POLYMERS

INDEX:

CLASSIFICATION OF POLYMERS:

1# On the basis of origin:

(a) Natural: (eg starch, cellulose, proteins etc.)

(b) Synthetic: (eg PVC, nylon, bakelite etc.)

2# On the basis of monomer composition:

(a) Homopolymer: $n(A) \rightarrow (A)_n$ (identical monomer)

(b) Copolymer: $n(A) + m(B) \rightarrow$ A – A – B – B – A – B (non-identical)

(i) Random Copolymer (–A – B – A – A – B – A – B – B–)

(ii) Alternating Copolymer (–A – B – A – B – A –)

(iii) Block Copolymer (–A – A – A – A – B – B – B – B –)

(iv) Graft Copolymer (–A – A – A – A – A –)

B
|
B
|
B

3# On the basis of chain structure:

(a) Linear polymer – Dense, packed well

(b) Branched polymer – low density

(c) Cross-linked polymer – 3-D network.

4# On the basis of chain composition:
(a) Homochain polymer - (all C-atoms in backbone)
(b) Heterochain polymer - (heteroatom in backbone)

5# On the basis of polymerization mechanism
(a) Addition polymers: Obtained by added monomers
(b) Condensation polymers: Obtained by two monomers condensed together.

6# On the basis of molecular force.
(a) Elastomers: > Weak intermolecular forces. (eg rubber)
(b) Fibres :> Strong intermolecular forces like hydrogen bonds.
> Crystalline with high tensile strength. (eg nylon66)
(c) Thermoplastics :> Intermediate intermolecular forces.
> Soften on heat, harden on cooling
> No cross linkage (eg. PVC, teflon)
(d) Thermosetting plastics: > Intermediate IMFOA
> Can't softened once hardened
> Hard & infusable due to cross-links.
(eg. bakelite, melamine)

7# On the basis of tacticity (spatial arrangement of substituent groups of asymmetric carbon)
ystalline { (a) Isotactic: All asymmetric-C have same arrangement
(b) Syndiotactic: Alternate asymmetric-C have same arr.
morphous { (c) Atactic: Random arrangement

$-(A\bullet)_n$ here, n is degree of polymerization

Date:
Page No:

8# On the basis of polymerization
(a) Oligopolymers: Low degree of polymerization
(b) Macromolecules: High degree of polymerization.

9# On the basis of chemical composition
(a) Organic : C as backbone (eg. nylon, PVC etc.)
(b) Inorganic: No C in backbone (eg. rubber of silicone)

FUNCTIONALITY OF POLYMERS
→ Defined as the no. of reactive sites in molecule
→ Monomers have ≥2 reactive sites
(Ethylene has 2, Acetylene has 4, Phenol has 3 (ortho, ortho, para))
→ Linear polymers arise from bifunctional monomers
→ Cross-linked polymers arise from trifunctional monomers
→ A mix of bi- & tri- leads to branched.

MECHANISM OF POLYMERIZATION:
A # Addition Polymerization
* Monomers are directly added without byproducts
→ Mechanism : (3-step)
(i) Chain Initiation:
> Active molecules called chain initiators attack monomer

$$M + \underset{(\text{initiator})}{I-I} \rightarrow 2I^+ + \underset{(\text{monomer})}{M} \longrightarrow \underset{(\text{initiated})}{I-M^+}$$

(ii) Chain Propagation:
> Initiated chain attacks more monomers

$$I-M^+ + M \longrightarrow I-M-M^+ + M \longrightarrow I-M-M-M^+ \longrightarrow \ldots$$

(iii) Chain termination :

> Active centres combine with each other.

$I-M-M-M^+ + M^+-M-M-I \longrightarrow I-M-M-M-M-M-M-I$

* Types of Mechanisms:

1.) Free radical mechanism

(i) Chain Initiation : Homolytic dissociation causes free radical formation.

(dissociation) $C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{\Delta} 2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow 2C_6\dot{H_5} + CO_2$

(initiator reaction) $I-I \longrightarrow 2I^\bullet$

$I^\bullet + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow I-CH_2-\underset{X}{\underset{|}{CH^\bullet}}$

(monomer) (initiated monomer)

(ii) Chain Propagation: Additional monomers added.

