The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

1984-1

International Workshop on Advanced Polymer Science and Turbulent Drag Reduction

10 - 20 March 2008

Characteristics of Polymer

Ram Prakash SINGH
University of Pune
Department of Physics
Ganeshkhind
411 007 Pune
INDIA

CHARACTERISTICS OF POLYMER

Dr. R.P.Singh
Former Vice-Chancellor
University of Lucknow
&
Head & Professor of Materials Science Centre, Indian Institute of Technology, Kharagpur

Characteristics of Polymers

- Low specific gravity and high specific strength
- Thermal and electrical insulations
- Corrosion and weather resistances
- Ease in design and manufacturing of complicated structures
- Outstanding aesthatic appeal due to ease in adoption of permanent colours
- Mass production with low energy intensive manufacturing techniques
- Ease in printability and adhesion
- Ease in handling and cleanliness
- Offering tremendous scope of physical and chemical modification to meet industrial and consumer requirement
- Tremendous adaptability to low cost production

Applications for Polymers

- Industrial
  - 1. Building and Construction
  - 2. Electrical, Electronics and Telecommunications
  - 3. Engineering
  - 4. Furniture
  - 5. Medical
  - 6. Packaging
  - 7. Textiles
  - 8. Transport

- Agriculture
  - 1. Water conservation and management
  - a. Reservoir and irrigation lining
  - b. Water tanks and containers
  - c. Mulching
  - d. Pipe for drip and sprinkler irrigation
  - 2. Plastics covered tunnels
  - a. Plastics covered tunnels
  - b. Green house covers
  - 3. Production collection and packaging
  - 4. Fertilizer, pesticides packaging, transport and distribution
  - 5. Livestock
  - 6. Machinery and Tools

The Application of Polymers in High Technology

- I. Polymers for advanced structures – polymers for high performance plastics / fibers (modules/high strength) Interpenetrating networks / Engineering / Polymer blends / Fiber reinforced materials.

- II. Polymers for Information Technology – Electro and photoconducting polymers / Information polymers for non-linear optics / piezo and pyroelectric polymers / organic semicondutor / photochronic and magnetic polymers /lithographic, packages and encapsulant polymers / polymers for separation technology / membranes (for industrial separations / for biomass and biological separation), flocculating polymers for selective recovery of minerals, drag reducing polymers / polymers for enhanced oil recovery.

- III. Polymers for Biosystems – Controlled release and targeted drug carriers, biosensors, biomaterials / biodegradable polymers.

Applications of Polymers

Applications have permeated all aspects of our life

- 1. Health
- 2. Medicine
- 3. Clothing
- 4. Transportation
- 5. Housing
- 6. Defence
- 7. Electronics
- 8. Energy
- 9. Employment
- 10. Trade

Low Density
High Specific Strength and Modulus
High corrosion resistance
High electrical and thermal
Conducting polymers
Easy and low energy processing into intricate shapes by fast processing techniques
Great aesthatic appeal
Moth and fungus resistance
Low permeability of water vapours and others gases
Controlled – Biodegradability; Biodegradable and non-biodegradable polymers

10 facts about plastics everyone should know…

- 1. Plastics are one of the most resource efficient and versatile materials available to society.
- 2. Plastics make a significant contribution to the vital goals of sustainable development :
  - Social progress plastics provide affordable products giving more people access to higher standards of living, healthcare and information
  - Economic development: the plastics industry chain in Europe adds value to society. It employs well over 1.5 million people and generates sales in excess of 159 billion euro.
  - Environment protection: plastics help save resources – fossil fuels and energy, plastics products save water and food.

- 3. Plastics consume only a tiny fraction – just 4% - of the world’s oil, as feedback.
- 4. Plastics products in use save oil:
  - 100kg of plastics parts in cars reduces oil consumption by about 12 million tonnes each year in Europe, reducing CO_2, emissions by 30 million tonnes a year.
  - Plastics help reduce fuel consumption and CO_2, emissions from our homes: the innovative use of plastics can reduce domestic fuel consumption to 3 litres per square metre, compared to an average of 20 litres.
- 5. Plastics are too valuable to waste – even at end-of-life. After serving a useful purpose, plastics can either be recyled or used as an alternative fuel. Plastic waste has a calorific value at least equal to coal and with lower CO_2 emissions.
- 6. Renewable energies rely on plastics: solar panels, wind turbines
- 7. Over 1 billion people in the world lack access to safe water. Plastics can preserve and distribute water economically, reliably and safety.

- 8. No other material can compete with plastics when it comes to meeting technological demands while preserving resources.
- 9. Plastics are the champions of prevention:
  - Plastics packaging represents 17% all European packaging and yet packages over 50% of the consumer goods.
  - Over a ten-year period it is estimated that plastics packaging per unit has been reduced by around 28% thanks to technology.
  - Without plastics packaging, the weight of packaging would increase four-fold, production costs and energy consumption would be doubled, and waste volume increased by 150%.
  - 10. Plastics make our lives safer: airbags, seatbelts, baby seats, bike helmets, medical devices …. Are just some examples.

The Use of Plastics in Automobiles

Plastics Content in Small Car (U.S.A.)

1980

↓

Double

↓

1990

↓

2000 (1.4 million tons)

Aerospace

- For each pound saved in the weight of the airframe, the pay load can be increased by a pound over the life of aircraft
- Further progress in manufacturing processes, repair procedures and failure mode control will enhance the use of polymers / composites in Aerospace applications

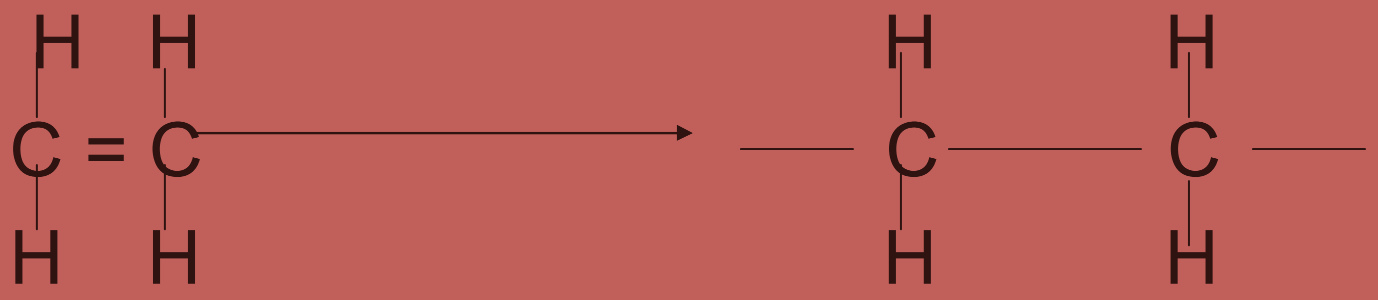
- Examples of the unexploited mechanical reserves of polymers in comparision with classical materials stiffness
- Percent achieved of the theoretically maximum value

	Injection Moulded	Fibres
Polypropylene	3%	40%
Polyamide	1%	3%
Glass	88%	
Steel	77%	
Aluminium	95%	

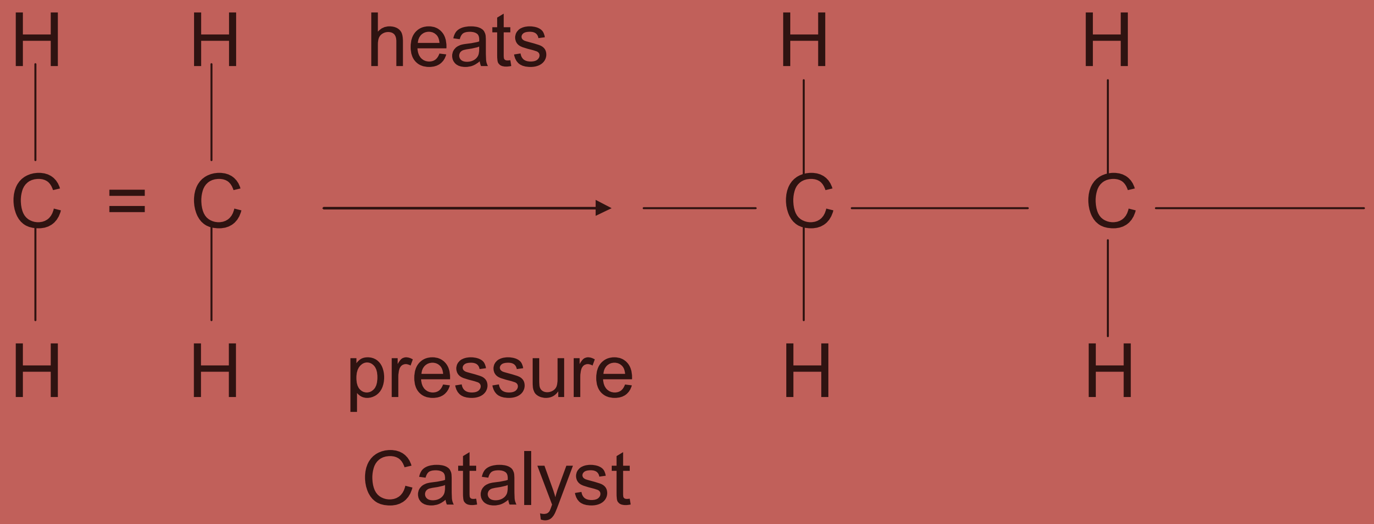
Monomers / Polymers / Mers

- Monomers: The simple molecules that are covalently bonded into long chains are called monomers. Long chain molecule formed from the monomer units is called a polymer.
- The chemical process by which the monomers are chemically combined into long chain molecular polymers is called

Chain –growth polymerization



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array} \longrightarrow -\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array}-\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array}-$$



$$\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \xrightarrow[\text{pressure, Catalyst}]{\text{heats}} -\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-$$

The repeat sub unit in the polymer chain is called a mer.

n- degree of polymerization (DP)= no. of such units or mers in the polymer molecular chain.

Average DP for polyethylene (PE) =3500-25,000

Molecular Weight = 1,00,000-7,00,000gm/mol.

Chain Polymerisation

- 1. Initiation, 2. Propagation, 3. Termination

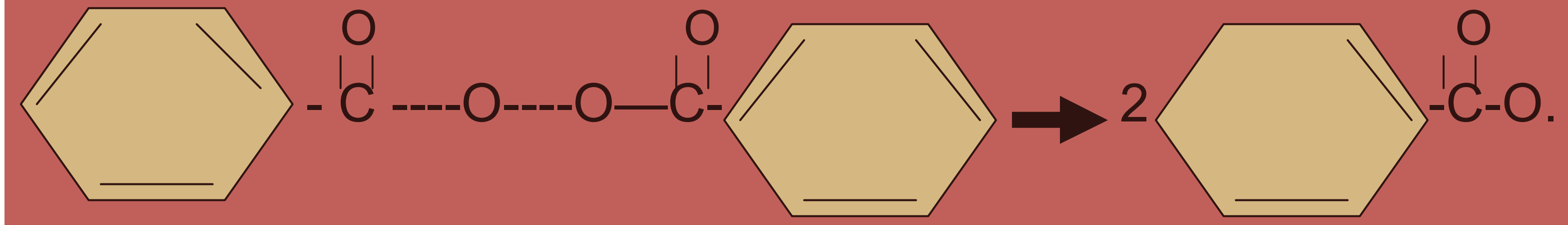
I – Initiation – Free radical – group of atoms having an unpaired electron (free electron), which can covalently bond to an unpaired electron (free electron) of another molecule.

$$H - O - O - H \xrightarrow{\text{heat}} 2H - O.$$

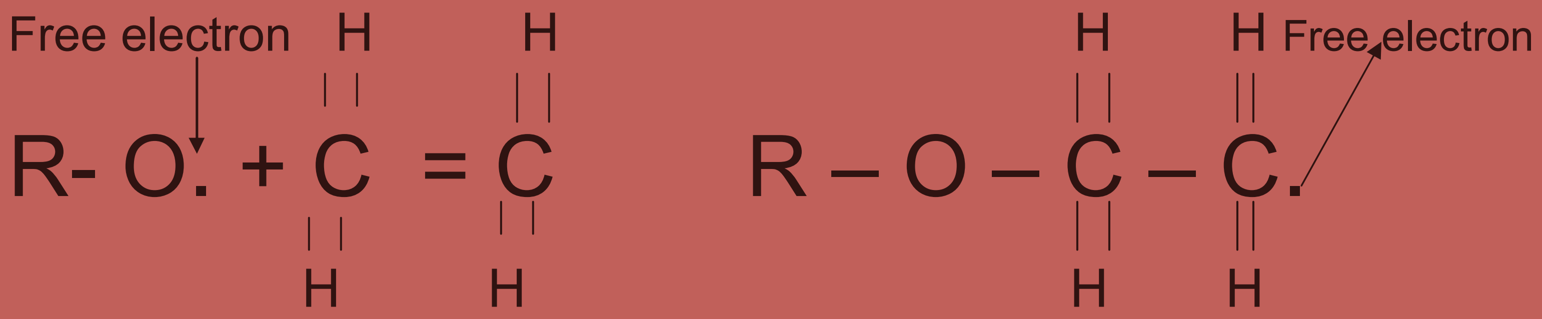
Hydrogen Peroxide

$$R - O - O - R \longrightarrow 2R - O.$$

Organic peroxide Free Radical



Benjoyal Peroxide Free Radicals



$$\mathrm{R\text{-}\,O.} + \underset{H}{\overset{H}{\mathrm{C}}} = \underset{H}{\overset{H}{\mathrm{C}}} \qquad \mathrm{R - O} - \underset{H}{\overset{H}{\mathrm{C}}} - \underset{H}{\overset{H}{\mathrm{C}}}.$$

II. Propagation:

$$R - CH_2 - CH_2 + CH_2 = CH_2 \longrightarrow$$

$$R - CH_2 - CH_2 - CH_2 - CH_2$$

III. Termination:

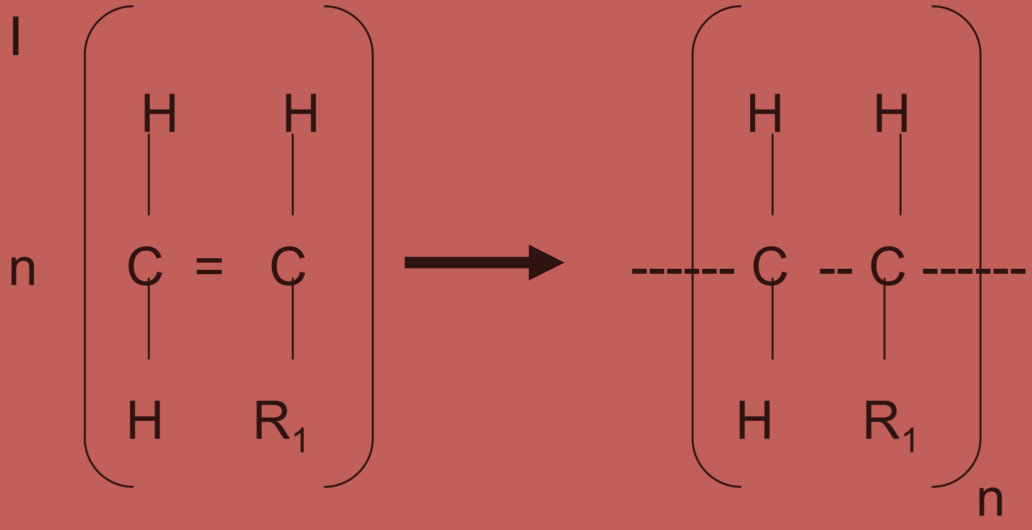
$$R(CH_2 - CH_2)^{\cdot}_{m} + R`(CH_2 - CH_2)^{\cdot}_{n} \longrightarrow$$

$$R(CH_2 - CH_2)_{m} - (CH_2 - CH_2)_{n} R`$$

Vinyl and Vinylidene Polymers.

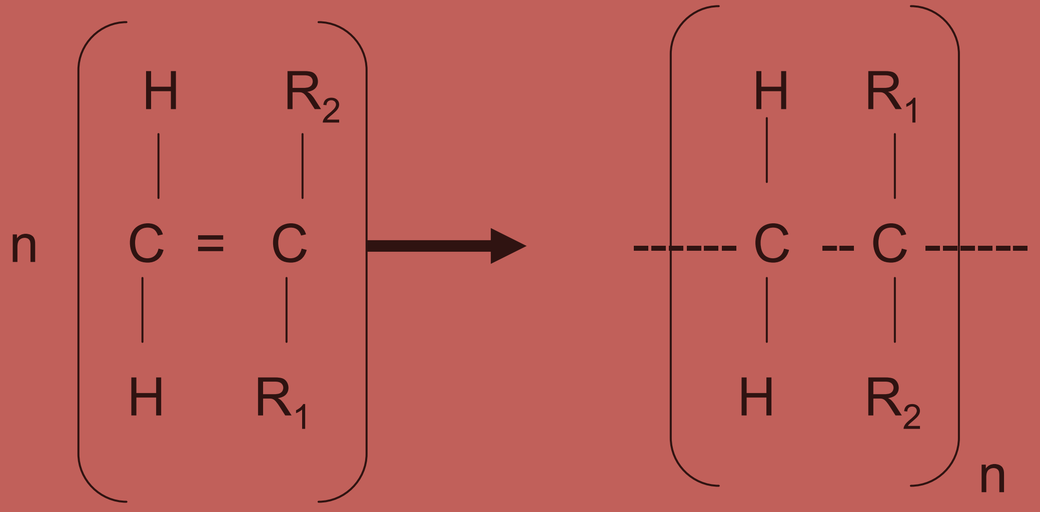
I) Vinyl Polymers

I



$$n\left(\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & R_1 \end{array}\right) \longrightarrow \text{------}\left(\begin{array}{ccc} H & & H \\ | & & | \\ C & \text{--} & C \\ | & & | \\ H & & R_1 \end{array}\right)_{n}\text{------}$$

