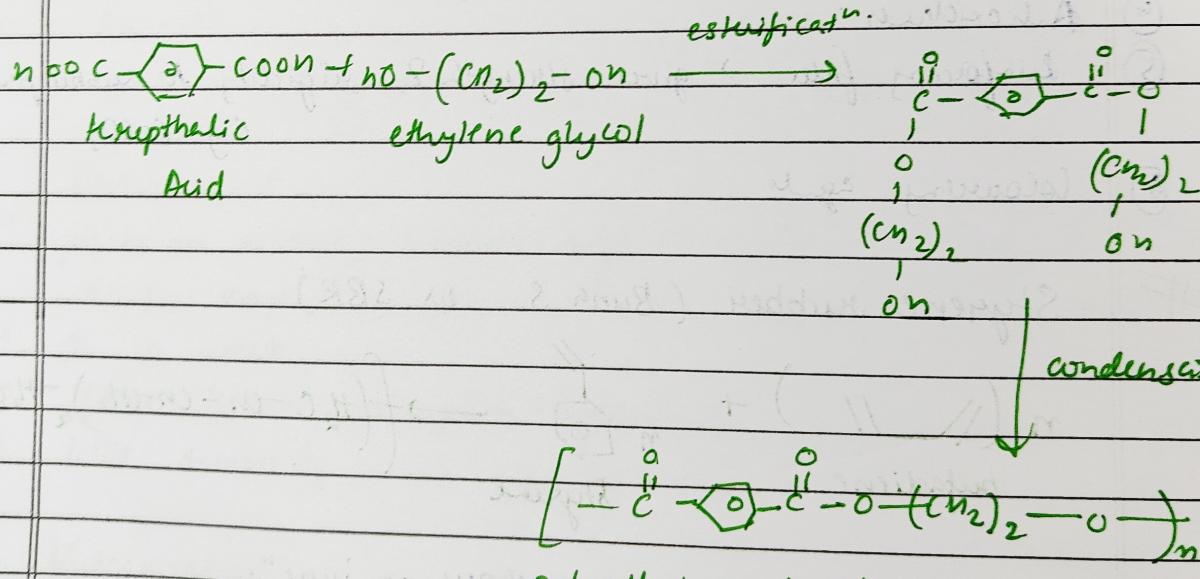
Properties of BUNA-N

- excellent resistance to heat, sunlight, oil & acid
but less resistant to alkalis than natural rubber.
- As proportion of acrylonitrile is ↑, the resistance to acids, salts, oils ↑.
- Vulcanized nitrile rubber is more resistant to heat & ageing than natural rubber.

Uses:

- for making conveyor belts, high altitude aircraft components, tank lining, gaskets

Polyester / Esteron / Polyethylene Sulfite



- properties.
- can exist both in amorphous & semicrystalline form.
- stable over temp. range of -40°C to 100°C.
- high mechanical strength & dimension stability.
- At room temp. it is resistant to water, dilute acids, salts etc.

Application :-

- for making video & audio tape.
- for making clear bottles for foods & beverages
- to make films for shank packet.
- As an electrical insulator, it is used for making molds for electrical appliances.

Degree of Polymerisation :

Mol. mass of polymer

Mol. mass of monomer

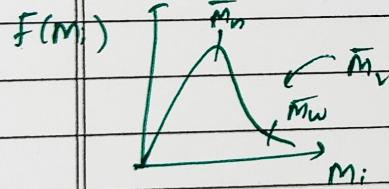
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Number-average molecular mass = total mass of all
(M_n) molecules

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{w_i}{\text{total no. of mol. present.}}$$

~~Molecular mass of polymer~~

$$\text{Weight average, } M_w = \bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum w_i M_i}{\sum w_i}$$



#

$$\text{Polydispersity Index (PDI)} = \frac{\bar{M}_w}{\bar{M}_n}$$

monodispersed $\bar{M}_w = \bar{M}_n$

②

COMPOSITE &

BIOMATERIAL

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Composite material :

A material composed of two or more physically distinct phases whose combination produces aggregate properties that are different from those of its constituents.