$I-CH_2-\underset{X}{\underset{|}{\dot{CH}}} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow I-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{CH}}}$ ----

$I\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_n CH_2-\underset{X}{\underset{|}{CH^\bullet}}$ or $I \sim\sim\sim CH_2-\underset{X}{\underset{|}{\dot{CH}}}$

* Types of propagation

→ $\sim\sim CH_2-\underset{X}{\underset{|}{\dot{CH}}} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow \sim\sim CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{CH}}}$

(head to tail)

→ $\sim\sim CH_2-\underset{X}{\underset{|}{\dot{CH}}} + \underset{X}{\underset{|}{CH}}=CH_2 \longrightarrow \sim\sim CH_2-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-\dot{CH_2}$

(Tail to Tail)

→ $\sim\sim \underset{X}{\underset{|}{CH}}-\dot{CH_2} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow \sim\sim \underset{X}{\underset{|}{CH}}-CH_2-CH_2-\underset{X}{\underset{|}{\dot{CH}}}$

(head to head)

→ $\sim\sim \underset{X}{\underset{|}{CH}}-\dot{CH_2} + \underset{X}{\underset{|}{CH}}=CH_2 \longrightarrow \sim\sim \underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-\dot{CH_2}$

(Tail to head)

(iii) Chain Termination : Growth of chain arrested

(a) By Coupling : Radicals of two active chains combine to complete the chain.

(b) By disproportion :

$$I\left[CH_2-\underset{X}{CH}\right]_n-CH_2-\underset{X}{\dot{C}H}+\underset{X}{\dot{C}H}-CH_2\left[\underset{X}{CH}-CH_2\right]_m I$$

$$I\left[CH_2-\underset{X}{CH}\right]-CH_2-\underset{X}{CH_2}+\underset{X}{CH}=CH\left[\underset{X}{CH}-CH_2\right]_m I$$

(c) Chain Transfer

$$R\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{\dot{C}H}+SH\rightarrow R\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{CH_2}+\dot{S}$$

This $\dot{S}$ acts as an initiator for other chain.

2.) Ionic Addition Polymerization

Following the same basic steps but the initiator is cation or anion ~~depends~~ instead of free radical.

(i) Cationic Polymerization :

Initiator → electrophile

Intermediate → carbocation

Inhibitor → nucleophile.

$$Y^+ + CH_2=\underset{X}{CH} \longrightarrow Y-CH_2-\underset{X}{\overset{\oplus}{C}H}$$

(ii) Anionic polymerization

~~Intermediate~~ Initiator → nucleophile

Intermediate → carbanion

Inhibitor → electrophile

Date:

Page No:

5) Co-ordination Polymerization

Neither radical nor ion, but the orientation of monomers in a specific way using catalysts (Zigler - Natta catalyst i.e. triethylaluminium)

$$Cat-R' + CH_2=CHR \longrightarrow Cat\,CH_2\,CH(R)R' \;(+\; n\,CH_2=CHR')$$

$$\longrightarrow Cat-CH_2-\underset{\substack{|\\R}}{C}-\left(CH_2-\underset{\substack{|\\R}}{CH}\right)_n R'$$

3# Condensation Polymerization

Monomers added with by-product removal.

$$n\,HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH + n\,H_2N-(CH_2)_6-NH_2$$

$$\longrightarrow \left[-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH\right] + 2n\,H_2O$$

Addition	Condensation
Chain growth polymerizaⁿ	Step-wise polymerizaⁿ
Monomers added together	Monomers condensed together
No eliminatⁿ	Eliminaⁿ occurs
Homopolymers formed	Heteropolymers formed
Thermoplastics "	Thermosetting plastics "
Take long time for yield	Take time for more molec. wt.
Eg: PVC	Eg: Nylon 6, 6.

Date:
Page No:

PLASTICS

Shapable to hard materials by heat & press.

Adv over metals :

> Lightweight yet strong
> Corrosion-resistant
> No moisture absorption
> low maintenance
> Easily mouldable
> less brittle than glass yet smooth / glossy
> Can take variety of colors.

Thermoplastics (Soften on heating)

> Resoften as they comprise of long-chain molecules

eg: polyethene, teflon, polypropylene etc.

Thermosetting (Once set, forever set)

> 3-D cross linked structure does not soften but disintegrate on heat.

eg: Bakelite, epoxy resins etc.