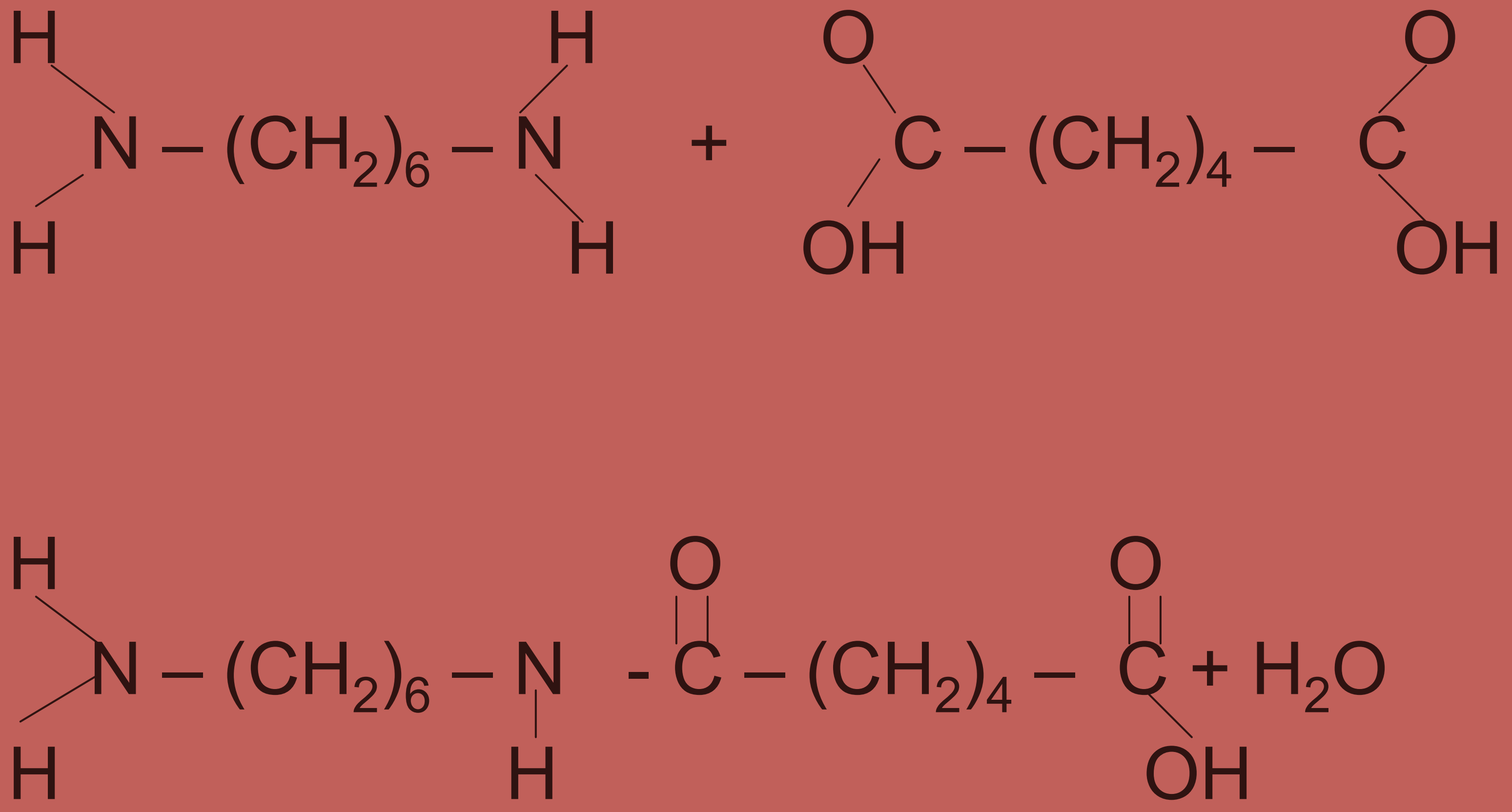
II) Vinylidene Polymers.



$$n\left[\underset{H}{\overset{H}{C}}=\underset{R_1}{\overset{R_2}{C}}\right]\longrightarrow\left[-\underset{H}{\overset{H}{C}}-\underset{R_2}{\overset{R_1}{C}}-\right]_n$$

Stepwise Polymerization

Hexamethylene Diamine Adipic Acid



$$\mathrm{H_2N-(CH_2)_6-NH_2 + HO(O)C-(CH_2)_4-C(O)OH}$$

$$\mathrm{H_2N-(CH_2)_6-NH-C(=O)-(CH_2)_4-C(=O)OH + H_2O}$$

Hexamethylene Adipamide (Nylone 6, 6)

I. Homopolymers : Polymers chain made up of single repeat units.

A-A-A-A-A-A-A

II. Copolymers : Poly (ACoB)

Random Copolymers AABBABBBBAABB Poly (A ran B) or Poly (A stat B)

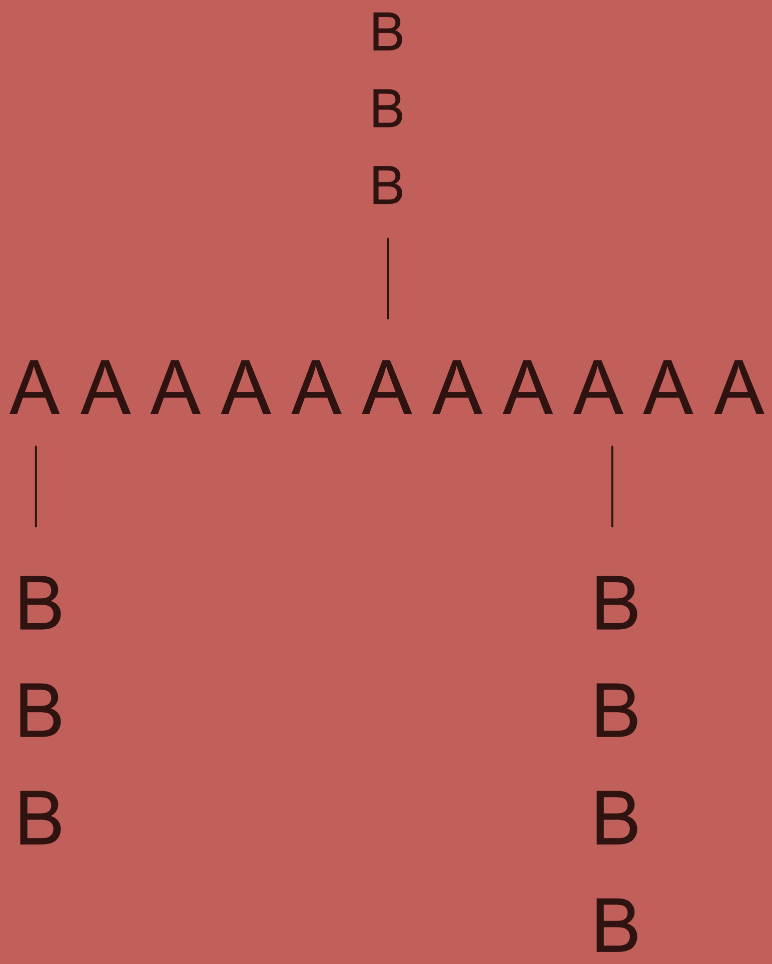
(i) Alternate Copolymers : Poly (A alt B)

ABABABABABAB ………..

(ii) Block Copolymers: Poly (A block B)

A-A-A-A-A-B-B-B-B-B ….

(iii) Graft Copolymers : Poly (A graft B)



B
B
B

A A A A A A A A A A A

B B
B B
B B
B

Classification

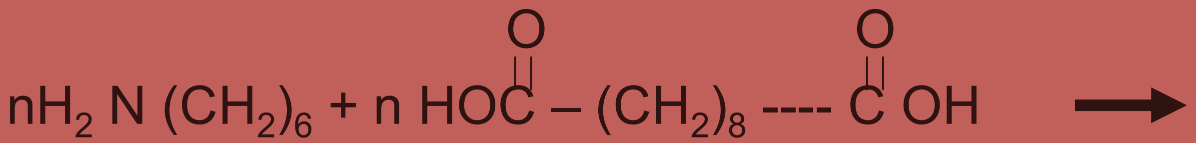
- **Nomenclature**

I) Common Name : Some names are derived from the place of origin or name of inventor.

Havea Brasilienses – rubber from Brazil

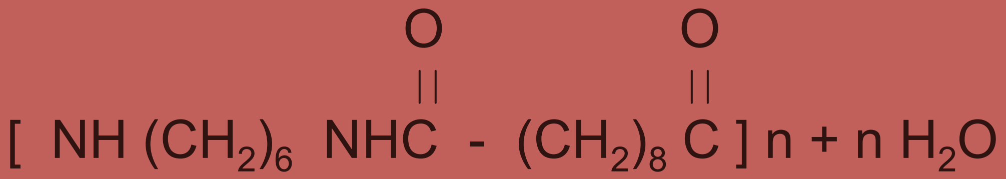
Bakelite – Leo Baekeland

Nylones were named according to number of carbons in diamine and carboxylic acid.



$$nH_2\,N\,(CH_2)_6 + n\,HO\overset{O}{\overset{\|}{C}} - (CH_2)_8 \text{----} \overset{O}{\overset{\|}{C}}\,OH \longrightarrow$$

1,6 Hexamethylene diamine Sebacic acid



$$[\ NH\,(CH_2)_6\ NH\overset{O}{\overset{\|}{C}} - (CH_2)_8\,\overset{O}{\overset{\|}{C}}\,]\,n + n\,H_2O$$

Nylon 6, 10

ii) Source – Based Names – Polymers are based on the common name of the reactant monomer preceded by the prefix “POLY” Polystyrene. Vast majority of polymers based on the vinyl group ($CH_2 = CHX$) or the vinylidene group ($CH_2=CX_2$) as repeat unit are known by their source-based names PE, PVC, PVA, PMMA etc.

Poly (vinylidene chloride)

Poly [styrene – Co – (methyl methacrylate)

PS – block – PB – block – PS

iii) Structure – Based Names – IUPAC system names the component of the repeat unit arranged in prescribed order.

Historic Perspectives

Before 1800 – Cotton, Flax, Wool and Silk Fibres, Bitumen, Leather, Cellulose Sheet, Natural Rubber (Havea Brasilienses)- Guttaparcha, Balata, Shellac

1839 – Volcanisation of Rubber (Charles Goodyear)

1846 – Nitration of Cellulose (Schonbein)

1851 - Ebonite (Hard Rubber: Nelson Goodyear)

1868 – Celluloid –Camphor Plasticised Cellulose nitrate (Hyatt)

1889 – Cellulose nitrate photographic films (Reichenbach); Regenerated Cellulose Fibres (Cardonnet)

1907 – Phenol Formaldehyde resin (Bakelite, Backeland)

1927 - PVC Wall Covering

1931 – PMMA Plastics

1932 – Concept of Polymer or Macro Molecule (H.Staudinger)

1937 – PS

1938 – Nylon 6, 10

1941 – LDPE

1943 – Teflon (Plunkett); Silicones; PU (Bayer)

1947 – Epoxy Resins

1950 - Polyester and PAN Fibres

1957 – HDFE; PP;PC

1962 – PI

1964 – PPO

1965 –Polysulphones, SB, Block Copolymers

1970 – PBT

1971 – PPS

1971 – Kevlar (Kwolek), LCP

1977 – Polyacetylene (Shirakawa)

1980 – Poly (P – Phenylene Benzobisthiazole)

1985 /

1986 - High Strength PE Fibre.

Plastics

1. Thermoplastics
2. Thermosetts

1. High Tonnage or Commodity Plastics
2. General Purpose Engineering Plastics
3. Supper Engineering Plastics / Speciality Plastics

Plastics

Commodity : PE, PP, PS, PVC, PMMA consumption 74%; HDT (^{0}C)≤ 100 ^{0}C strength (MPa) ≤ 50; Price US $/Kg = 0.9-2.2

Engineering; PA, PEST, PC, POM, PPE Consumption – 9%; HDT> 100^{0}C; strength > 50 MPa; Price US $/Kg = 8-3.5

Specialty; PPS, PSF, PEI, PAI, PEEK, LCP; Consumption = 1%; HDT > 150^{0}C; strength ≥ 70 MPa; Price US $/Kg ≥10

High Tonnage or Commodity Polymers

Polyethelene (PE), Polypropylene (PP), Poly (Vinyl Chloride) (PVC), Polystyrene (PS), Poly (Methyl Methacrylate) (PMMA), Polybutadiene (PB), Poly (Vinylacetate) (PAC)

Engineering Plastics

Polyamide (PA), Polycarbonate (PC), Polyacetal(PA), Poly (Butylene Terepthalate) (PBT), Para Poly (Phenylene Oxide) (Para PPO - PPE) and Poly (Ethylene Terepthalate) (PET)

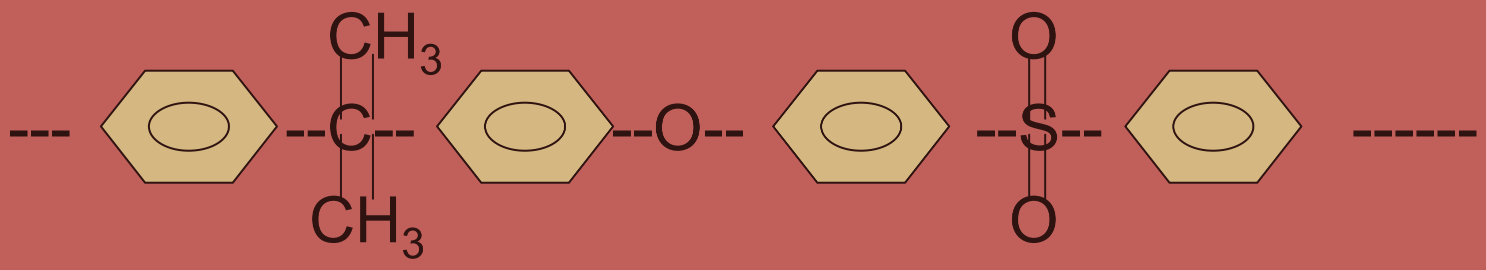
Speciality Engineering Plastics

Poly(Phenylene Sulphide)	(PPS)
Polysulphone	(PSF)
Polyacrylate	(PAC)
Poly(Ethersulphones)	(PES)
Poly(Ether Ether Ketone)	(PEEK)

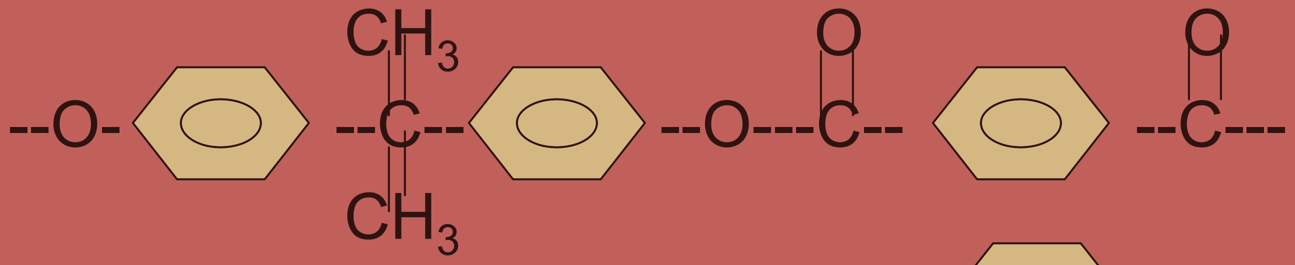
Polyimide (PI), Poly (Amide-Imide) (PAI)
Poly (etherimide), Phenol – Alkalkyl and
Ionomer, Perfluoroalkoxy (PFA),
Copolymer Resins and Fluorinated Ethylene
Propylene (FEP), Copolymer Resins.

Engineering / Speciality Polymers

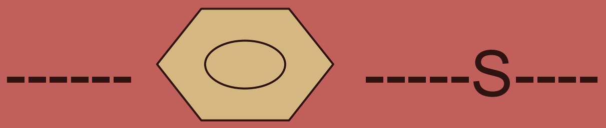
1. Poly (ether Ketone)



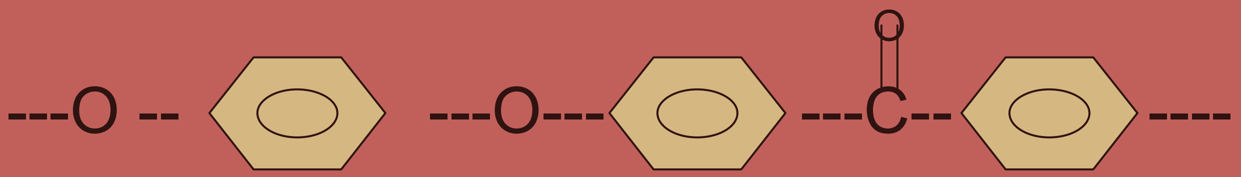
2. Polyacrylate



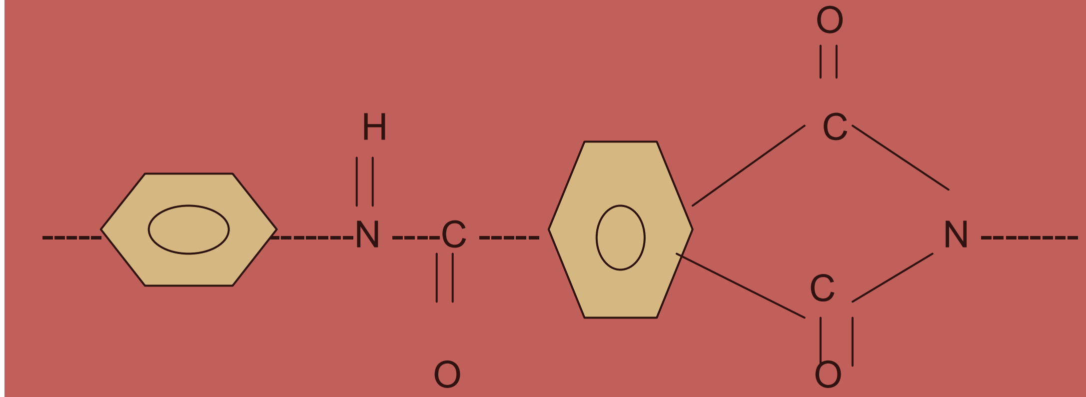
3. Poly (Phenylene Sulfide)



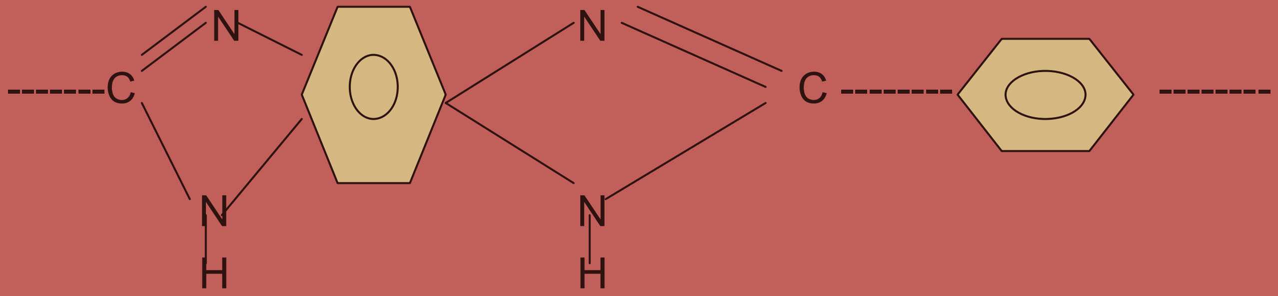
4. Poly (Ether Ether Ketone)