Eg: cemented Carbides (WC) with Co binder
plastic molding compounds containing fillers

⇒ Composite → filler + Matrix

Matrix

1. Material component that surrounds the fiber.
2. usually a ductile, or tough, material with low density.
3. strength usually ≈ 1 (or less) than that of fiber

Eg: thermoplastic resin thermoset (most common epoxy, phenolic)

4. Serve to hold the fiber (filler) in a favorable orientation.

Fiber:

→ Material that are strong with low densities.

→ Eg: glass, C, paracryl

⇒ Eg: fibreglass acquire strength from glass & flexibility from polymer.

#

Advantages :-

- High strength to weight ratio.
- High creep resistance
- High toughness
- Corrosion resistance
- High tensile strength at elevated temperatures.
- Anisotropic - bidirectional properties can be design advantage (i.e. helicopter blades).
- Dimensional changes due to temp. changes can be much less.

#

Disadvantages :-

- Material costs
- Repair can be difficult
- fabrication / manufacturing difficulties.
- properties non-isotropic makes design difficult.
- Wider range of variability (statistical spread).

#

Classification of Composition :

Based on Matrix material

1) Metal Matrix Composites (MMC)

- Composed of a metallic matrix (Al, Mg, Fe, Co, Cu) & a dispersed ceramic (oxides, carbides) or metallic phase (Pb, W, Mo) e.g. $\text{Al-Al}_2\text{O}_3$
- High strength, high stiffness, abrasion resistance etc.

2)

Ceramic Matrix Composites (CMC):

composed of ceramic matrix & embedded fibers of other ceramic material. (dispersed phase)

e.g. SiC-SiC

3) Polymer Matrix Composite (PMC) :

composed of matrix from thermoset (epoxy) or thermoplastic (PVC) & embedded glass, C, steel or kevlar fibers.

e.g. GFRP aka fiberglass (polyester or epoxy & glass).

⇒ CFRP (Carbon fiber reinforced composite)

GFRP (glass fiber reinforced composite).

BIOMATERIALS

→ Biomaterial is used to make devices to replace a part or a function of body in a safe, reliable, economic & physiologically acceptable manner.

→ It is a non-viable material used in medical device, intended to interact with biological systems.

⇒ Treatment option → transplantation

→ reconstruction

→ mechanical devices

Evolution of Biomaterial

1st generation (1950s) - Goal: Biocompatibility

2nd generation (1980) - Goal: Bioactivity

3rd generation (2000) - Goal: Regeneration

1st Generation →

1st generation implants

Gold fillings, wooden teeth, PMMA dental prostheses -
steel, gold, ivory, bone plates etc - glass eyes & other

body parts.

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2nd Generation Implants

- Collaborations of physicians & engineers
- Used advances in materials science.
- 2nd generation Implants - Titanium alloy dental & orthopedic implants - Co-Cr implants - UHMW polyethylene bearing surfaces for total joint replacements
- Heart valves & pacemakers.

3rd generation Implants:

- bioengineered implants using bioengineered materials
- Some modified & new polymeric devices
- Eg: Tissue engineered implants designed to re-grow rather than replace tissues - Some resorbable bone repair cements - Genetically engineered 'biological' components.