	Thermoplastic	Thermosetting
1.	Resoften	Don't resoften
2.	Reusable scrap	Non-reusable scrap
3.	Addition polymerizaⁿ	Condensaⁿ polymerizaⁿ
4.	Low molec. wt.	High molec. wt.
5	Soluble in organic solvent	Insoluble in organic solvent
6.	Linear	3-D
	eg: PVC	eg: Bakelite

Date:
Page No:

Moulding Constituents

1) Resin: They hold all other constituents
2) Plasticizers: > Increase flexibility
   > Neutralize IMFOA
   > eg: veg. oils, oleic acids.
3) Fillers: > Improve hardness / tensile strength
   > eg1: carbon black in natural rubber
   eg2: Asbestos in plastic
4) Lubricant: Prevent sticking to mould
5) Catalysts: Accelerate polymeriza^n (for thermosetting)
   eg: Ag, Cu, Pb.
6) Stabilizers: Improve thermal stability
   eg: Pb salts
7) Coloring materials: Impart color.

Moulding Processes

1) Compression Moulding

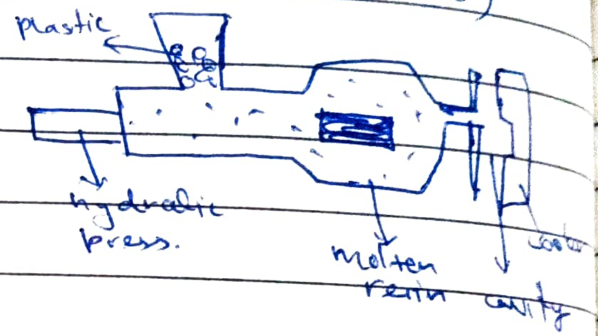
> For thermosetting (switches, handles etc.)
> Mould is of 2 halves
> Upper half has projection, lower half has cavity
> Material in lower half is heated
> Both parts closed under pressure and excess comes out as flash.

2) Transfer Moulding

> For thermosetting
> A piston forces material into mould cavity through sprue and runner system

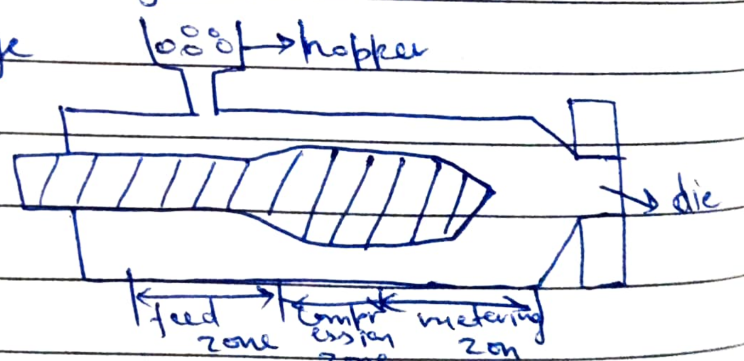
#3) Injection Moulding

> For thermoplastics (mugs, buckets, bins etc)
> Plastic as granules is molten
> Piston injects molten part to cavity
> Material cooled & solidified
*> High speed



#4) Extrusion Moulding

> For elongated articles (pipes, rods, tubes, etc)
> Same as injection but cavity is replaced by die and piston is replaced by helical screw
> • feed zone recieves charge
• compression zone melts charg
• metering zone injects molten paste to die



> hot material is then extruded out as long article.

THERMOPLASTIC RESINS (Polyethylene)

(a) Low - density Polyethylene (LPDE)

> polymerization of ethylene @ 250°C 1000-3000 atm with benzoyl peroxide initiators.

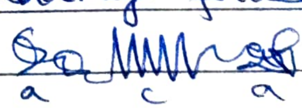
$$n(CH_2=CH_2) \longrightarrow -(CH_2-CH_2)_n$$

> Waxy solid that floats on water
> Low density due to less branching.

> Non polar
> Tough, flexible, inert, ~~electrical insulator~~
> Usage: bags, mugs, toys, ink tubes etc.

(b) High - density Polyethylene (HPDE)
> Polymerizaⁿ of ethylene @ 60-70°C 6-8 atm with Ziegler-Natta catalyst
> High density due to packed chains
> High softening temp. (135°C)
> Low water/gas permiability, inert, non-toxic.
> Usage: pipes, bottles, drug packing, crates, containers, tanks, sheets to pack.