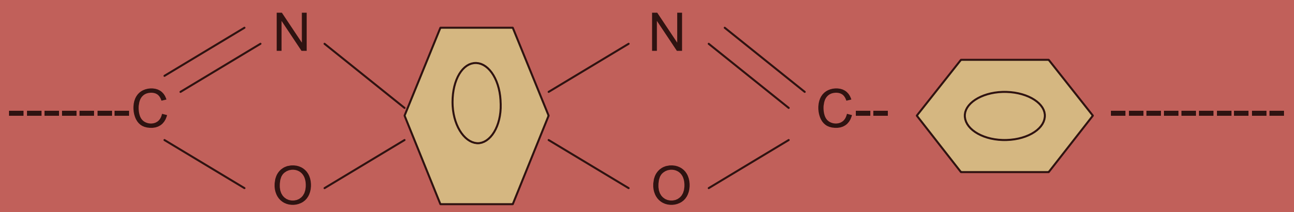
5. Poly (Amide-imide)



6. Poly (Para Phenylene Benzo bis imidazole) PBI



7. Poly (Para Phenylene Benzobis Oxazole) PBO



8. Poly (Para Phenylene Benzobis thiazole) PBT

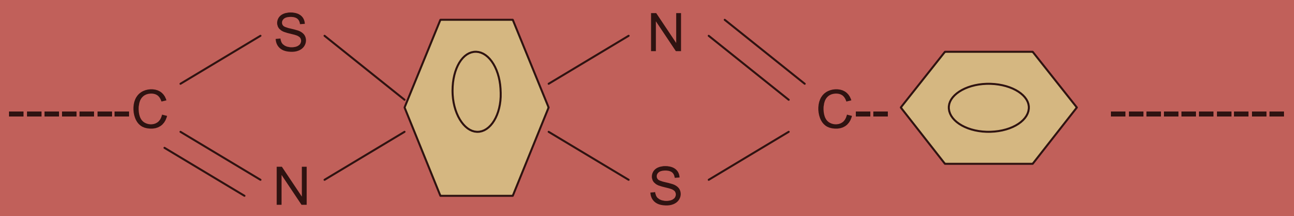


Table 4. Typical Properties of Commodity Resins

Polymer	**ρ (kg/m^3)**	**T_g (^0C)**	**T_m (^0C)**	**HDT (^0C)**	**σ (MPa)**	**E (GPa)**	**ε_b (%)**
LDPE	915-935	-126	108	41-44	7-17	0.1-0.3	100-700
LLDPE	910-925	-130	125	6-66	14-21	0.1-0.2	200-1200
HDPE	941-967	-130	135	65-93	19-30	0.7-1.6	100-1000
UHMWPE	930	-130	132	79	20-41	110	300
PP	903	-20-0	165	101	35.5	1.38	100-600
PS	1040-1050	105	NA	82-112	32-56	3.1-3.3	1.2-3.6
HIPS	1050	100	NA	73-85	16-41	1.6-2.6	1.0-2.5
PVC-F	1180-1700	Vary	NA	VARY	5.5-26	0.005-0.01	150-450
PVC-R	1320-1580	81	NA	63-82	41-52	0.07-0.11	40-80
PMMA	1170-1190	85-105	NA	79-107	48-76	2.2-3.2	2-6
HI-PMMA	1110-1180	80-100	NA	82-102	55-76	2.4-3.1	2-40

Note: The symbols used in Tables 4 to 6 are:

ρ – Density

T_g – Glass Transition temperature

T_m – Melting Point

HDT – Heat deflection temperature at 66 psi

σ – Tensile stress

E – Tensile modulus

ε_b – Maximum strain at break and

NA – "Non Applicable".

Table 5. Typical Properties of Engineering Resins

Polymer	**ρ (kg/m^3)**	**T_g (^{0}C)**	**T_m (^{0}C)**	**HDT (^{0}C)**	**σ (MPa)**	**E (GPa)**	**ε_b (%)**
PA-6 (dry)	1130	75	219	>160	80	3.0	50-100
PA-66 (dry)	1140	57	255	>200	90	3.4	20
PETG	1270	81	NA	71	50	1.7	180
PBT	1400	80	245	167	172	4.3	30-300
PBT	1310	40	225	154	55	2.55	50-300
PBT+ 30GF	1520	40	225	221	124	9.65	2
PC	1200	149	NA	138	62	2.38	110
POM	1420	-30	175	172	69	3.1	25-75
POM+ GF	1650	-30	165	166	110	8.28	3
PPE	1050-1100	100-150	NA	93-138	41-110	0.2-0.3	2-3
PPE + GF	1270	165	NA	158	117	8	3-5

Table 6. Typical Properties of Speciality Resins

Polymer	**ρ (kg/m^3)**	**T_g (^{0}C)**	**T_m (^{0}C)**	**HDT (^{0}C)**	**σ (MPa)**	**E (GPa)**	**ε_b (%)**
PSF	1240	185	NA	181	70	2.5	50-100
PEI	1270	217	NA	210	105	3.0	7-8
PEI+ GF	1610	217	NA	216	186	11.7	2-5
PES	1370	230	NA	207	84	2.44	40-80
PES + GF	1600	230	NA	220	140	10.6	3
PEEK	1320	145	335	-	92	3.6	50
PEEK + GF	1490	145	335	615 (?)	157	9.7	2.2
PPS	1350	93	285	199	48-86	3.3	1-4
PPS + GF	1670	93	285	279	121	7	0.9
PAI	1400	275	NA	NA	186	4.5	12
PAI + GF	1610	275	NA	NA	207	11	7
LCP	1700	NA	410	-	94	13	1.8

Speciality Polymers and Composites (High Performance Polymers)

1. Hydrophilic Polymers
2. Polymers with Electrical, Electronic and Photonic Properties
3. High Temperature and Fire-Resistant Polymers
4. Liquid Crystalline Polymers
5. Ionic Polymers
6. Advanced Elastomers
7. Speciality Blend
8. Advanced Composites
9. Biopolymers and Composites

Table 1. World Market Share By Resin Type

No.	Resin Type	Market Share (%)
1.	Low density polyethylene, LDPE + LLDPE	20
2.	High density polyethylene, HDPE	12
3.	Polypropylene, PP	12
4.	Polystyrene homopolymers and copolymers, PS + ABS	10
5.	Poly (vinylchloride), PVC	17
6.	Other thermoplastics, TP	13
7.	Thermosets, TS	16

Table 3. Typical Properties of Commodity Resin

No.	Category	Polymers	Consumption %	HDT (^{0}C)	Strength (MPa)	Price (US`$/ KG)
1.	Commodity	PE, PP, PS, PVC, PMMA	74	≤ 100	≥ 50	0.9-2.2
2.	Engineering	PA, PEST, PC, POM, PPE	9	≥ 100	➢40	1.8-3.5
3.	Speciality	PPS, PSF, PEI, PAI, PEEK, LCP	1	> 150	>70	> 10

Table 7. Competing Engineering and Speciality Resins

No.	Newer Resin	Older Materials	Applications
1.	PAr	PC, PSF,PET/PBT	Appliances, transportation, electrical & electronic, industrial
2.	PES	PSF, PAI, PPS	Medical, transportation, electrical & electronic
3.	SMA	ABS, PPE / HIPS	Appliances, transportation, business machines
4.	PEC	PAr, PC	Appliances, transportation, electrical, industrial, aircraft
5.	PI	PAI, thermoset PI	Industrial, machinery
6.	PAI	PI, PPS	Transportation, machinery, industrial
7.	PE, PEST-elatomers	Elastomers, PU	Electrical, chemical, medical
8.	PEEK	PSF, PI, PPE/HIPS	Aerospace, automatic, electrical, appliances
9.	PEI	PC, ABS, PPE/HIPS	Aerospace, automotive, electrical appliances
10.	PEBA	PC, ABS, PPE/HIPS, PEST	Automotive, electrical, business machines, recreational
11.	PISU	PC, PSF, PPE/HIPS, PI	Transport, electrical& electronic, Industrial
12.	PAE	PSF	Structural, aerospace, electrical
13.	LCP	PPS, thermosets	Automotive, outdoor, electrical & electronic, oil fields

No.	Newer Resin	Older Materials	Applications
14.	PC/LCP	PC/ABS	Economic replacement as thin wall housing for portable telecommunication devices
15.	PPE/PA	PVC-R	Extruded, power-coated window profiles
16.	PEI/PPS	LCP	Electronic components for surface mounting
17.	PA -11	PE	Gas piping applications with excellent quality of connectors and joints
18.	PPS/ Fluoro polymer	PA-46	Injection molded parts for automotive pumps, and electronic office machines
19.	PA/PPE	PBT/PC or PBT/PET	Automotive exterior parts, electrical equipment and plug & socket connectors
20.	PET/PEN	PET	Hot fill or reusable bottles
21.	PC/SMA	POM	Scuff plates, camera components, automotive
22.	SMA/ABS	ABS, PC, PPE / HIPS	Automotive consoles, door trim, instrument panels cowl vents, wheel covers
23.	PPS/PPE	PPE/HIPS	Electrical & electronic and mechanical parts
24.	PBT/ABS	PC/ ABS; PO/ PBT	Automotive instrument panels, cowl vent grill appliances (air conditioner grills, consoles, boxes), electrical & electronic housings, frames parts
25.	PEI/PC	PSF	Microwave-able cookware, electrical connectors, raceways, headlamps

Thermoplastics

The thermoplastics have the following characteristics:

1. They soften when heated and harden when cooled irrespective of the number of times the process is achieved.
2. They flow with pressure and heat
3. No chemical changes take place in them upon heating
4. The temperature to use is limited to Tg for amorphous polymers and the melting temperature for crystalline polymers
5. Can be reprocessed a number of times
6. Due to reprocessability the composites based on thermoplastics are also amenable to repair and recycle.
7. The environmental stability is enhanced with crystallinity
8. Low density, low energy requirement for manufacture and low product – processing cost.

9. The engineering plastics have the following properties.

i) High tensile strength (Strong)
ii) High modulus (Stiff)
iii) High impact strength (Tough)
iv) Low creep under load (High T_g)
v) High service temperature

Thermosetting Polymers

The thermosetting resins are chemically reactive substances, which undergo hardening to produce insoluble and infusible products. The polyesters, epoxies, and polyimides are widely used as matrix materials in FRP.

Characteristics

1. The thermosetting polymers are generally produced by reaction of resin consisting of linear long-chain molecules with hardner, which results in three –dimensional highly cross-linked structure.
2. Once heated they react irreversible to form inter-molecular covalent bonds generally to form cross linked structure.
3. Do not soften or flow upon second heating even upon application of pressure.
4. Cannot be reprocessed
5. Use temperature limit is higher than the thermoplastics and is governed by degradation temperature.

6. Generally dimensionally more stable than thermoplastics
7. These resins have combined products of high modulus, creep resistance and hardness
8. Dense cross-linking generally leads to brittle materials that are subjected to failure by the growth of internal flaws and crack propagation. They are amorphous.

9. The cross link densities of common cross-linked resins are:

   i) Approximately uniform

   ii) Non uniform with interconnecting chain segments

   iii) Networks consisting of densely cross linked resins dispersed in uncross linked matter.

10. Prior to crosslinking, thermosetting resins may be low viscous liquids or they may be glassy solids which have been powdered.

11. Initial formation of a cross linked insoluble network occurs at a point called gelation. Crosslinking of curing process is generally carried out at higher temperature. After gelation, the resin becomes soft, weak gel and later slightly rubbery like before finally becoming brittle hard solid.

12. Specific gravities of thermosetting matrix are in range of 1.1-1.4
13. As a matrix for composites they serve the following purposes:

    i) Transfer load in and out of fibres

    ii) It prevents continuous crack propagation through brittle fibres. The fibres may also prevent continuous crack propagation through brittle matrix.

    iii) It protects the fibres from the environment

14. The properties of the composites that are significantly affected by the properties of the matrix and the fibres to matrix bond strength include:

i) Temperature and environmental resistance

ii) Longitudinal compression strength

iii) Transverse tensile and compressive strength

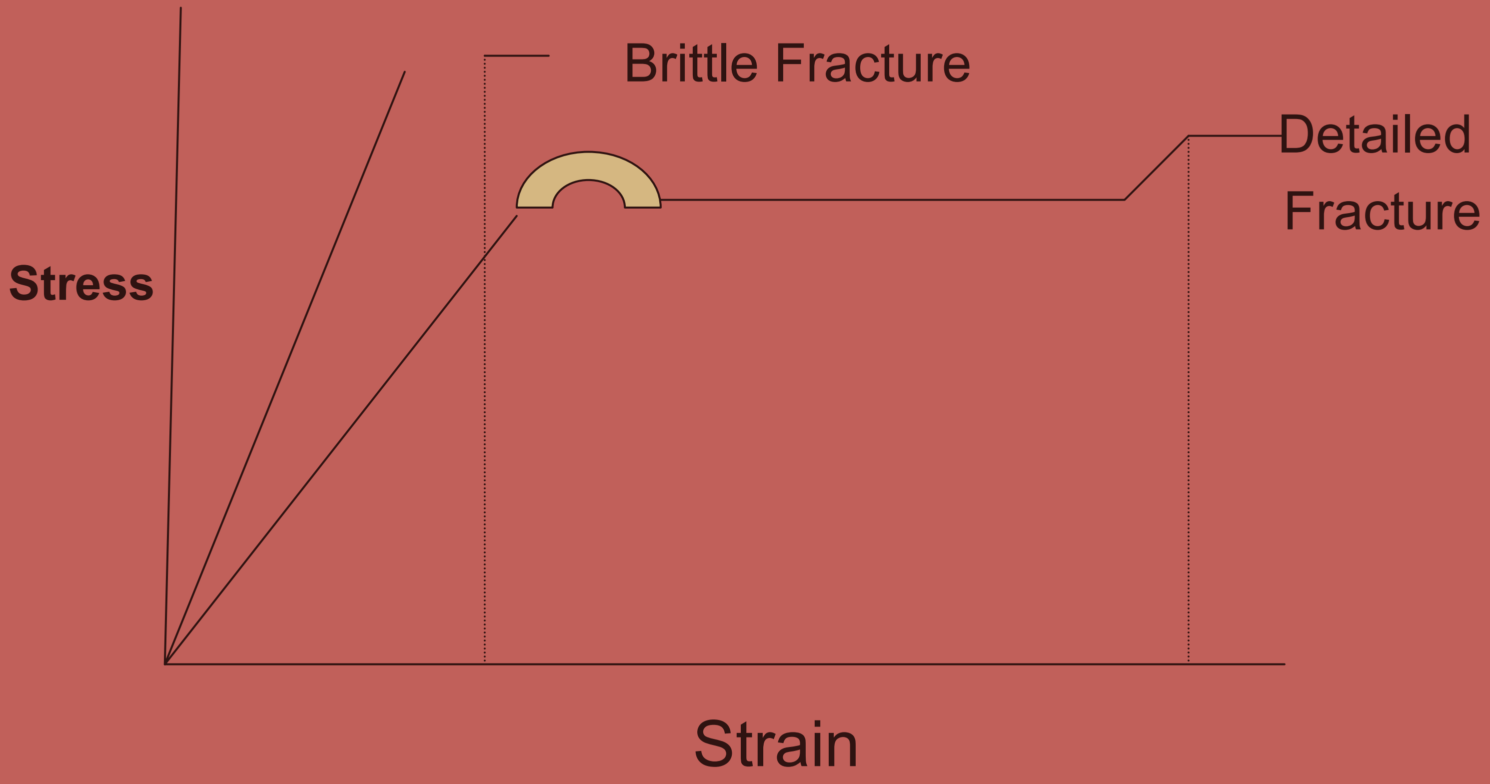
iv) Interlaminar shear strength

v) Toughness and impact strength

vi) Fatigue strength and

vii) Creep resistance

15. Polymeric thermosetting materials come closer to the ideal matrices at least for application upto 200^0C.



Classification of Thermoplastic Polymers

Commodity	Transitional	Engineering	Performance
PET (Unfilled)	ABS / SAN	Modified PPO	Fluoro Polymers
Polyethylene	Acrylics	Nylon	Poly (amide-imide)
Polypropylene	SMA copolymer	PBT	Polyarylate
Poly (vinylcholoride)		PET	Poly (ether ether ketone)
		Polyacetal	Poly (etherimide)
		Poly carbonate	Poly(ether sulfone)
		SMA terpolymer	Polyimide
			Poly (phenylen esulfide)
			Polysulfone

Volume

Price

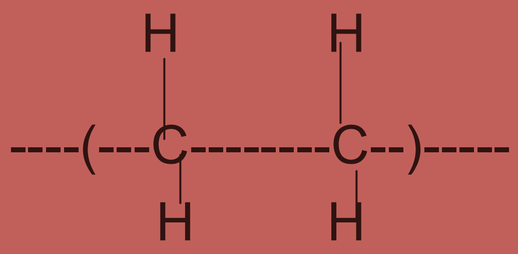
Thermal Resistance

Themoplastics

i) Low Density

ii) Low energy requirement for manufacture

iii) Low product processing cost



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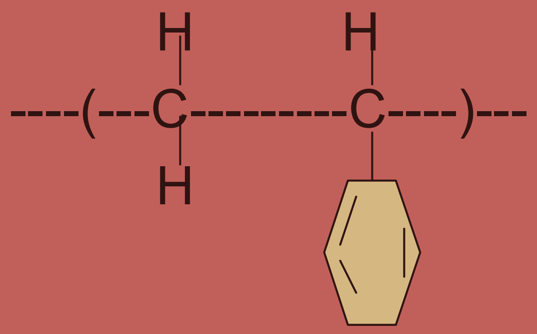
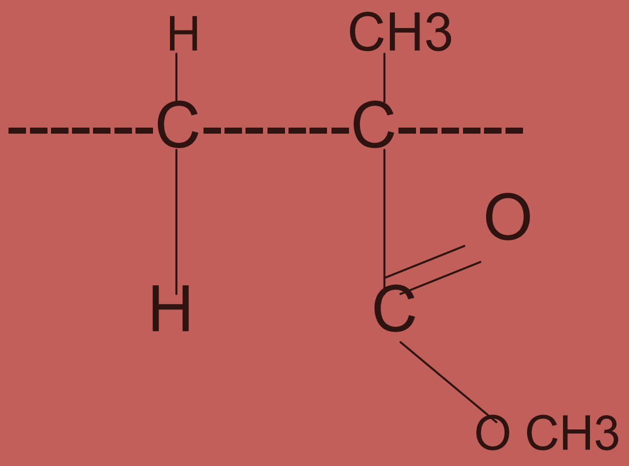
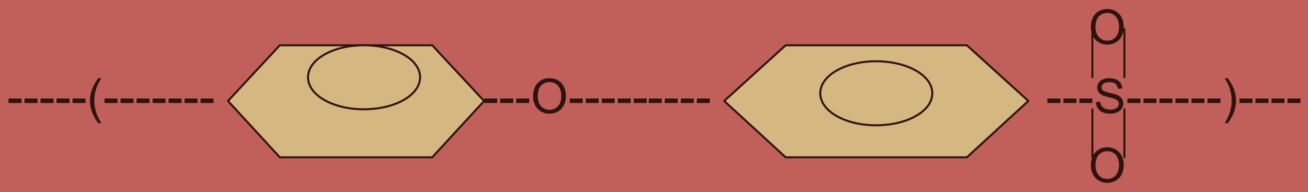
Polyethylene



Polystyrene



PMMA



Poly (ether sulphone)

Hydrophilic Polymers

1. Natural polymers, carbohydrates or proteins
2. Semisynthetic Polymers

   Cellulose (Wood Pulp, Cotton Linters) modified with functional groups of Petrochemical origin.