Characteristics of Biomaterials:-

Physical Requirements

- Hard Material
- Flexible Material

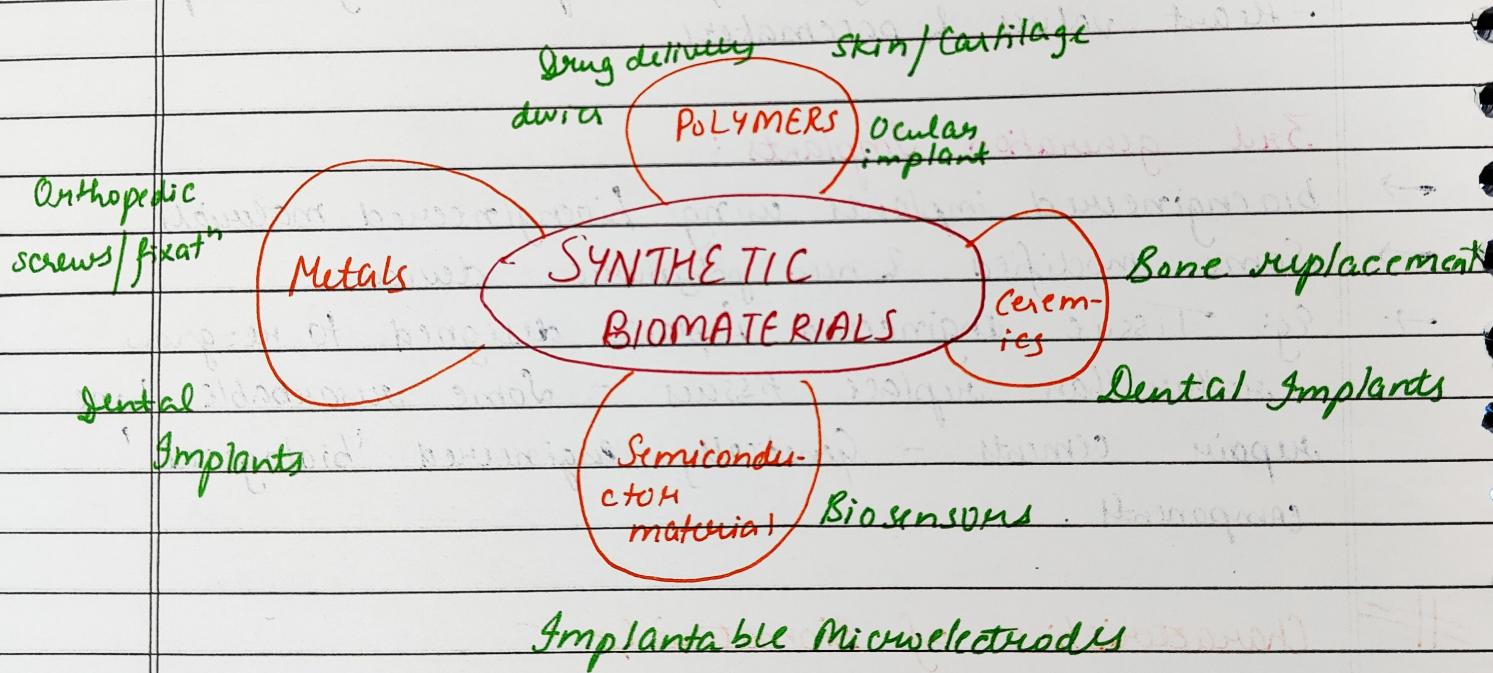
Chemical Requirements

- Must not react with any tissue in the body.
- Must be non-toxic to the body.
- Long-term replacement must not be biodegradable.

diisopropyl benzene
sulphonate

Features of a Biomaterial :-

- absence of carcinogenicity (the ability to produce cancer)
 - Absence of immunogenicity
 - Absence of teratogenicity (ability to cause birth defects)
 - Absence of toxicity.



CERAMICS

Ceramics :-

- These are mostly silicates, oxides, nitrides & carbides
- insulative do the passage of electricity & heat
- resistant to high temp & harsh environment than metals & polymers.
- hard but very brittle.

Properties of Ceramics:-

- Extreme hard
- Heat, corrosion resistance
- High wear resistance
- Low electrical, thermal conductivity.
- Low thermal conductivity
- Low thermal expansion
- Poor thermal shock resistance.
- Low ductility (very brittle & high elastic modulus)
- Low toughness

(Low fracture toughness indicates the ability of a crack or flaw to produce a catastrophic failure.)

- Low density
- High strength at elevated temperature

Classification of Ceramics.