(c) Linear low-density polyethylene (LLPDE)
> Copolymer of ethylene & 1-butene
> Uses: golf balls, blending with LPDE, packing films, bottles etc.

(d) Ultra high molecular weight polyethylene (UHMWPE)
> Linear polymer with amorphous (randomly folded) & crystalline (neatly oriented folded) region 

> Uses: surgical prostheses, machine parts, heavy-duty liners.
~~> eg: Poly~~

* Polypropylene
> Homopolymer of propylene
Prop.
> Low density, stiff, heat resistance, inert

> transparent, rigid, glossy
> recyclable, weldable

Uses:

> Rope fibre, carpet, bags, water-pipes etc.

* Polyvinyl Chloride (PVC)

> Radical polymerization of ~~poly~~ vinyl chloride with atactic substitution. $\{CH_2-CHCl\}_n$

Prop:

> Colorless, odorless, non-flammable, inert, light resistant.

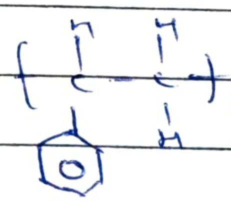
(i) Rigid PVC: Brittle, rigid, used for sheets

(ii) Plasticised PVC: Based on esters of poly carboxylic acids

Uses:

> Pharma package, water/juice packs, blood bags, gloves etc.

* Polystyrene



> polymerization of styrene

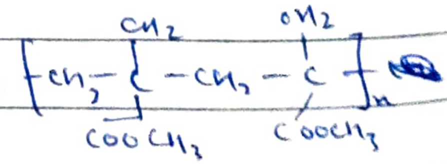
Prop:

> light, transparent, moisture-resistant, brittle

Uses:

> Use n throw cups/bottles, toys, disposables, medical uses.

* Polymethylmethacrylate (PMMA)



> methyl metha acrylate polymerisaⁿ

Prop:

> Known as plexi glass for transparency/strength.

> inert but dissolves in some organic solvents.

Uses:

> Glass substitute in lens, windscreen, signboards, windows etc

* Polytetrafluoroethylene (PTFE) (Teflon)

$$CF_2 = CF_2 \xrightarrow[(NH_4)_2S_2O_8]{\text{pressure}} \left[CF_2 - CF_2 \right]_n$$

Prop:
> higher softening temp. (350°C)
> Strong & inert
> Doesn't dissolve in acids or corrosive alkali

Uses:
> Non-stick utensils, pump valves/ pipes, motor insulators etc.

* Polyvinyl acetate (PVA)

$$CH_2 = CH - COOCH_3 \longrightarrow \left[CH_2 - \overset{COOCH_3}{\overset{|}{CH}} \right]_n$$

Prop:
> insoluble in water but soluble in organic solv.
> difficult to saponify
> air, water, chem resistant

Uses:
> Adhesive/ paint, chewing gums, surgical dressings.

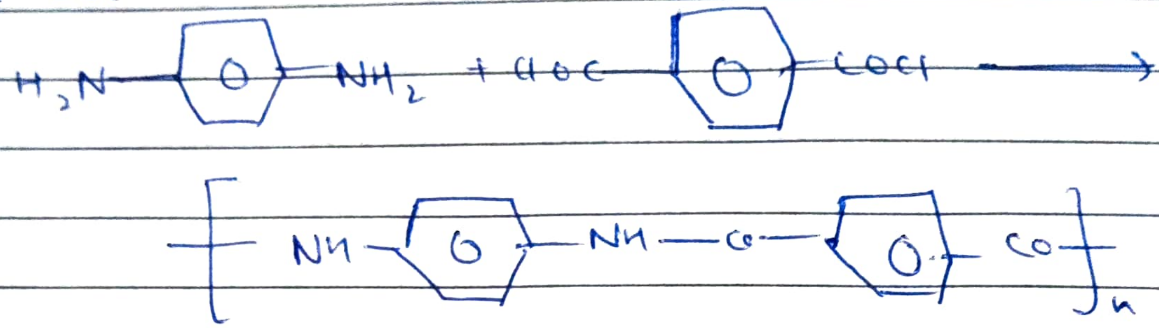
* Nylon 6,6 (Polyamide)

$$HO - \overset{O}{\overset{||}{C}} - (CH_2)_4 - \overset{O}{\overset{||}{C}} - OH + H_2N - (CH_2)_6 - NH_2 \longrightarrow \left[\overset{O}{\overset{||}{C}} - (CH_2)_4 - \overset{O}{\overset{||}{C}} - HN - (CH_2)_6 - NH \right]$$

Prop:
> Strong, rigid, stable

Uses:
> fibre, automotive parts, hinges, conveyer belts, parachutes.