3. Synthetic Polymer

   Polymerization products or monomers of petrochemical origin.

Physical States of Polymer

Glassy State : Segmental, whole chain motions frozen; only vibration of molecules and localized mode of motion are possible.

T_g

Rubbery State: Segmental motions are like place whole chain motion frozen; vibrations are there; localized mode of motion.

T_f

Viscofluid State : Whole chain motion, segmental motion, vibrational motion ; localized mode of motion, all take place.

Glass Transition is the passage of molecules in mobile liquid state into solid state with no change of phase i.e. with retention of short – range order.

Motion in Amorphous Polymers

1. Transitional motion of entire molecule, which permits flow.
2. Cooperative wriggling and jumping of segments of molecules approximately 40-50 carbon atoms in length permitting flexing and uncoiling – normal mode motion.
3. Motions of few atoms along the chain (five or six or 80) or of side groups on the main chain – Localized mode of motion.
4. Vibration of atoms about their equilibrium positions.

Motions 1-4 are arranged in order of decreasing activation energy that is smaller amounts of thermal energy (RT) are required to produce them.

Crystallisation in Polymers

Factors affecting crystallinity are as follows :

1. Regularity in polymer chain
2. Flexibility of polymer chain
3. Packing – close packing, globular proteins, helical macromolecules long extended chains (rigid chains)

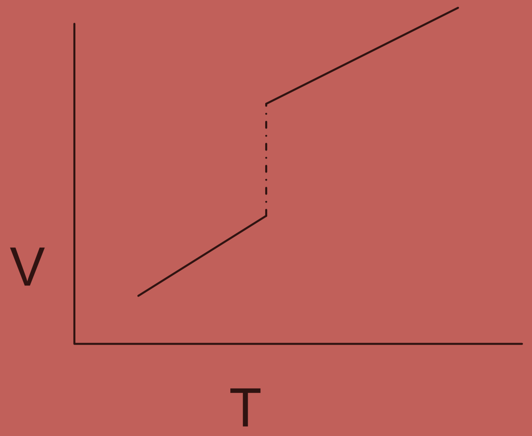
Thermodynamics Transitions

First Order Transition: Discontinuity in the first derivative of Gibb's Free Energy

$\Delta G = - SdT + VdP$

$(\delta G / \delta T)_P = - S$

$(\delta G / \delta P)_T = V$



Discontinuity in Volume

Second Order Transition : Discontinuity in second derivatives of Gibb's Free Energy.

- $(\delta^2 G / \delta T^2)_P = (\delta S / \delta T)$;
  $(\delta^2 G / \delta P^2)_P = (\delta V / \delta P)_T$

and $[(\delta / \delta T\ (\delta G / \delta T)_T)_P = (\delta V / \delta T)_P$

$C_P = T\ (\delta H / \delta T)_P$

$C_P = T\ (\delta S / \delta\ T)_P$

i.e. **Second Order Transition** $\longrightarrow$ Discontinuity in Specific Heat

$\beta = (1 / V)\ (\Delta v / \delta P)_T$

Compressibility coefficient

$\alpha = (1 / V)\ (\delta V / \delta T)_P$

Thermal expansion coefficient

Characteristics of Glass Transition Temperature (T_g)

1. Pendent groups pose restrictions on the Torsion about σ bonds in the backbone chain i.e. that is the backbone chain becomes less flexible and this increases the T_g.
2. T_g increases with increasing polarity ($T_g \propto$ Cohesive Energy Density)

$$T_g = 2\,\delta^2 / mR + C_1$$

m ---- Parameter; internal mobility of the group in a single chain.

The T_g and T_m of crystallisable polymers increase with decreasing chain flexibility and increasing CED

$T_g / T_m = ½$ (Symmetrical Polymers)

$T_g / T_m = 2/3$ (Asymmetrical Polymers)

$\approx 0.5 – 0.8$

3. $T_g = C_5 – C_0 / M$ (Fox, 1956)
4. T_g increases with increasing cross link density

   $T_g \approx C_9 + C_{10} / M_C$

   $T_g \approx C_4 – C_5 / M + C_9 / M_C$
5. In case of incompatible blends (amorphous), Two T_g corresponding to each of the two different phases are exhibited. For compatible blend single T_g is obtained

$1 / T_g = W_1 / T_g + W_2 / T_{g2}$

Where W_1 and W_2 are weight fractions respectively of polymer 1 and 2.

6. Plasticizing effect on polymer decreases T_g

7. The hydrostatic pressure (P) affects the T_g according to the following equation

$$(dT_g / dP) = \Delta\beta / \Delta\alpha$$

Where Δβ and Δα are respectively the changes in compressibility and volume expansion coefficients associated with glass transition.

$\approx 0.2 – 0.8$ KM P_a^{-1}

Polymers with less flexible chains have very high T_g and their $T_f – T_g$ is so small that they don’t display rubber like properties even at increased temperature.

Glass – Rubber Transition

Glass Rubber Transition Temperature T_g.

Glassy State of Polymer is a State of Frozen Disorder

\- Flory

I. Glass Transition

- ➢ Pseudo 2nd order transition
- ➢ Kinetics of glass formation depends upon the rate of cooling / heating
- ➢ Discontinuity in slopes of V and Cp are gradual

Viscosity – 10^{12} PaS (10^{13} Poise) – Isoviscous State

II. **Glass Transition is a typical relaxation** process (Kinetic Approach).

Relaxation time in rubbery state – 10^{-1} to 10^{-6} sec.

Kovacz – $(V_t - V_\infty)$ V_s. time.

V_t = polymer volume at temperature, t.

V_∞ = equilibrium volume at the same temperature

With increasing temperature, the polymer approaches its equilibrium state faster.

III. Thermodynamic Transition

Gibb’s and DImarzio- Isoentropic State,
conformational entropy – 0 at T_2
T_2 – below 50^0C of T_g, 2nd order transition,
conformational entropy is zero.

IV. Free Volume Theories

$V_f^g = V_{sp}^g - V_0$
V_0 is the volume occupied by molecule
V_f^g and V_{sp}^g are free and specific volumes
$V_{sp}^g = V_0 + V_f^g$
$f_g = V_f^g / V_{sp}^g = 0.025 + 0.003$
$f_g = 0.025 \pm \alpha_s (T - T_g)$
α_s – Coefficient of Thermal Expansion

When free volume reaches its lower limit, polymer becomes glass upon cooling at this temperature, free volume stops changing with temperature …. Iso Free Volume State.

V. Effect of Molecular Mass of Polymer on its T_g

$T_g = T_{g\,\infty} - k / M$

$1 / T_g = 1 / T_{g\,\infty} + k' / M$

k and k …… Constant

T_g ------- T_g at Mass M

$T_{g,\,\infty}$ ------- T_g at infinite chain length.

i) At low molecular mass, polymer can exist only in glassy and liquid state – T_g and T_f coincide.

ii) Higher the molecular mass of polymer, the greater is the difference Tf – Tg.

iii) More rigid the chain, the higher will be the molecular mass at which the transition temperature splits.

PIB ; M ≈ 1000

PS ; M ≈ 40,000

VI. Effect of Molecular Flexibility and Geometry

i) Polymers with low hindrance potentials to internal rotation show very low T_g.

PE – T_g = - 120^0C

Stiff chain polymers have high T_g

PET = + 70 ; PC = 150

ii) Bulky side groups decrease the mobility of the chain hence the raise T_g.

PP ; T_g = -18^0C PS; T_g = 100^0C

iii) Flexible side groups tend to decrease the T_g – Internal Plasticization

iv) Molecular Symmetry tends to lower T_g

PVC; T_g = 87 ^{0}C

PVDF; T_g = -10^0C

PP; T_g = -18^0C

PIB = -65 ^{0}C

VII. Intermolecular Forces

The presence of polar groups, hydrogen bonding or other factors tend to raise T_g.

PP = -18^{0}C; PVC = 87^{0}C ; PAN =103^{0}C

Polyacrylic Acid T_g > 100^{0}C

VIII. Effect of Plasticizers on T_g

Plasticizer lower the T_g.

IX. Effect of cross-linking, cross-linking increases the T_g.

Melting of Polymers

Melting – first order transition

$T_m^0 \ - \ (\Delta H_m)_p / (\Delta S_m)_p$

ΔH_m and ΔS_m, enthalpy and entropy differences between the ordered (crystalline) and disordered (liquid) phases. They are known as enthalpy and entropy of melting.

The presence of defects increases the entropy of crystalline state. Hence actual T_m is much lower than its equilibrium melting temperature T_m^0.

$(1 / T_m) \ (1 / T_m^0) = R / \Delta H_m (1 / XW_a + 1 / X\text{-}Z + 1)$

W_a – weight fraction of noncrystalline material, X – degree of polymerization. Z is parameter associated with crystalline size.

ΔH_m heat of fusion per mole of crystalline repeat unit.

Since Z and X cover a range of values within a polymer sample, the melting process is expected to take place over a finite temperature range.

$T_m \infty 1 / d$

D – lamellar thickness of polymer samples crystallized isothermally at different temperatures T_X

$T_m \infty T_X$

Effect of Structure

1) Polymers with rigid molecules melt at higher temperatures than flexible chain molecule.
2) Polar chains form crystalline structure with high T_m

$T_m = KT_g$

K = 2 For symmetrical

= 1.4 For asymmetrical polymer

1) For a given mass or volume of polymers, shorter the chain, more randomized they become upon melting, thus giving higher ΔS_m . Hence crystalline melting point decreases with deceasing chain length and poly-disperse polymer the distribution of chain lengths gives a distribution of melting points.

2) Equation 1 indicates that the chains, which are strongly bonded in the crystal lattice have high ΔH_m , hence they have high T_m.

3) The rigid (stiffer) and less mobile chains randomize less upon heating and therefore have a low ΔS_m will tend to have higher T_m's.

4) The crystallinity affects melting point. Less crystalline imperfect matters have lower melting temperatures.

Factors Encouraging Crystallinity in Polymers

1. An increase in regularity of chains allows them to align more easily.
2. A reduction in rigidity or stiffness of chains allows chain to align more easily but T_g will reduce.
3. Reducing the number and size of side chains will allow chains get closer together.
4. The introduction of polar groups (as in PTFE) or introduction of hydrogen bonding sites (as in PA) will increase the intermolecular forces.

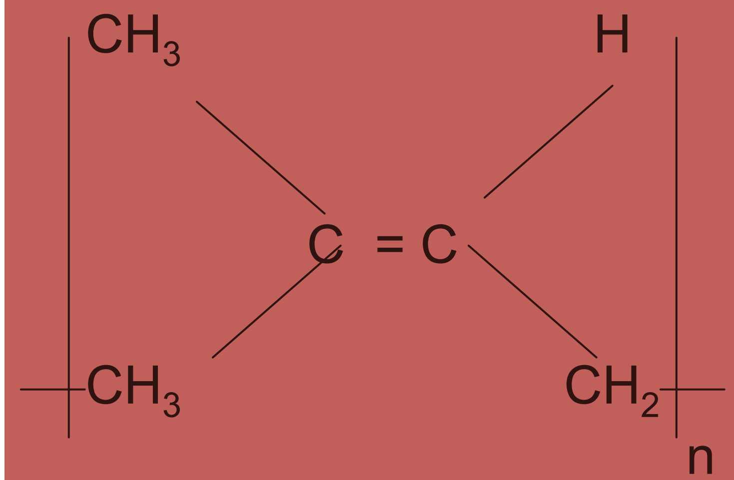
The Following Sources of Irregularity Discourage Crystallization

1. **Random co polymerization**
2. **Bulky side groups**
3. **Chain branching**
4. **Lack of stereo regularity i.e. atactic**
5. **Certain geometrical isomers.**

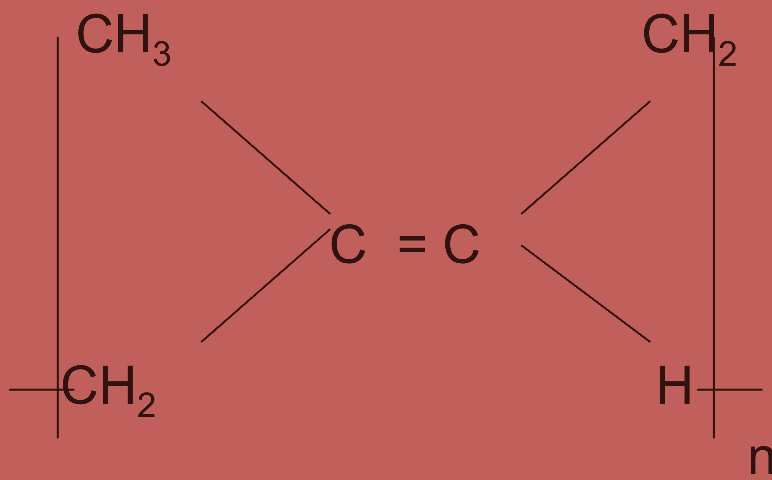
Streeo Isomerism (Tacticity) in Thermoplastics

1) Atactic : The pendent CH_3 randomly arranged on either side of main carbon chain.
2) Isotactic : CH_3 on the same side of main chain
3) Syndiotactic : CH_3 alternates regularity on either side of main chain.

Isomers: The substituent groups on the carbon atoms linked by double bonds can in reality be on same side of chain. This is C is Isomer. Alternatively they may be on opposite sides. This is the trans isomer.

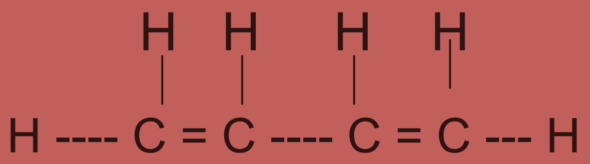


CIS



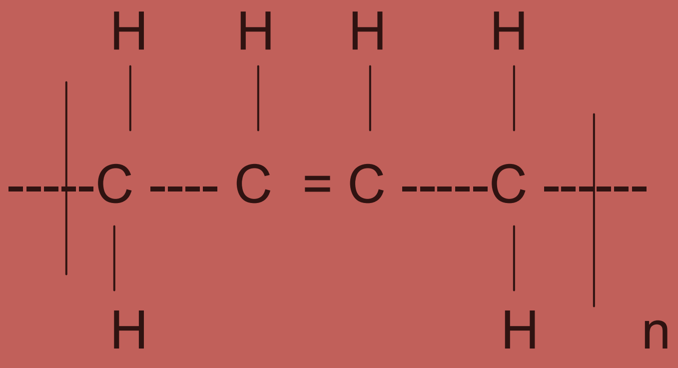
Trans

Diene Polymers



$$H{-}\overset{H}{C}{=}\overset{H}{C}{-}\overset{H}{C}{=}\overset{H}{C}{-}H$$

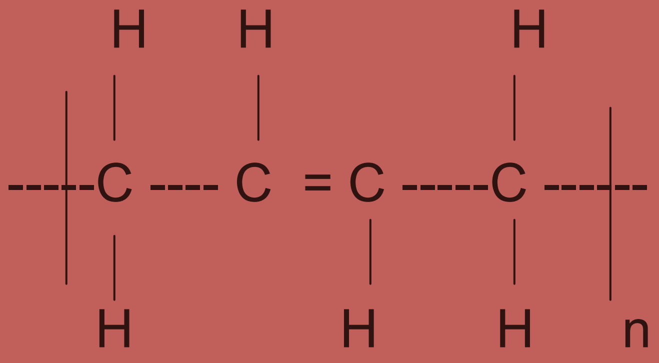
1, 3 butadiene



$$\left[-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\right]_n$$

C is 1-4

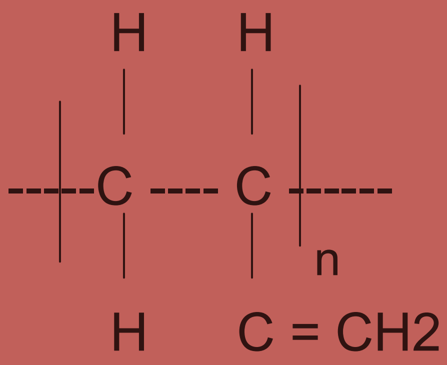
1,4 poly (1,3 butadiene)



$$\left[-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-\right]_n$$

Trans 1-4

1,4 poly (1,3 butadiene)



$$\left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{C=CH_2}{C}}- \right]_n$$

1,2- poly (1,3 butadiene)

Crystallisation in Polymers

1) Fringed Micelle Model
2) Folded Chain Model

Lamella ⟶ Super Molecular Structures

⟶ Spherulite

T_g PE = - 110^0c
PP = - 18^0c
PVAC = 29^0c
PVC = 80^0c
PS = 75 – 100^0C
PMMA = 72^0C

- Singh crystal of polymers Lamellae Thickness ≈ 100 nm lateral dimensions ≈ several μ_m lamellae are about 50-60 carbon atoms, each fold contains 5 carbon atoms.