Classes.	Clay products	Refractories	Abrasives	Cements	Advanced ceramics
→ optical	→ whiteware	→ bricks for	→ sandpaper	→ composite	ceramics
→ containers	→ structures	high T (furnaces)	→ cutting	→ structures	→ Zirconia, BN, SiC etc
→ composite reinforce			→ polishing		

1. Refractories :-

→ these are used at high temp. (e.g. in furnaces)

→ Silica (SiO_2) - Alumina (Al_2O_3)

→ Silica refractories - silica rich - small additions of alumina depress melting temp. (

2. Cutting tools :-

→ Tools :-

for oil drilling

for cutting Si wafers

→ Materials :-

manufactured single crystal or polycrystalline diamond in a metal or resin matrix.

3. Sensors :-

Eg: ZnO_2 as O_2 sensors.

→ principle: ↑ diffusion rate of O_2 to produce rapid response of sensor signal to change in O_2 concentration

→ Approach: add Ca impurity to ZnO_2 :

↑ O^{2-} vacancies

↑ O^{2-} diffusion rate.

→ Operation:

magnitude of V.D \propto pp of O_2 at external surface.

4. Advanced Ceramics: Materials for Automobile engine

Advantages

- Operate at high temp.
- Low frictional losses
- Operate without cooling system
- Lower weight than current engines

Disadvantages

- Ceramic materials are brittle.
- Difficult to remove internal voids.
- Ceramic parts are difficult to form & machine.

→ e.g. Si_3N_4 , SiC , ZrO_2 (used in engine block & piston coating)

5. Materials for ceramic Armor:

Components: Outer facing plates, Backing sheet

- | | |
|---|--|
| → properties: hard & brittle
fracture high velocity projectile
e.g. Al_2O_3 , B_4C , SiC | Soft & ductile
deform & absorb remaining energy
e.g. Al, Synthetic fiber laminates |
|---|--|

#

Ceramic Fibration Methods:

Glass forming particulate forming Cementation

1) Blowing of glass Glass forming:

Blowing of pressing:

- pressing → plates, cheap glass.
- glass formed by application of press
- mold is steel with graphite lining

Heat treating glass

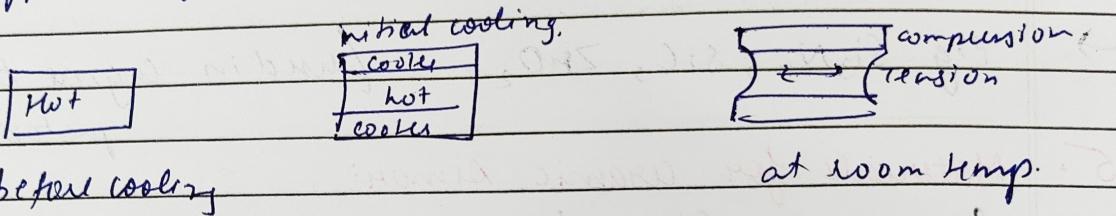
→ Annealing:

~~Annealing removes internal stress caused by uneven cooling.~~

→ Tempting:

out surface of glass part into compression.

suppresses growth of cracks from surface scratches.



2. Particulate forming:

Hydroplastic farming:

→ Mill & screen constituents desired particle size.

Slip Casting:

Same film

→ Mix with water & other constituents to form slip.

typical porcelain composition

50% clay

25). filter (finely ground) quartz

425-1. fluxing agent

Drying as water is removed - interparticle spacings ↓

- shrinkage.

- drying too fast causes sample to warp or crack.

fixing: heat treatment b/w 900 - 1400 °C.

Vitrification: liquid glass forms from clay & flux flows b/w SiO_2 particles. (flux ↓ melt temp).

Powder pressing:
powder (plus binder)

Sintering occurs during firing of a piece that has been powder pressed.

e.g. Al_2O_3 powder sintered at 1700°C for 6min

Tape casting:

- Thin sheets of green ceramic cast as flexible tape.
- Used for integrated circuits & capacitors.

3. Cementation:

- Hardening of paste: paste formed by mixing cement material with water.
- Formation of rigid structures having varied & complex shapes.
- Hardening process: hydration (chemical rxn involving polymer)
- portland cement →
mix clay & lime bearing minerals
calcine (heat to 1400°C)
grind into fine powders