* Kevlar



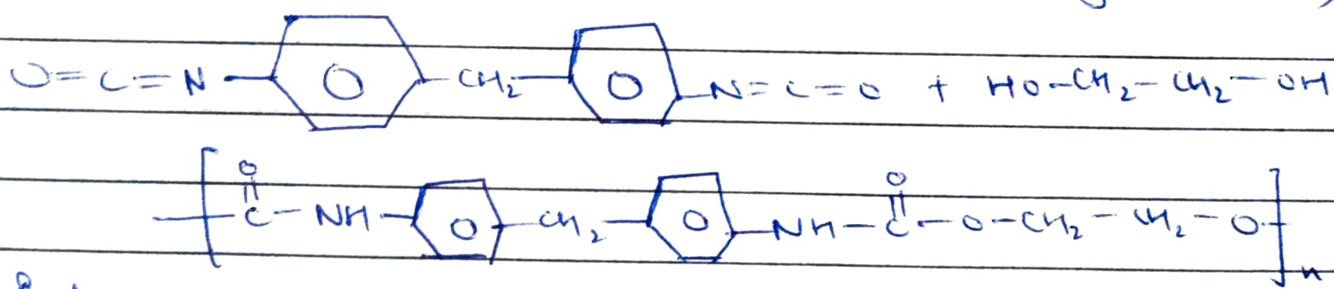
Prop:

> Gajab ka strong

Uses:

> helmets, vests, safety clothings in sports, ~~...~~ etc.

THERMOSETTING RESINS (Polyurethane)



Prop:

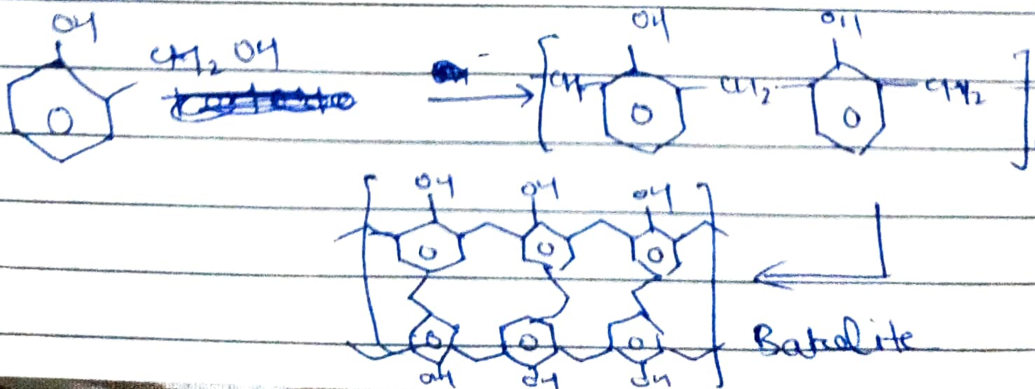
> Resillient, flexible, durable

> Affordable, safe

Uses:

> Footwear, Coatings, Furniture / buildings etc.

* Bakelite



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Bakelite

Prop:

> Quick moulding, smooth moulding

> Insulator, non-flexible, scratch-resistant

> swells in extreme humidity

> fishy odor on rubbing & burning

Uses:

> Electric insulator parts: switch/plugs etc

> Paints/Adhesives, telephon/TV parts.

* Silicone Resins

$$\left[O - \underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}} - O \right]_n \longleftarrow SiCl_4 + CH_3MgCl$$

Prop:

> Water / chem resistant

> Antifoaming agents

Uses:

> All weather lubricants, electric condensers.

Polymer Composites

Mixture of two polymers (thermoset or thermoplastic) with synergistic properties

(i) Advanced Composites (ii) Engineering composites

Adv.

> Lightweight

> Ability to tailor prop.

> Fatigue resistant

> Easy to mold

Disadv:

> High cost
> Complex manufacturing
> Low ductility
> Less damage noticeability

* Rubber (Elastomers)

> Stretchable to 4–10 times length
> Molecule has coil shape (amorphous but stretch to cryst.