  PE or through mic with $a = 0.749$, $b = 4.94$ and $c = 2.55$

Characteristics of Crystalline and Amorphous Polymers

Crystalline	Amorphous
Properties	**Properties**
Excellent chemical resistance	Dimensional stability and
Sharp melting point	Warpage resistance
Low viscosity	Maintenance of properties at elevated temperatures
Significant tensile flexural and heat distortion improvement with reinforcement	Clarity Generally good impact strength Melting range
Polymers	Polymers
Polypropylene	ABS
Polyacetal	Polycarbonate
Nylon 6,6	Polysulfore
Polybutylene terephthalate (PBT)	Polyarylate

Molecular Architecture

1 – Increasing backbone stiffness *

2 – Increasing Decomposition temperature **

For SC $T_d > T_m$; $T_d > T_g$ ($T_d = T_d + 100$)

3 – Introduction of cyclic units in the backbone

4 - Introduction of heterocyclic units in the backbone chain

High strength, high modulus polymer at high temperature yet tractable below T_d

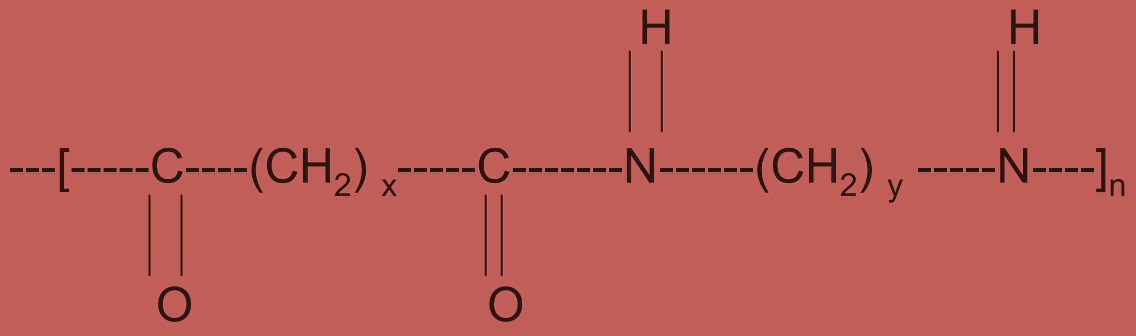
*A – Incorporation of bulky side group to the backbone

B – Use of hydrogen bonding between chains

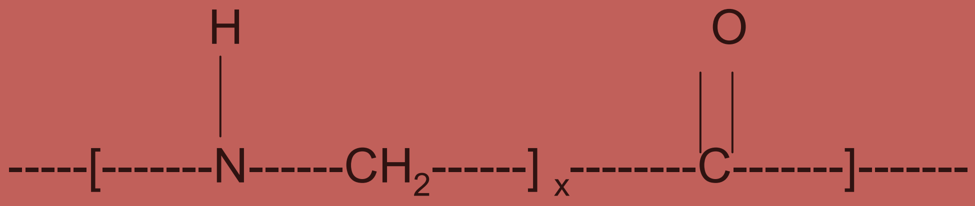
C – Incorporation of cyclic rings in the backbone

D – Incorporation of non-cyclic rings in the backbone

** Reduction of C-H bonds, introduction of high strength bond Si – O, C – F.



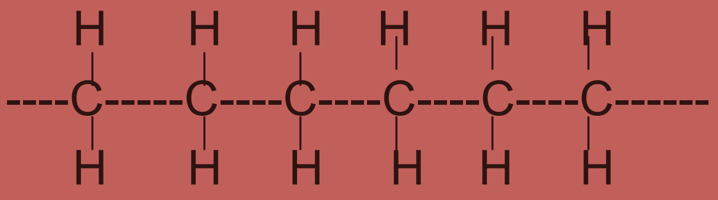
$$---[-----\underset{\underset{O}{\|}}{C}----(CH_2)_x-----\underset{\underset{O}{\|}}{C}-------\overset{\overset{H}{\|}}{N}------(CH_2)_y-----\overset{\overset{H}{\|}}{N}---]_n$$

b 

$$-----[-------\overset{\overset{H}{|}}{N}------CH_2------]_x--------\overset{\overset{O}{\|}}{C}-------]-------$$

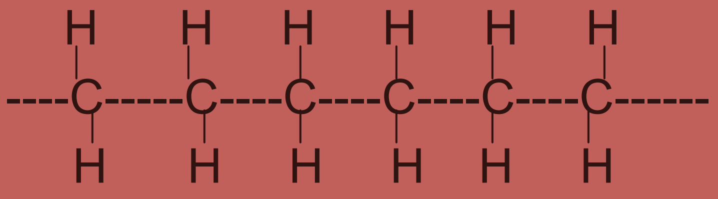
a) Repeat unit of dyadic polyamide and

b) Monoadic polyamide



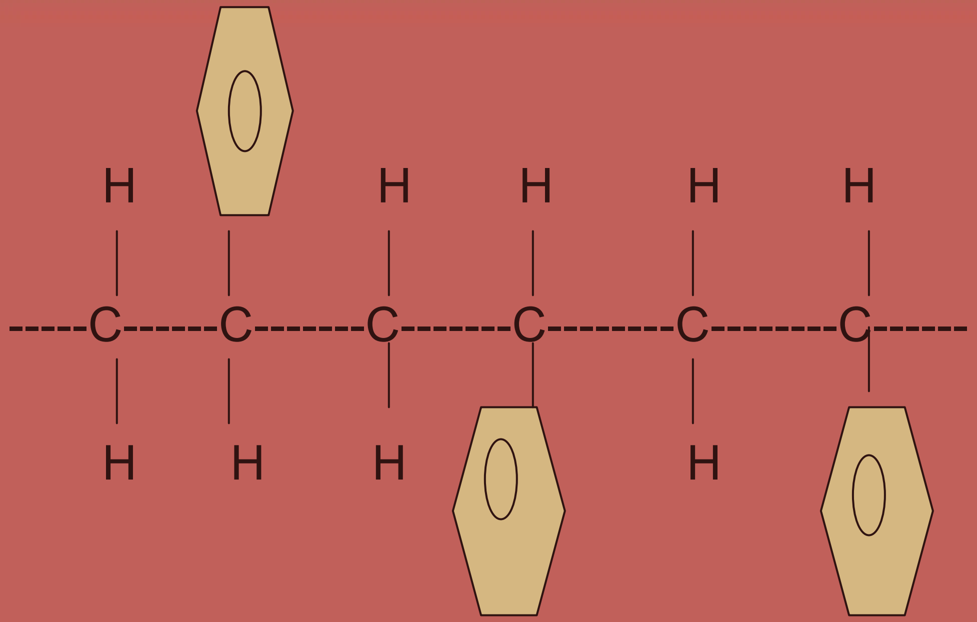
$$----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}------$$

Polyethylene

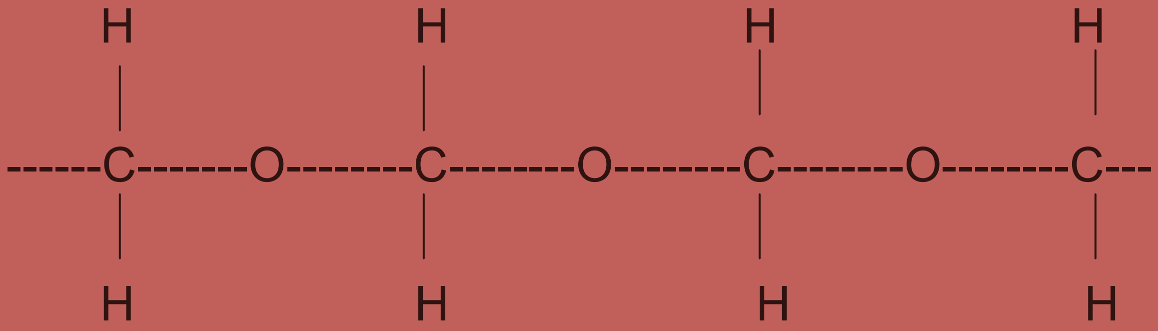


$$----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}----\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}------$$

Polypropylene



Polystyrene



$$\cdots\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}\cdots O\cdots\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}\cdots O\cdots\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}\cdots O\cdots\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}\cdots$$

Polyacetal

Table 7. Property date for some fluoropolymers

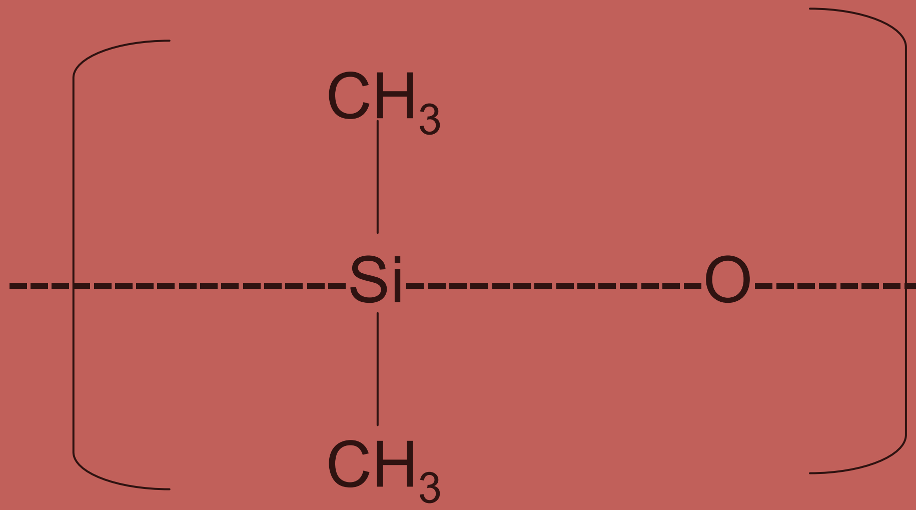
	PTFE	PTFE / 30% Glass Fibre	PCTFE
Specific gravity	2.1.2.2	2.22.2.35	2.1.2.15
Tensile strength / MNm^{-2} (yield)	19.20	16.20	24.25
Elongation –to-break %	250-400	250-300	125-175
Tensile modulus / GN m^{-2}	0.27-0.6	1.6	1.3.2.0
Flexural modulus / GN $^{-2}$	0.6	1.3.1.6	1.5
Continuous service Temperature / ^{0}C	288	288	199

I. Increasing Td (decomposition temperature), reduction of CH bonds & increasing in Si-O, C-F bonds

Increasing Backbone chain stiffness

Table 6. Typical bond lengths and dissociation energies for some selected primary bonds.

Bond	Bond length R	Dissociation energy Kcal mol $^{-1}$	kJ mol $^{-1}$
O-O	1.32	35	146
Si-Si	2.35	42.5	178
S-S	1.9.2.1	64	268
C-N	1.47	73	305
C-Cl	1.77	81	339
C-C	1.54	83	347
C-O	1.46	86	359
N-H	1.01	93	389
C-H	1.10	99	414
C-F	1.32.1.39	103.123	431.514
O-H	0.96	111	464
C=C	1.34	146	610
C=O	1.21	179	748
C=N	1.15	213	890



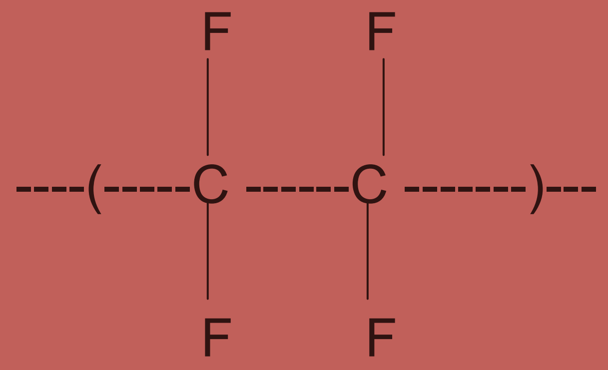
$$-\left[\;-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{\mathrm{Si}}}}}-O-\;\right]-$$

$T_g = - 123^0C$

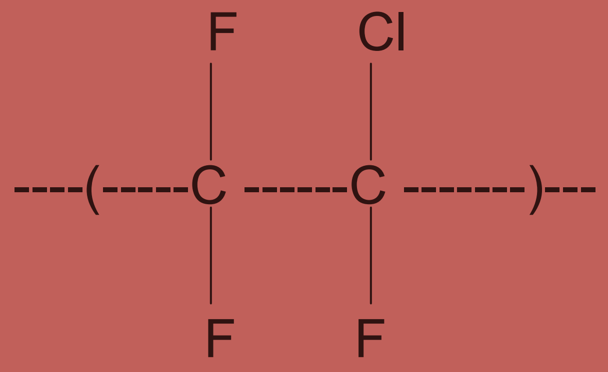
by replacing
CH_3 groups
by phenyl
groups

Figure 4. The repeat unit of poly (dimethylsiloxane) (PDMS)

PTFE



$$-(-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-)-$$



$$-(-\overset{F}{\underset{F}{C}}-\overset{Cl}{\underset{F}{C}}-)-$$

Material	Specific Gravity (g/cm^{-3})	Modulus (GN / $^{m-2}$)	Specific Modulus (MN/m/kg^{-1})	Strength (MN/m^{-2})	Specific Strength (MN /m^{-1} /kg)
Aluminium	2.7	71	26	80	30
Brass (70Cu/30Zn)	8.5	100	12	550	65
Mild steel	7.86	210	27	460	59
Polyamide 66	1.41	3	2.6	80	70
Polycarbonate	1.24	2.3	1.9	60	48
Polyamide 66 /30% glass	1.38	8	5.8	160	116
Poly(phenylens sulphide) / glass	1.72	14.0	8.1	131	76
Poly(etherether ketone)	1.4	13.7	9.8	240	171
Liquid crystal polymer	1.38	12.9	9.3	230	164

Table 2. shows the energy requirements to make various engineering materials (3.4). On a volume basis plastics materials compare favourably with other engineering materials.

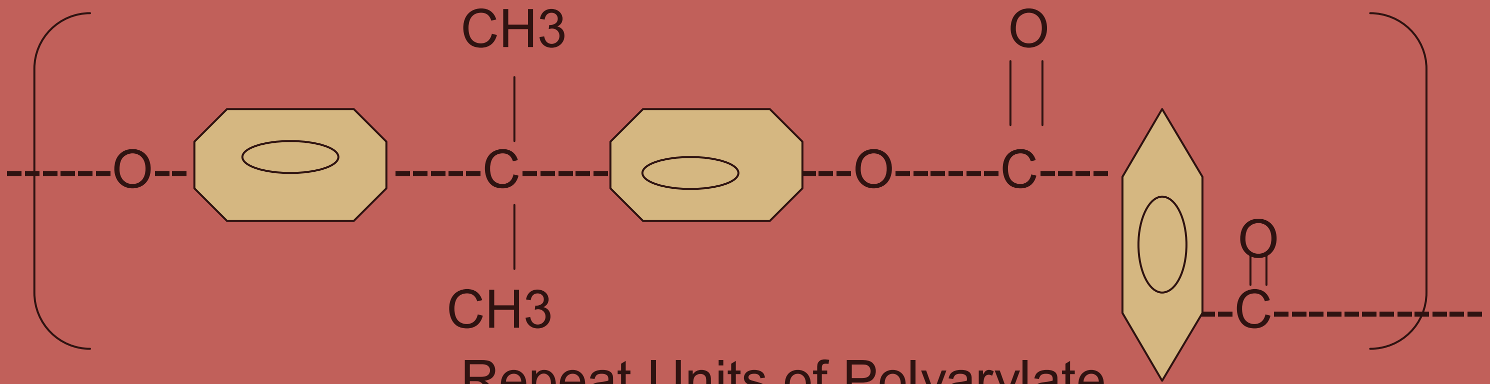
Table 2. The energy required for the production of different engineering materials (3.4)

Material	**Energy**	
	(KJ / Kg $^{-1)}$	(KJ / m^3/10)
Bottle glass	18	41
Low-density polyethylene	69	64
High-density polyethylene	70	67
Polypropylene	73	68
Polyvinylchloride	53	69
Polystyrene	80	84
Polyurethane	130	100
Polypropylene / 30% glass fibre	90	100
Polyester / 30% glass fibre	90	150
Phenoplast	150	200
Steel	45	350
Aluminium	>200	>540
Brass	95	600

Cyclic units in Backbone….

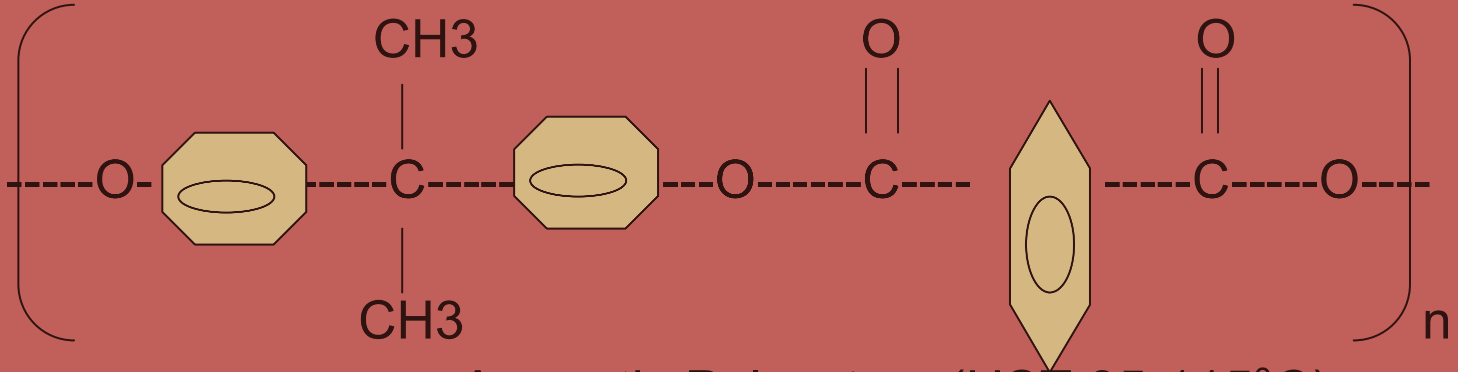
3)Partially Aromatic Thermoplastic Polyesters and Polyacrylates

a)



Repeat Units of Polyarylate

b)



Aromatic Polyesters (UST 85-115^{0}C)

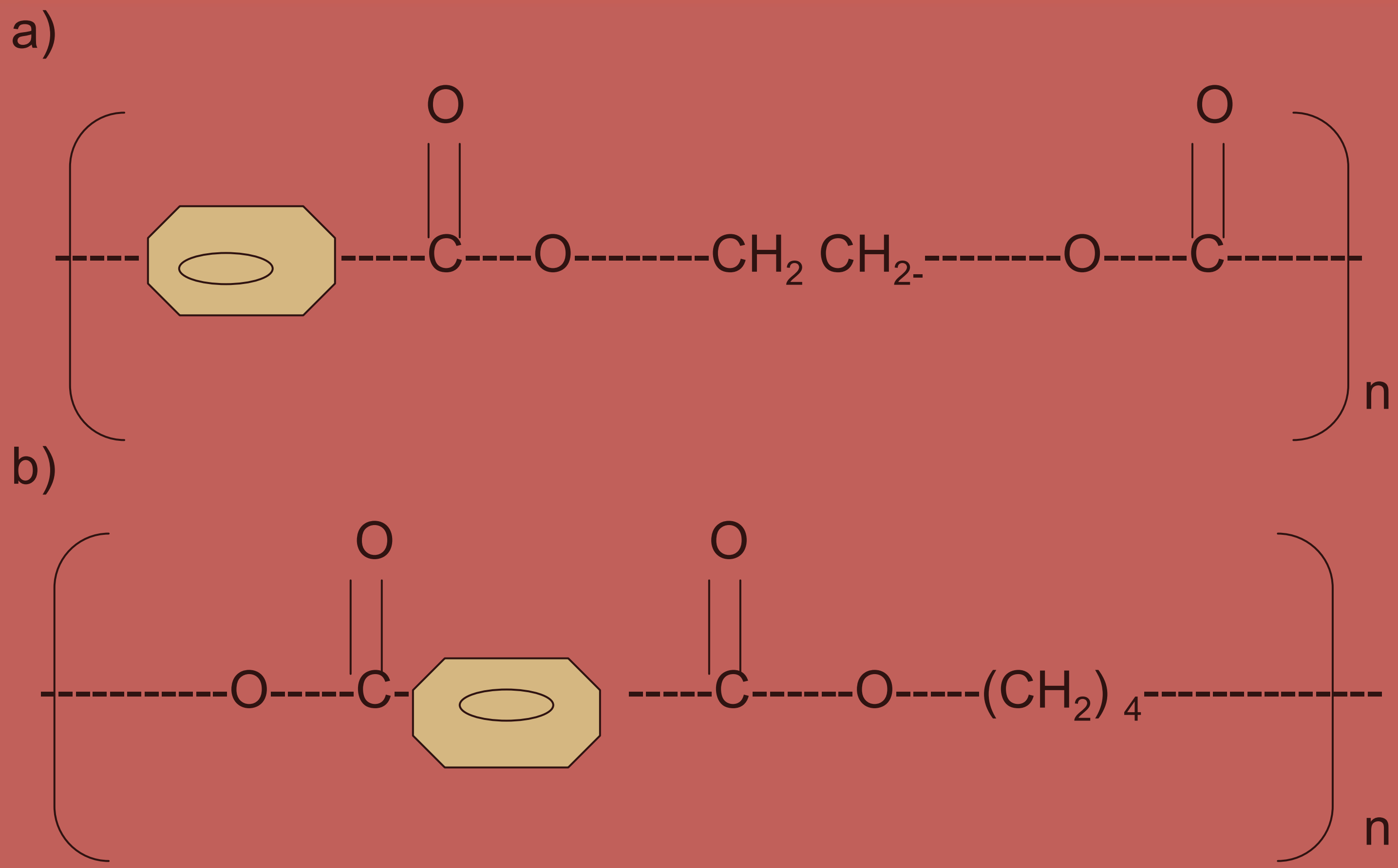


Figure 9. The repeat units of (a) polyethyleneterephthalate (PET) and (b) polybutyleneterephthalate (PBT)

