International Workshop on Advanced Polymer Science and Turbulent Drag Reduction

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Characteristics of Polymer

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CHARACTERISTICS OF POLYMER

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University of Lucknow
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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 aesthetic 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
II. Polymers for Information Technology –
 Electro and photoconducting polymers / Information polymers for non-linear optics / piezo and pyroelectric polymers / organic semiconductor / 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

<table>
<thead>
<tr>
<th>Applications</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Health</td>
<td>Low Density</td>
</tr>
<tr>
<td>2. Medicine</td>
<td>High Specific Strength and Modulus</td>
</tr>
<tr>
<td>3. Clothing</td>
<td>High corrosion resistance</td>
</tr>
<tr>
<td>4. Transportation</td>
<td>High electrical and thermal</td>
</tr>
<tr>
<td>5. Housing</td>
<td>Conducting polymers</td>
</tr>
<tr>
<td>6. Defence</td>
<td>Easy and low energy processing into intricate</td>
</tr>
<tr>
<td></td>
<td>shapes by fast processing techniques</td>
</tr>
<tr>
<td>7. Electronics</td>
<td>Great aesthetic appeal</td>
</tr>
<tr>
<td>8. Energy</td>
<td>Moth and fungus resistance</td>
</tr>
<tr>
<td>9. Employment</td>
<td>Low permeability of water vapours and others</td>
</tr>
<tr>
<td></td>
<td>gases</td>
</tr>
<tr>
<td>10. Trade</td>
<td>Controlled – Biodegradability; Biodegradable and</td>
</tr>
<tr>
<td></td>
<td>non-biodegradable polymers</td>
</tr>
</tbody>
</table>
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 CO₂ emissions by 30 million tonnes a year.
   - Plastics help reduce fuel consumption and CO₂ 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 recycled or used as an alternative fuel. Plastic waste has a calorific value at least equal to coal and with lower CO₂ 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)
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 comparison with classical materials stiffness

- Percent achieved of the theoretically maximum value

<table>
<thead>
<tr>
<th></th>
<th>Injection Moulded</th>
<th>Fibres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>3%</td>
<td>40%</td>
</tr>
<tr>
<td>Polyamide</td>
<td>1%</td>
<td>3%</td>
</tr>
<tr>
<td>Glass</td>
<td>88%</td>
<td></td>
</tr>
<tr>
<td>Steel</td>
<td>77%</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>95%</td>
<td></td>
</tr>
</tbody>
</table>
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.
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 = 1,00,000-7,00,000 gm/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.

\[
\text{heat} \\
H - O - O - H \rightarrow 2H - O.
\]

Hydrogen Peroxide

\[
R - O - O - R \rightarrow 2R - O.
\]

Organic peroxide \quad Free Radical
Benjoyal Peroxide

Free Radicals

Free electron $\cdot O + C = C$

$\cdot O + C = C$

II. Propagation:

$R - CH_2 - CH_2 + CH_2 = CH_2$

$R - CH_2 - CH_2 - CH_2 - CH_2$
III. Termination:

\[ R(CH_2 - CH_2)_m + R'(CH_2 - CH_2)_n \rightarrow R(CH_2 - CH_2)_m - (CH_2 - CH_2)_n R' \]

Vinyl and Vinylidene Polymers.

I) Vinyl Polymers

\[ \begin{array}{c}
H \\
C = C \\
H \\
\hline
R_1 \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
H \\
C - C \\
H \\
\hline
R_1 \\
\end{array} \]
II) Vinylidene Polymers.

\[
\begin{array}{c}
\begin{array}{c}
\text{H} \\
\text{C} = \text{C} \\
\text{H} \\
\end{array} \\
\begin{array}{c}
\text{H} \\
\text{R}_1 \\
\end{array}
\end{array}
\longrightarrow
\begin{array}{c}
\begin{array}{c}
\text{H} \\
\text{R}_2 \\
\end{array} \\
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{H} \\
\text{R}_1 \\
\end{array} \\
\begin{array}{c}
\text{H} \\
\text{R}_2 \\
\end{array}
\end{array}
\end{array}
\]
Stepwise Polymerization

Hexamethylene Diamine + Adipic Acid

\[
\text{Hexamethylene Diamine: } \text{N} - (\text{CH}_2)_6 - \text{N} + \text{C} - (\text{CH}_2)_4 - \text{C}
\]

\[
\text{Adipic Acid: } \text{O} + \text{C} - (\text{CH}_2)_4 - \text{C} \quad \text{OH}
\]

\[
\text{Hexamethylene Adipamide (Nylone 6, 6)}: \text{N} - (\text{CH}_2)_6 - \text{N} - \text{C} - (\text{CH}_2)_4 - \text{C} + \text{H}_2\text{O}
\]

\[
\text{OH}
\]
I. Homopolymers: Polymers chain made up of single repeat units.