> Natural Rubber

> Obtained from Hevea Brasiliensis tree.

$$\underset{\text{Isoprene}}{CH_2=\underset{|}{\overset{}{C}}(CH_3)-CH=CH_2} \longrightarrow \underset{\text{Polyisoprene}}{\left[CH_2-\underset{|}{C}(CH_3)=CH-CH_2\right]_n}$$

Prep:

> Taken from tree latex as milky liquid
> Coagulated with acetic / formic acid
> Bleached with $NaHSO_3$, washed, dried
> Heavy gummy mass passed in machine to make sheets
> Dried @ 50°C and called crepe rubber

Gutta-Percha (trans, 1,4-polyisoprene)

> It is unstreched as crystalline thus, rigid.
> Biologically inert, insulating.

Uses:

> Golf balls, submarine cables, adhesives

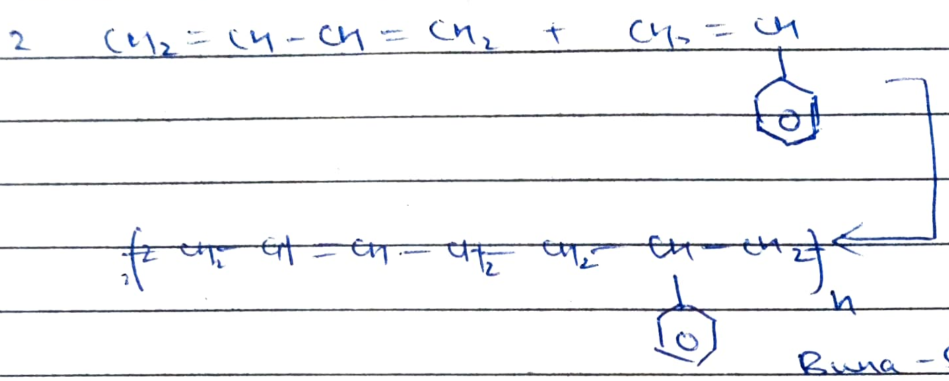
Date:
Page No:

Prop (Natural Rubber)
> Hardens @ 5°C
> Tacky @ 30°C (Two piece join to one)
> Water absorbant, soluble in organic sol.$^{\text{n}}$
> Non-resistant to oils.
Drawbacks:
>
> Decays in air
> Less durable
> Permanent deformation if stretched too much.

+ Vulcanization of Rubber
> Process of improvement in rubber elastisity by heating it in compounding chemicals, resulting in 3-D chains.
> Compounding chem – Sulphur, H_2S, Benzoyl chloride
Activator — ZnO, stearic acid
Prop:
> Higher tensile strength & break point
> Short permanent set
> Rapid retraction
> Less water absorption
> Large temp. range
> Chemical inertness.

> Synthetic Rubbers

* {Styrene Butadiene Rubber or Buna-S / GR-S}



Buna-S
(vulcanized by sulphur / S_2Cl_2)

Prop:

> Same as natural rubber

> Carbon black added for abrasion resistance

Uses:

> Tyres, footwear, adhesives ~~etc~~, insulation of wires etc.

* Nitrile Rubber (NBR / Buna-N / GR-A)

$$CH_2=CH-CH=CH_2 + \left(CH_2=\underset{CN}{CH}\right) \longrightarrow \left[CH_2-CH=CH-CH_2-CH_2-\underset{CN}{CH}\right]_n$$

Uses

> Couplings, rollers, washing machine parts, hoses, adhesives etc.

Prop:

> Oil resistant

> Weak

↑ Acrilonitrile → oil resistant tensile strength

↑ Butadiene → flexibility @ temperatures

* Neoprene (GR-M / polychloroprene / duprene)

$$CH_2 = CH - \overset{Cl}{\overset{|}{C}} = CH_2 \longrightarrow \left(CH_2 - CH = \overset{Cl}{\overset{|}{C}} - CH_2 \right)_n$$

Prop.:
> Similar to natural rubbers but oil / chem resistant
> Non-permeability for gases

Uses:
> Heavy-duty conveyer belts, hose covers, footwears etc.

* Butyl Rubber (GR-I / polyisobutyl - isoprene)

Uses:
> ~~Ty~~ Tyre tubes, hoses, diaphragms, cable insulation, seals.