2. Polycarbonate and Polyphthalate Carbonate

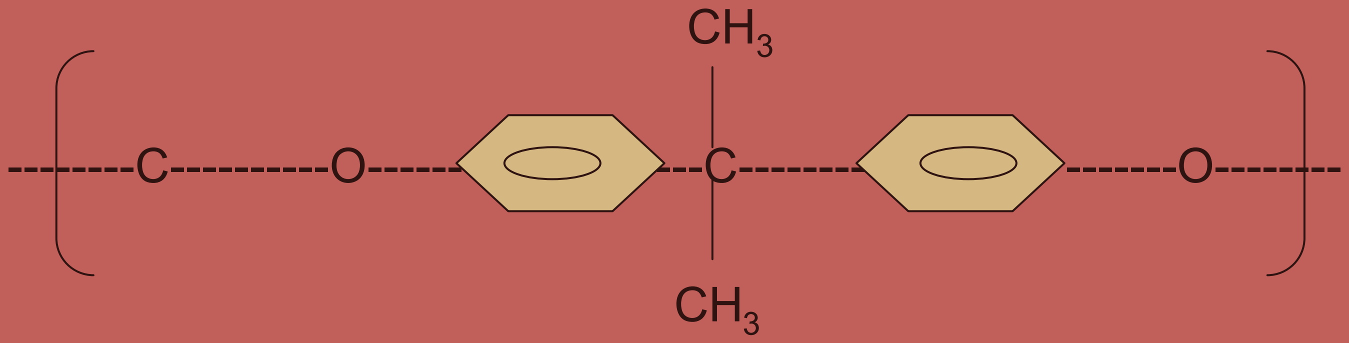
Table 8. Property data for thermoplastic polyesters and polyarylates

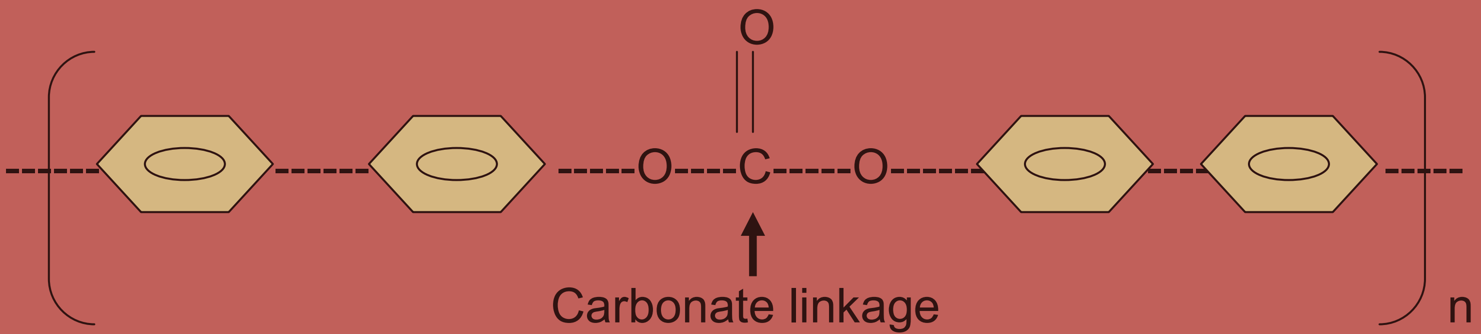
	PET	PBT	'Ardel' Polyarylate	PBT /30% glass fibre
Specific gravity	1.34-1.39	1.31	1.21-1.26	1.71
Tensile strength/MNm^{-2}	58-71	52	69	1.80
Elongation-to-break %	3-300	250	50-100	2
Tensile modulus/GN m^{-2}	2.7-4.0	2.7	2.07-2.28	16.0
Flexural modulus/GN m^{-2}	2.4-3.1	2.1	2.14-2.23	9.0
Heat deflection temperature at 1.82 MN m^{-2}/^{0}C	37-40	50-85	110-170	200
Continuous service temperature/^{0}C	85-115	120	-	140

Table 9.Property data for polycarbonates and blends

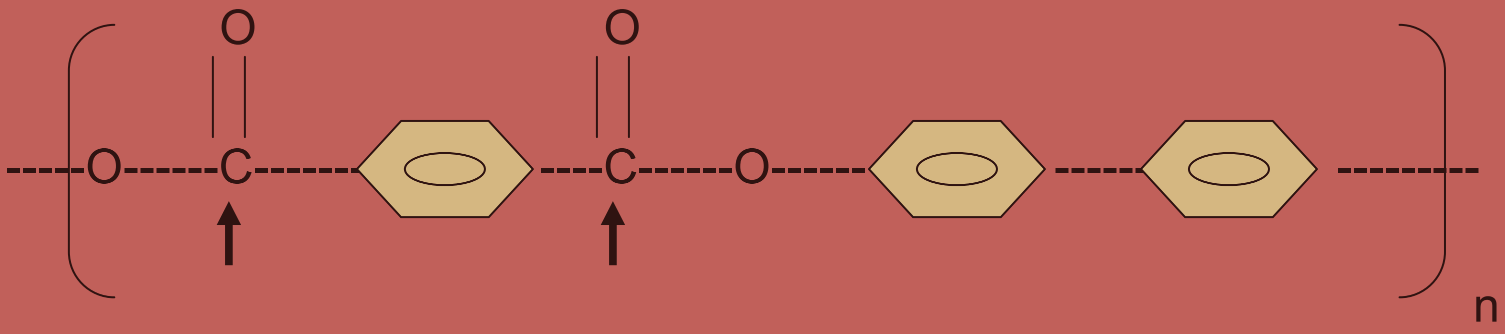
	PC	PPC	PC/40% glass fibre	PC/PBT/ modifier
Specific gravity	1.2	-	1.52	1.22
Tensile strength/MNm^{-2}	70	70	120	.50
Elongation-to-break / %	100	80	2	100
Tensile modulus/$GN\ m^{-2}$	2.3	2.1	10.0	1.8
Flexural modulus/$GN\ m^{-2}$	2.5	2.2	100	1.9
Heat deflection temperature at 1.82 MN $m^{-2}/{}^0C$	135-140	163	150	95
Continuous service temperature/${}^0C$	-	-	-	-

2. Polycarbonate and Polyphthalate Carbonate





Carbonate linkage

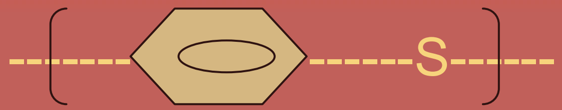


Ester linkage

Table 10.

	Trogamid T	Grilamid TR55
Specific gravity	1.12	1.06
Tensile strength/MNm^{-2}	68	75
Elongation-to-break / %	132	-
Tensile modulus/GN m^{-2}	3.0	-
Heat deflection temperature at 1.82 MN m^{-2}/^{0}C	124	124
Continuous service temperature/^{0}C	130	140

1. Poly (m-phenylene Isophtalamide)
2. Poly (p – phenylene terephthalamide)
3. Partially Aromatic and Aromatic polyamides
4. Poly phenyle oxide (PPO)
5. Poly phenylene sulfide and poly arylene sulfide (PAS)
6. Poly ether ether ketone (PEEK) and polyether ketone (PEK)
7. Polysulphones



Excellent chemical resistance crystalline --- Flame Retarding

PAS ---- Aromatic content > PPS; $T_g = 215^0C$

	PPS glass fibre	PPS mineral	PAS 2	PAS2 glass fibre
Specific gravity	1.57-1.72	1.9-2.0	-	-
Tensile strength/MNm^{-2}	110-131	72-96	96	117
Elongation-to-break / %	1.0-0.8	0.5-0.7	-	-
Tensile modulus/GN m^{-2}	-	-	2.9	10.2
Flexural modulus/GN m^{-2}	9.6-14.0	14.0-17.0	3.4	9.6
Heat deflection temperature at 1.82 MN m^{-2}/^0C	240	-	198	200
Continuous service temperature/^0C	220-220	200-240	-	-

Table 13. Property data for some of the polysulphones

	PSO	PES	PES/30 % glass fibre	PES HTA	PSO/ABS Blend
Specific gravity	1.24	1.37	1.67	1.36	1.14
Tensile strength/MNm^{-2}	70	83	156	86	51
Elongation-to-break / %	50-100	30-80	3.0	19	3.7
Tensile modulus/GN m^{-2}	2.48	-	-	2.3	-
Flexural modulus/GN m^{-2}	2.65	2.55	8.0	2.5	2.5
Heat deflection temperature at 1.82 MN m^{-2}/^{0}C	174	202	216	234	150
Continuous service temperature/^{0}C	160	180	180	200	125

Table 14. Property data for thermoplastic polyimides

	Polyimide	Polyimide galss fibre	Polyamide-Imide	Polyether-imide	Polyether-imide/40 % glass fibre
Specific gravity	1.4	1.9	1.4-1.45	1.27	1.51
Tensile strength/MNm^{-2}	118	186	83-110	105	186
Tensile modulus/GN m^{-2}	-	-	4.9-6.7	3.0	11.7
Flexural modulus/GN m^{-2}	3.3	16.5	4.58	3.3	11.7
Heat deflection temperature at 1.82 MN $m^{-2}/^{0}C$	270-280	348	260	200	210
Continuous service temperature/^{0}C	260	260	250	170	170

Characteristics of Rubber

1) Rubber elasticity means a large deformability with almost complete reversibility. Rubbers are resilient. Rubbers are also characterized by high elongation at break. Rubbers thus have all around ability to be used in extension, compression, shear, torsion or combination of these stresses.
2) Owing to small atomic masses of atoms and insufficient chain packing, rubber densities are low.
3) Rubber dissolve slowly in appropriate solvent to give solutions high viscosity even at low concentrations.
4) Rubbers are viscoelastics and show creep, stress relaxation and permanent deformation in rubber parts after distorting load has been removed.
5) Rubbers show Joule Effect at moderate strains. When it is stretched, then heated it tries to contract. Its elastic modulus increases with rise in temperature. Rubbers absorb heat when allowed to contract rapidly.

6) Rubbers are poor conductor of heat and electricity with high coefficient of expansion. Large application of rubber is in insulation applications with large flexibility.

7) Rubbers have high friction coefficient when dry, this is greatly reduced when rubber is wet with water.

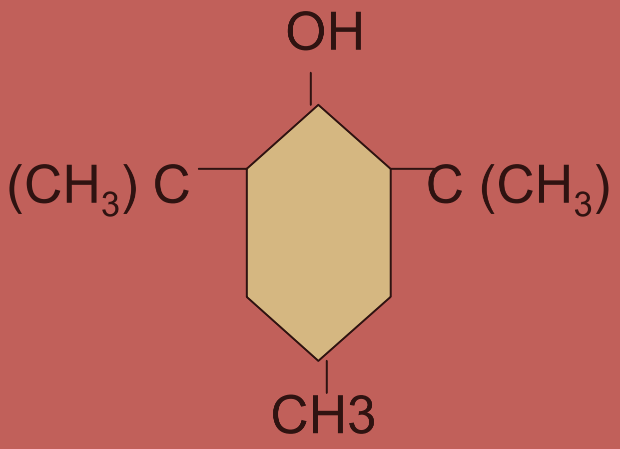
8) Properties of rubber can be improved by compounding with fillers and adjusting the conditions of vulcanization. Thus greater abrasion resistance, tear, high modulus or elasticity, hardness and tensile strength can be obtained in rubbers by the above operations.

9) When new samples of gum and carbon filled rubber vulcanizates are stretched and then allowed to retract, subsequent extensions to same strain require a lower stress. Most of this softening occurs during the first deformation and after a few stretching cycles, a steady state is reached. This phenomenon has been termed a Mullin's Effect.

In addition to these additives, typical formulations for commercial rubber may include anti oxidants and reinforcing fillers (usually carbon black). A typical formulation for vulcanization of a diene elastomer includes the following :

Component	phr
Sulfur	0.5 - 4
Fatty Acid	1 – 4
Zine Oxide	2 – 10
Accelerator	0.5 – 2

(A free radical Scavanger, 4-methyl-2, 6-di-tertiary butylphenol)



The probable reaction is as follows :

Activators form a salt which complexes with the accelerator. Accelerator forms monomeric polysulfide. Monomeric Polysulfide reacts with an unsaturated eleatomer chain, ----- rubber Polysulfide, rubber polysulfide + another chain --- polysulfide bridge.

Vulcanization

- The vulcanization is the chemical process by which unsaturated elastomer polymers are joined together by crosslinking using sulfer alone or with accelerators to restrict molecular movement. In 1939 Charles Goodyear discovered a Vulcanization process for rubber by using sulphur and basic lead carbonate. Goodyear found that when a mixture of natural rubber, changes from thermoplastics to an elastomer material. Besides sulfur, diene elastomers are crosslinked by use of peroxides, ionizing radiations and sulfur containing compounds. The concentration of sulfur in the vulcanized product is typically 3 parts per hundreds (pph) parts of elastomer compared to about 30pph in highly crosslinked hard rubber such as ebonite.

- The traditional vulcanization process is slow and inefficient as long bridges & cyclic sulfur structures may form. The vulcanization process can be improved by addition of accelerators such as thuriam disulfides, dithiocarbamades and benzothiazoles. Further addition of activators such as zine oxide and stearic acid serve to reduce the concentration of cyclic sulfide units and promote the formation of shorter chain sulfide bridges.

rubber

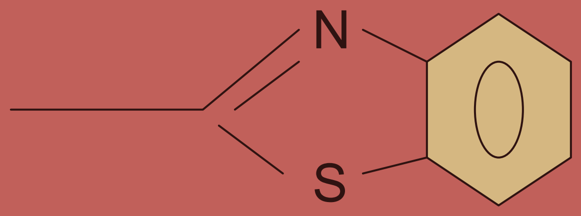
A. Ac----------Sx------Ac----→-rubber-------Sx--------

Ac-----→-rubber---------Sx--------rubber.

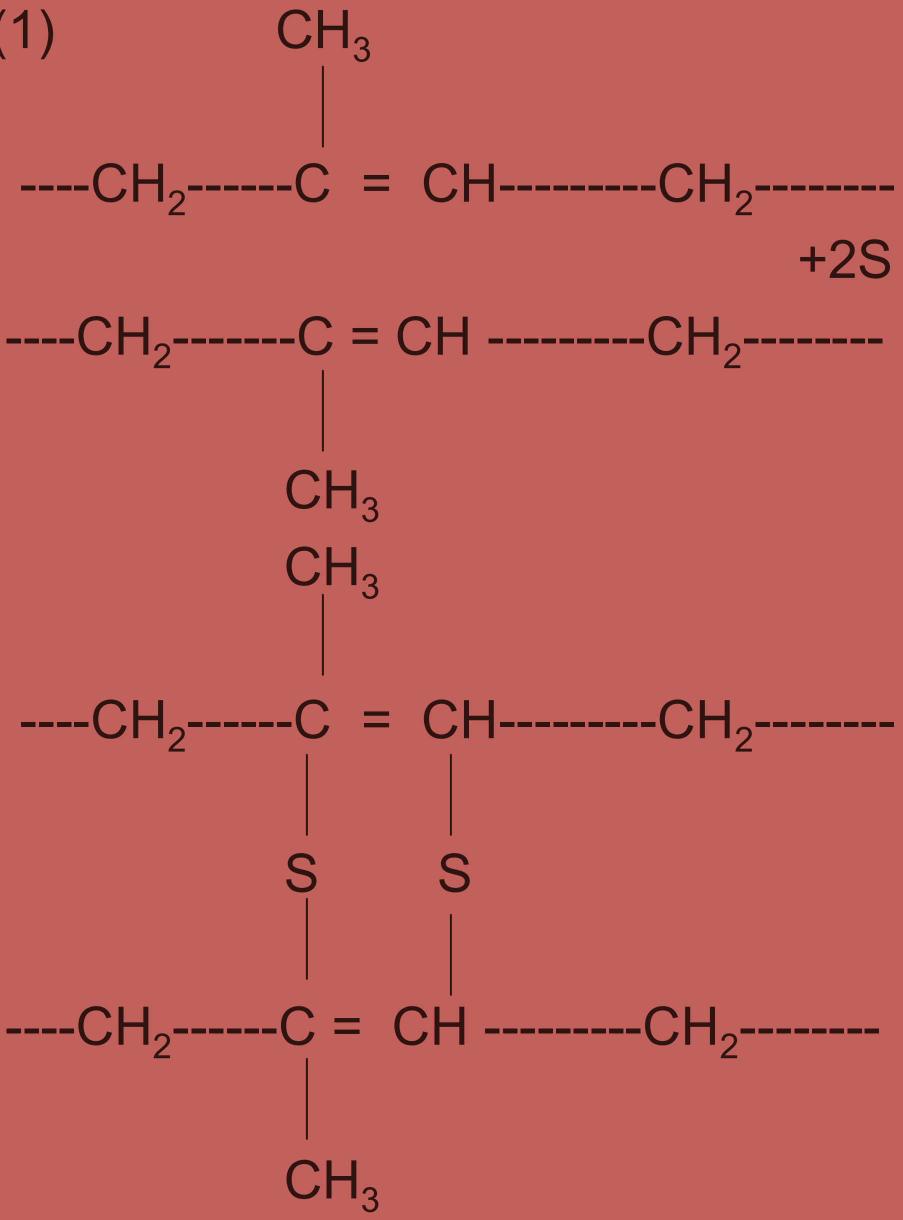
rubber

Ac group ---- Organic radical derived from accelerator i.e.

Benzothiazolyl group



(1)



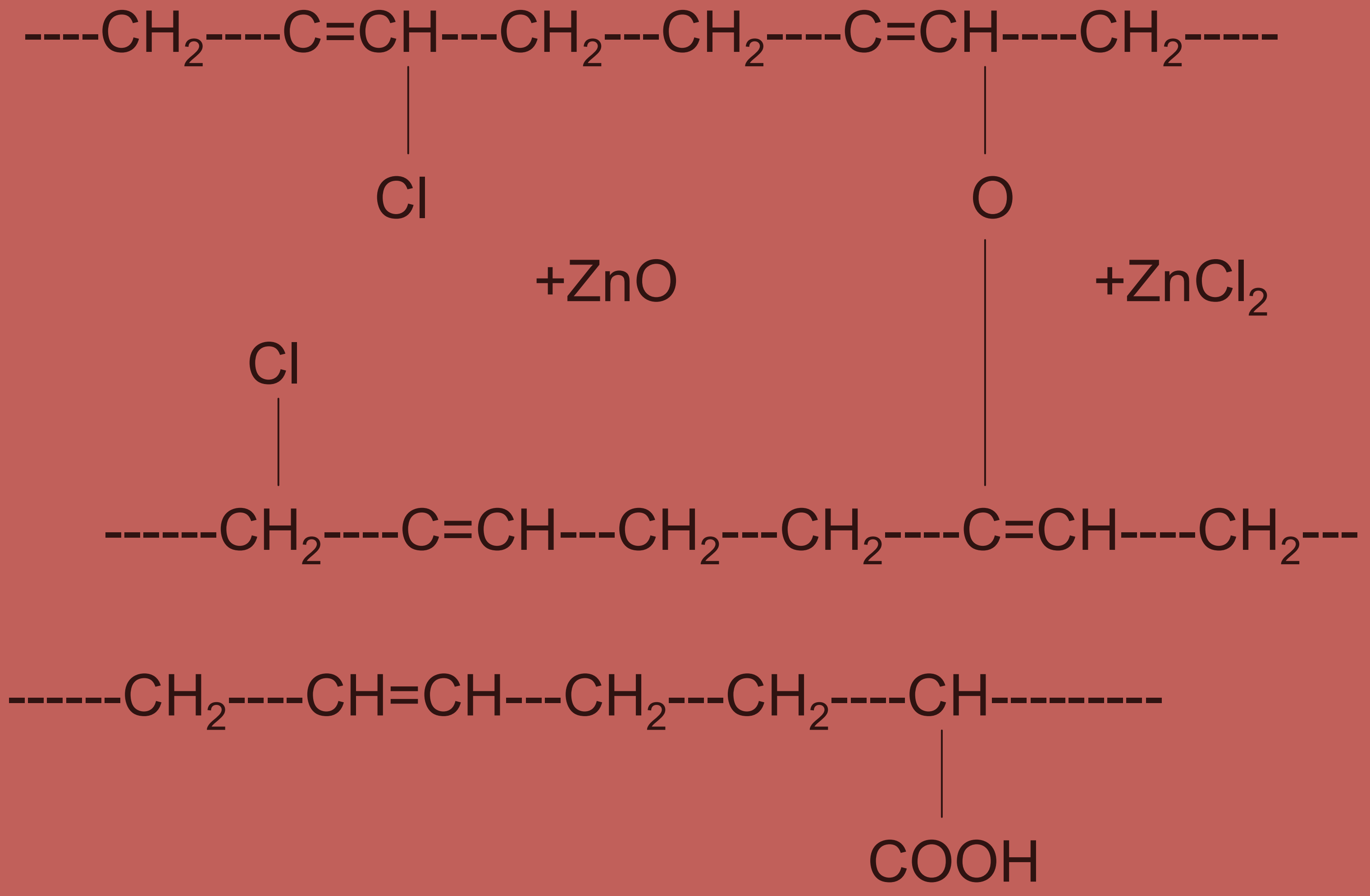
$$\begin{array}{cccccc}
 & CH_3 & & & & \\
 & | & & & & \\
\text{----}CH_2\text{------} & C & = & CH & \text{---------} & CH_2\text{--------}
\end{array}$$

$$+2S$$

$$\begin{array}{cccccc}
\text{----}CH_2\text{-------} & C & = & CH & \text{---------} & CH_2\text{--------} \\
 & | & & & & \\
 & CH_3 & & & &
\end{array}$$

$$\begin{array}{cccccc}
 & CH_3 & & & & \\
 & | & & & & \\
\text{----}CH_2\text{------} & C & = & CH & \text{---------} & CH_2\text{--------} \\
 & | & & | & & \\
 & S & & S & & \\
 & | & & | & & \\
\text{----}CH_2\text{------} & C & = & CH & \text{---------} & CH_2\text{--------} \\
 & | & & & & \\
 & CH_3 & & & &
\end{array}$$

(2)



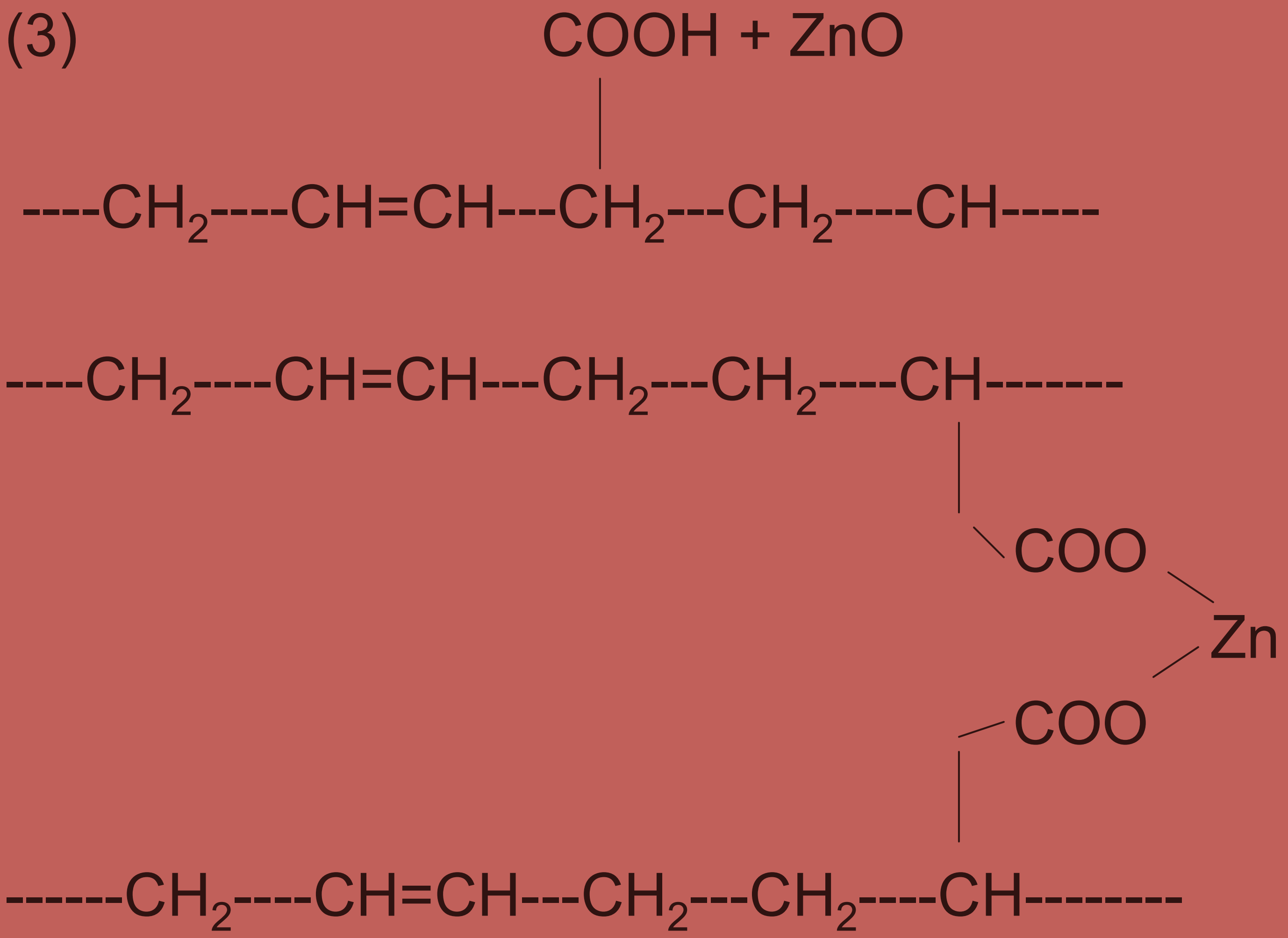
$$\text{----}CH_2\text{----}\underset{\underset{Cl}{|}}{C}=CH\text{---}CH_2\text{---}CH_2\text{----}C=\underset{\underset{O}{|}}{CH}\text{----}CH_2\text{-----}$$

$$+ZnO \qquad\qquad +ZnCl_2$$

$$\text{------}\overset{\overset{Cl}{|}}{CH_2}\text{----}C=CH\text{---}CH_2\text{---}CH_2\text{----}\overset{|}{C}=CH\text{----}CH_2\text{---}$$

$$\text{------}CH_2\text{----}CH=CH\text{---}CH_2\text{---}CH_2\text{----}\underset{\underset{COOH}{|}}{CH}\text{---------}$$

(3)



$$\overset{\displaystyle COOH + ZnO}{\vert}$$

$$----CH_2----CH{=}CH---CH_2---CH_2----CH-----$$

$$----CH_2----CH{=}CH---CH_2---CH_2----CH-------$$

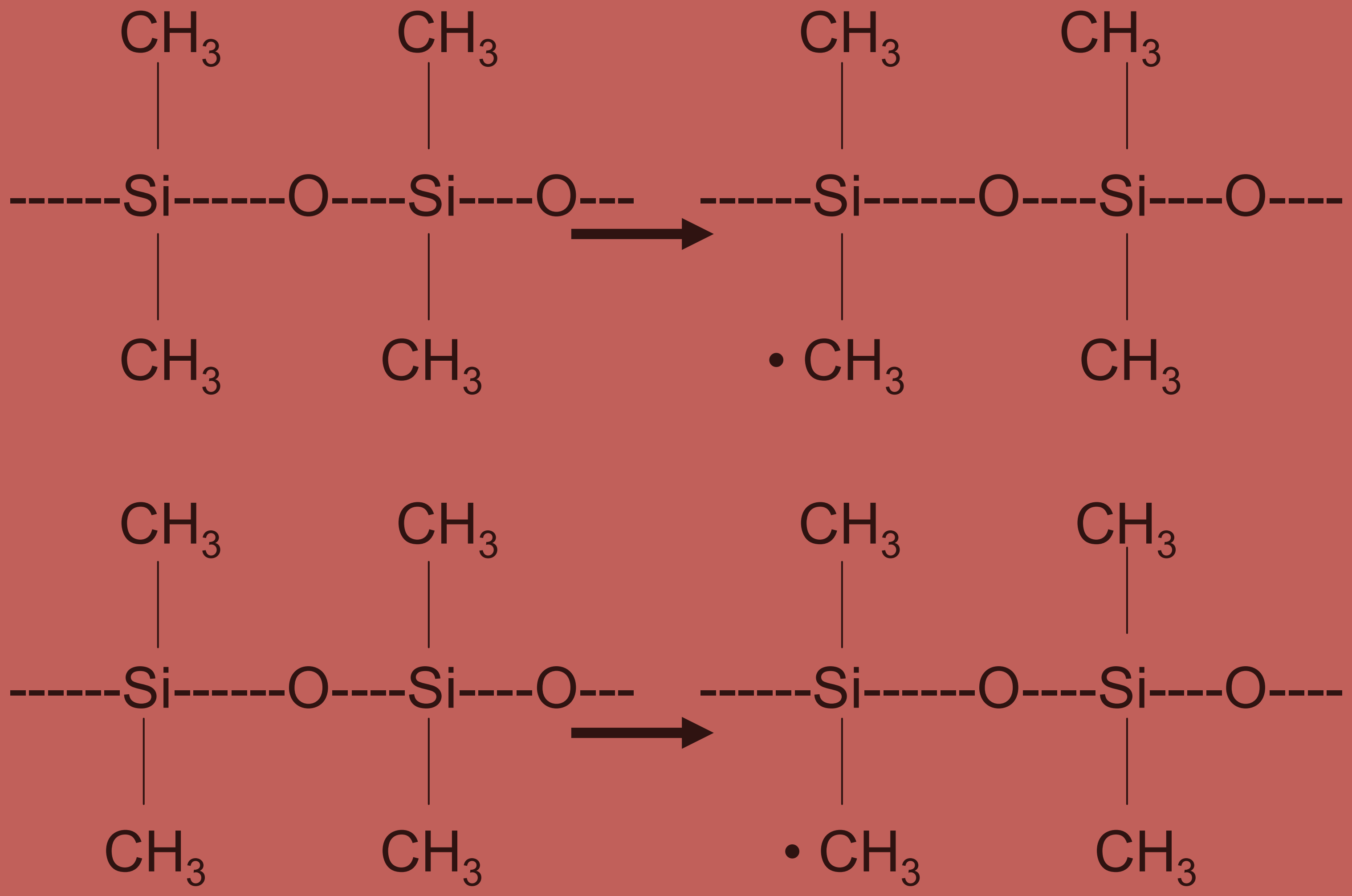
COO

Zn

COO

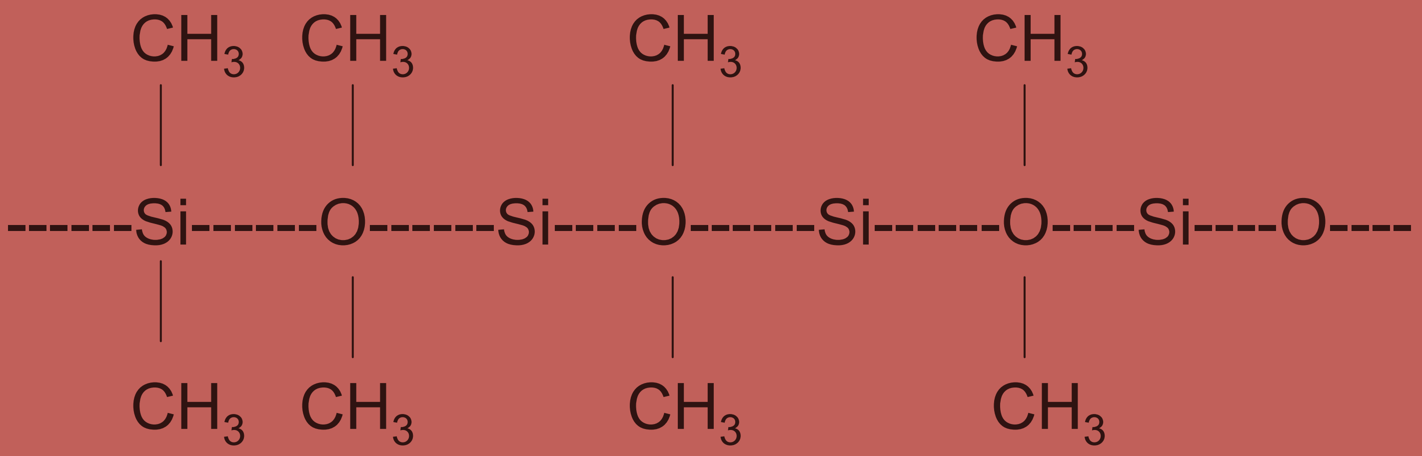
$$------CH_2----CH{=}CH---CH_2---CH_2----CH--------$$

(4)

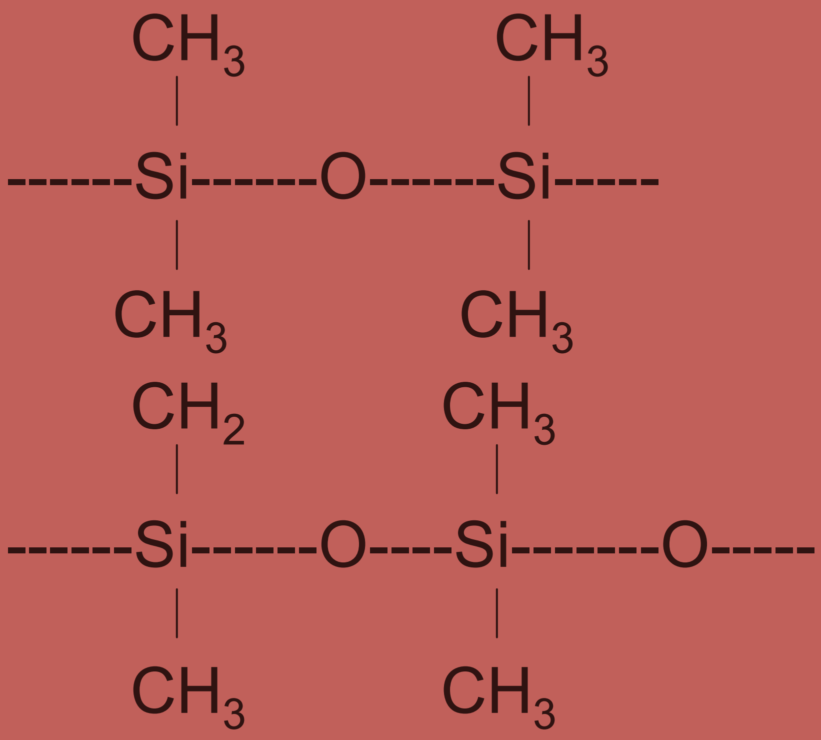


$$\text{------}\underset{CH_3}{\overset{CH_3}{Si}}\text{------}O\text{----}\underset{CH_3}{\overset{CH_3}{Si}}\text{----}O\text{---} \longrightarrow \text{------}\underset{\bullet\, CH_3}{\overset{CH_3}{Si}}\text{------}O\text{----}\underset{CH_3}{\overset{CH_3}{Si}}\text{----}O\text{----}$$

$$\text{------}\underset{CH_3}{\overset{CH_3}{Si}}\text{------}O\text{----}\underset{CH_3}{\overset{CH_3}{Si}}\text{----}O\text{---} \longrightarrow \text{------}\underset{\bullet\, CH_3}{\overset{CH_3}{Si}}\text{------}O\text{----}\underset{CH_3}{\overset{CH_3}{Si}}\text{----}O\text{----}$$



$$\text{------}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{------}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{O}}\text{------}Si\text{----}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{O}}\text{------}Si\text{------}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{O}}\text{----}Si\text{----}O\text{----}$$



$$\text{------}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{------}O\text{------}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-----}$$

$$\text{------}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{|}}{Si}}\text{------}O\text{----}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-------}O\text{-----}$$

Elastomers or Rubbers

- Formation of network structure on fabrication → Network → covalent bond or physical links that connect individual molecules.

↓

Thermosetts or Elastomers

Elastomers :

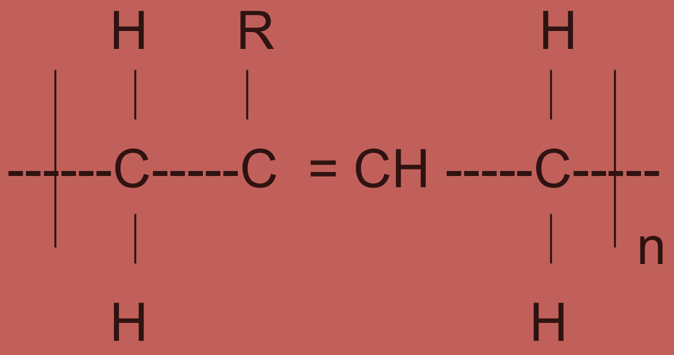
Polymers that have limited or no crystallinity, have low glass transition temperature (-50 - -70^0C) and can be crosslinked such that when deformed but will return to its original form upon release of applied force provided the force is not so great as to rapture the bonds are called Elastomers ----- They have few crosslinks.

Polymers having high density of crosslinks are therefore infusible, insoluble and dimensionally stable under load → Thermosetts.

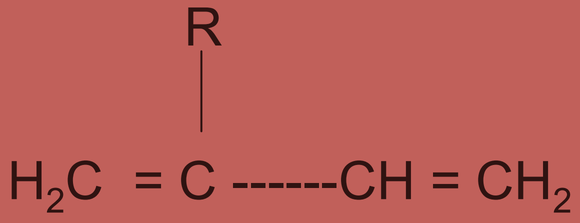
Elastomers

1) **Diene Elastomers**
2) **Non Diene Elastomers**
3) **Thermoplastic Elastomers**

- Dience Elastomers : Such as polybutadiene, polyisoprene and polychloroprene are polymerized from monomers containing two segmental double bonds (a diene) having the structure.



$$-\left[\,\overset{H}{\underset{H}{C}}-\overset{R}{C}=CH-\overset{H}{\underset{H}{C}}\,\right]_n-$$



$$H_2C=\overset{R}{C}-CH=CH_2$$

R = H	PB
= Cl	PCP
= CH_3	PIP

Polymerization → Single double bond in repeat unit → site for subsequent crosslinking (Vulcanization)

1) Homopolymers as above
2) Diene copolymers styrene butadiene elastomers / rubber (SBR); NBR – nitrile rubber copolymer of butadiene and acrylonitrile.

Non Diene Elastomers:

Polyisobutylene, polysiloxanes (Silicon Rubber), polyurethane (Spandex), fluoroelastomers (Viton)….. don't have unsaturated sites.

Crosslinking : Trifunctional Monomers (Polysiloxanes) use of free radical initiators, copolymerisation with small amount of a diene monomer (e.g. PB).

- **Thermoplastics Elastomers (TPE) :**

SBS terpolymer are TPE that contain rigid (glassy polystyrene) and soft (rubbery) PB segments can thermally processed upon cooling, the soft and rigid segments phase separate into physical distinct domains whereby the rigid domains serve as physical anchors for rubbery segments and thereby provide a restoring force when thermoplastic elastomers are stretched.

Butadiene – Based Elastomers:

Of all synthetic elastomers; PB and butadiene copolymers enjoy largest sale.

PB and SBR : Production of tyres and tyre products, blends of natural and synthetic rubbers.

PB: Good resilience, abrasion resistance, low heat buildup.

NBR or NITRILE RUBBER : Improved oil and aromatic solvent resistance materials for gasket, tubing, o rings, gasoline hoses.

Polyisoprene: Occurs in nature can also be synthesized.

NR – Natural Rubber :

Used in tyre is also Cis 1,4 polyisoprene – and is obtained from tree Hevea Brasiliensis (Havea Rubber) as a latex containing about 35% rubbers and 5% solids (e.g. proteins, sugars, resins and salts). Rubber is obtained by coagulation of the latex. Another source of NR is shrub GUAYULE, which is found in parts of USA and MEXICO.

Trans –Content polyisoprene is also obtained from tree products. (Gattaparcha and Balata) – Golf balls orthopaedic splints.

Polychloroprene:

Has good resistance to attack by O_2, ozone oil and gas – gaskets, tubing, O-rings and gasoline hoses.

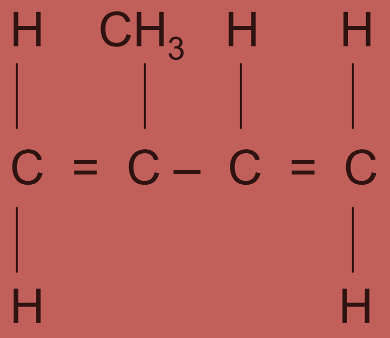
Vulcanization :

Uncrosslinked rubber is gummy material like chewing gum. To obtain network structure, diene elastomers are crosslinked by use of peroxides, ionizing radiation and sulfur or sulfur containing compounds.

Concentration of sulfur – 3 pph (parts per hundred) – 30 pph (Ebonite).

Elastomers

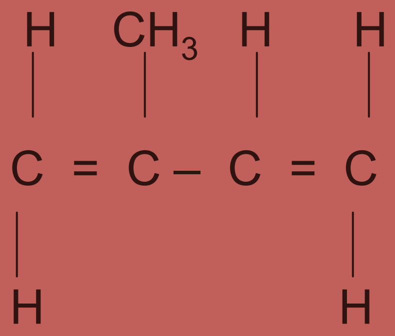
1. Isoprene Natural Rubber



$$\begin{array}{ccccccc} H & & CH_3 & & H & & H \\ | & & | & & | & & | \\ C & = & C & - & C & = & C \\ | & & & & & & | \\ H & & & & & & H \end{array}$$

---- C ---- C = C ------ C ------

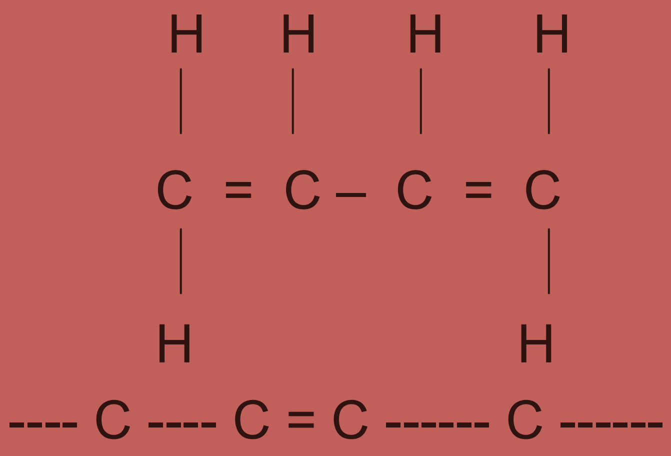
2. Chloroprene or Neoprene



$$\begin{array}{ccccccc} H & & CH_3 & & H & & H \\ | & & | & & | & & | \\ C & = & C & - & C & = & C \\ | & & & & & & | \\ H & & & & & & H \end{array}$$

---- C ---- C = C ------ C ------

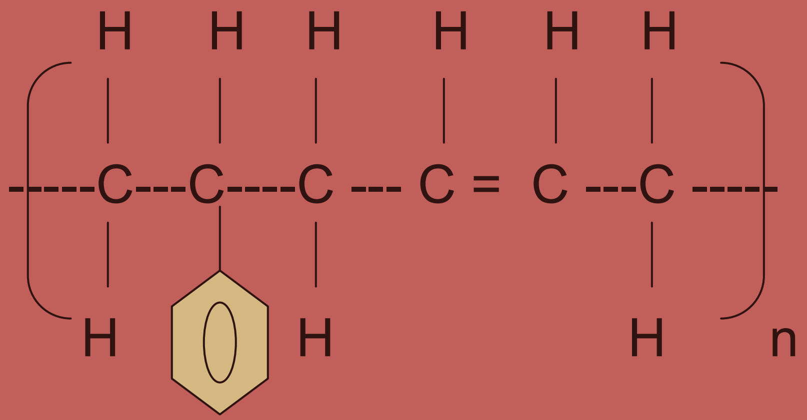
3. Butadiene



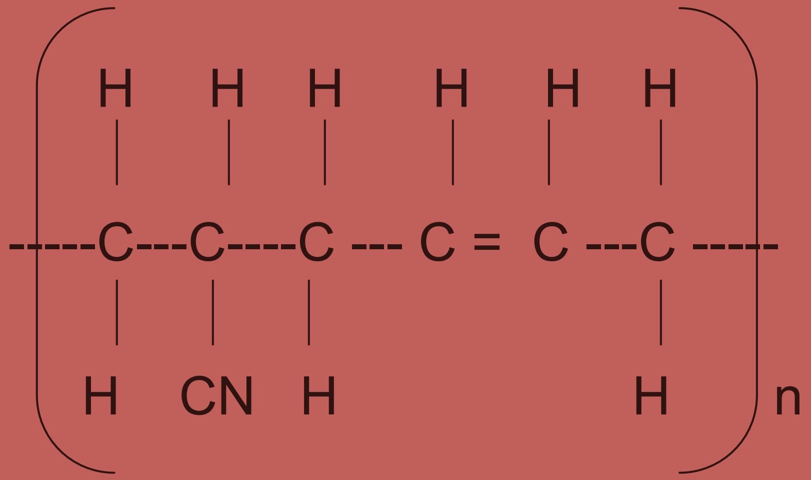
$$\underset{H}{\overset{H}{C}} = \overset{H}{C} - \overset{H}{C} = \underset{H}{\overset{H}{C}}$$

---- C ---- C = C ------ C ------

4. Styrene butadiene

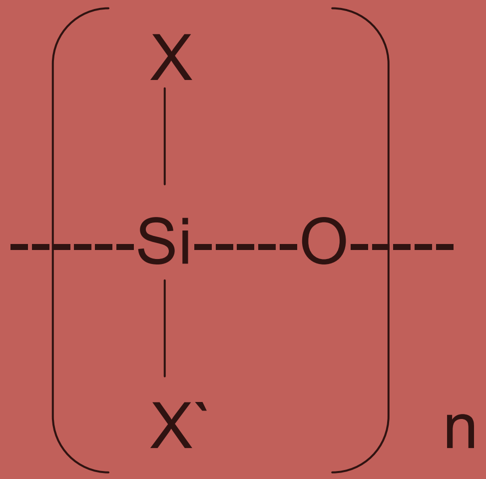


5. Nitrile Rubber

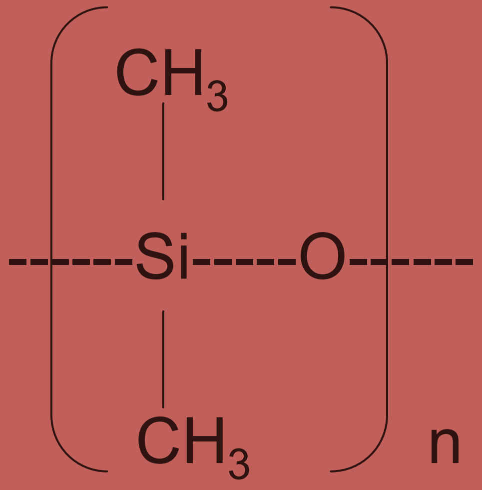


$$\left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CN}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}- \right]_n$$

6. Silicon Rubber



$$\left[-\overset{X}{\underset{X`}{Si}}-O- \right]_n$$



$$\left[-\overset{CH_3}{\underset{CH_3}{Si}}-O- \right]_n$$

(-100 -250^{0}C)

Table 13.5 Properties of Different Rubbers (Ealstomers)

Common Name	Chemical Name	Tensile, strength, psi	Percent Elongation	Resistance to Oil, Gas	Useful Temperature Range ^{0}F (^{0}C)
Natural Rubber	Cis-Polyisoprene	3,000	800	Poor	-60 to 180 (- 51 to 82)
GR-S or Buna S	Butadiene styrene copolymer	250	3,000	Poor	(- 60 to 180) (- 51 to 82)
Isoprene	Polyisoprene	3,000	400	Poor	(- 60 to 180) (- 51 to 82)
Nitrile or Buna N	Butadiene-acrylonitrile copolymer	700	400	Excellent	(- 60 to 300) (- 51 to 149)
Neoprene [GR-M]	Polychloroprene	3,500	800	Good	(- 40 to 200) (- 40 to 93)
Silicon	Polysiloxane	700	300	Poor	(- 178 to 600) (-117 to315)
Urethane	Diisocyanate polyester	5,000	600	Excellent	(- 65 to 240) (- 54 to 115)

Polydispersity

Number Average Molecular Weight

$$\overline{M}_n = \sum N_i m_i / \sum N_i$$

Weight Average Molecular Weight

$$M_n = \sum W_i m_i / \sum W_i ; W_i = N_i M_i$$

$$= \sum N_i M_i^2 / \sum N_i M_i$$

$$[] = K M_v^a$$

For rigid molecular a =2

θ solvent, a = 0.5, common a = 0.5 – 0.8

Viscosity Average Molecular Weight

$$\overline{M}_v = [\sum N_i m_i^{(1+a)} / \sum N_i m_i]^{1/a}$$

a – measure of polymer – solution interaction

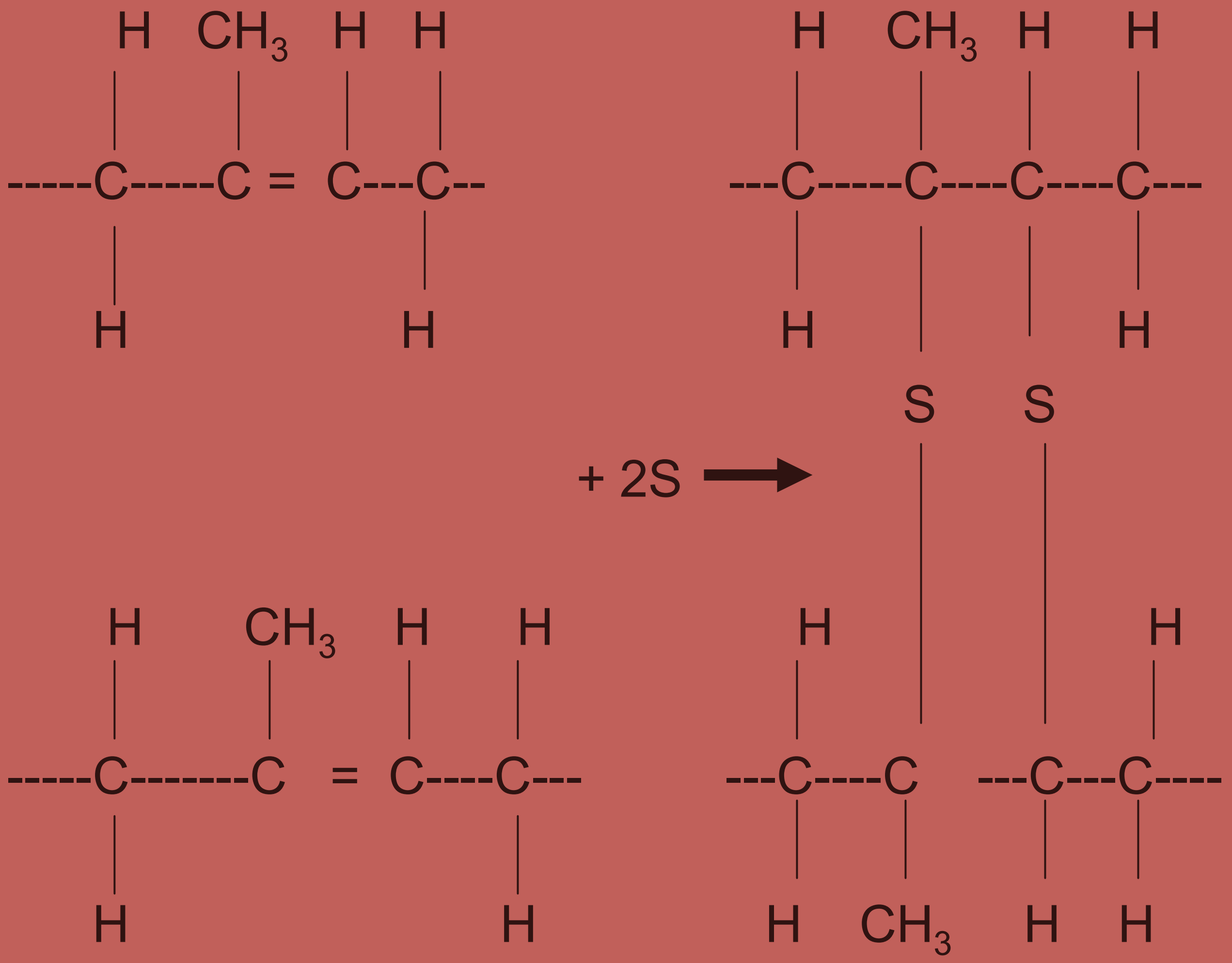
Polydispersity Index (PDI) :

Measure of breadth of the molecular weight distribution and is given by:

$$\overline{M}_w / \overline{M}_n$$

For monodisperse polymer, all molecules have the same value of M_i and thus $\overline{M}_w$ and $\overline{M}_n$ are equal i.e. PDI = 1. For polydisperse polymers $\overline{M}_w / \overline{M}_n$ can be as high as 25 although the more typical values are in the range of 2 – 10.

VULCANIZATION



Polymer Additives

1. Fillers : Wood Flour, SiO_2, glass, clay, tale, limestone, carbon black, ZnO.
2. Palsticizers : To improve flexibility, ductility and toughness ---- DOP; DEHP; DBP; DEP.
3. Stabilizers : Di tertiary – butyl – para creysol, carbon black, aliphatic thiols or disulphide, Mn and Ca stearates, organic phosphite.
4. Flame retardants : Halides
5. Colorants

Length, End – End Distance and Radius or Gyration

Contour Length – Full contour length (I_{count}) is obtained by multiplying the length of the segments (1) by number of segments (N) i.e.

$I_{count} = N\ 1$

End – End Distance – The statistical method is used to calculate the end-end distance of polymers.

Applying random flight model where it is assumed that all segment lengths 1 are equal in length and infinitely thin and that the angle θ between adjacent segments can take any value (freely jointed).

The root mean square of end-end distance ($\sqrt{L^2}$) is given by following equation.

$< L^2 > = N\ 1^2$

For a definite valence angle, which occur in real macromolecular chains.

$I_{max} = N\ 1 \sin (0.5\ \theta)$

l_{max} = maximum possible chain length assigned to a constant valence angle, chain in all – trans conformation.

Radius of Gyration : -

It is directly measurable as the mean square radius of gyration, which is defined as the second moment of mass distribution around radius of gyration, simply called radius of gyration is thus :

$$<R_G^2>^{1/2} = [\sum m_i R_i i^2 / m_i]^{½}$$

A definite relationship exists between the end-to-end chain distance and radius of gyration for linear chains with or without fixed valence angles in the limiting case of infinitely high molecular weight.

$$< L^2 >_0 = 6 < R_G^2 >_0$$

Text Books

1. W.D.Callister Jr. Materials Science and Engineering : An Introduction
2. William F Smith, Foundations of Materials Science and Engineering
3. J.R.Fried, Polymer Science and Technology
4. V. Raghvan, Materials Science and Engineering : A First Course
5. J.S.Anand, Applications of Plastics

THANK YOU