II. Copolymers: Poly (ACoB)
Random Copolymers AABBABBBBBBAABB Poly (A ran B) or Poly (A stat B)

(i) Alternate Copolymers: Poly (A alt B)
   ABABABABABABAB ………..

(ii) Block Copolymers: Poly (A block B)
(iii) Graft Copolymers : Poly (A graft B)

```
B
B
B
|
A A A A A A A A A A A A A A
|
  B
  B
  B
  B
```
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.

\[
\text{nH}_2 \text{N} (\text{CH}_2)_6 + \text{n HOC} - (\text{CH}_2)_8 \rightleftharpoons \text{C} \text{OH} \\
\]

1,6 Hexamethylene diamine \hspace{1cm} \text{Sebacic acid}

\[
\left[ \text{NH} (\text{CH}_2)_6 \text{NHC} - (\text{CH}_2)_8 \text{C} \right] \text{n} + \text{n H}_2\text{O} \\
\text{Nylon 6, 10}
\]
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
3. Supper Engineering Plastics / Speciality Plastics

1. High Tonnage or Commodity Plastics
2. General Purpose Engineering Plastics
Plastics

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

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

Specialty: PPS, PSF, PEI, PAI, PEEK, LCP; Consumption = 1%; HDT > 150°C; strength ≥ 70 MPa; Price US $/Kg ≥10
High Tonnage or Commodity Polymers

Polyethylene (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 Terephthalate) (PBT), Para Poly (Phenylene Oxide) (Para PPO - PPE) and Poly (Ethylene Terephthalate) (PET)
Speciality Engineering Plastics

Poly(Phenylene Sulphide) (PPS)
Poly(Phenylene Sulphur) (PSF)
Poly(Phenylene Sulphones) (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.
1. Poly (ether Ketone)

\[
\begin{array}{c}
\text{CH}_3 \quad \text{---C---O---S---} \\
\text{CH}_3
\end{array}
\]

2. Polyacrylate

\[
\begin{array}{c}
\text{CH}_3 \quad \text{O} \quad \text{---O---C---} \\
\text{CH}_3
\end{array}
\]

3. Poly (Phenylene Sulfide)

\[
\begin{array}{c}
\text{S}
\end{array}
\]

4. Poly (Ether Ether Ketone)

\[
\begin{array}{c}
\text{O} \quad \text{---O---C---} \\
\end{array}
\]
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>
<thead>
<tr>
<th>Polymer</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>HDT (°C)</th>
<th>$\sigma$ (MPa)</th>
<th>$E$ (GPa)</th>
<th>$\varepsilon_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>915-935</td>
<td>-126</td>
<td>108</td>
<td>41-44</td>
<td>7-17</td>
<td>0.1-0.3</td>
<td>100-700</td>
</tr>
<tr>
<td>LLDPE</td>
<td>910-925</td>
<td>-130</td>
<td>125</td>
<td>6-66</td>
<td>14-21</td>
<td>0.1-0.2</td>
<td>200-1200</td>
</tr>
<tr>
<td>HDPE</td>
<td>941-967</td>
<td>-130</td>
<td>135</td>
<td>65-93</td>
<td>19-30</td>
<td>0.7-1.6</td>
<td>100-1000</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>930</td>
<td>-130</td>
<td>132</td>
<td>79</td>
<td>20-41</td>
<td>110</td>
<td>300</td>
</tr>
<tr>
<td>PP</td>
<td>903</td>
<td>-20-0</td>
<td>165</td>
<td>101</td>
<td>35.5</td>
<td>1.38</td>
<td>100-600</td>
</tr>
<tr>
<td>PS</td>
<td>1040-1050</td>
<td>105</td>
<td>NA</td>
<td>82-112</td>
<td>32-56</td>
<td>3.1-3.3</td>
<td>1.2-3.6</td>
</tr>
<tr>
<td>HIPS</td>
<td>1050</td>
<td>100</td>
<td>NA</td>
<td>73-85</td>
<td>16-41</td>
<td>1.6-2.6</td>
<td>1.0-2.5</td>
</tr>
<tr>
<td>PVC-F</td>
<td>1180-1700</td>
<td>Vary</td>
<td>NA</td>
<td>VARY</td>
<td>5.5-26</td>
<td>0.005-0.01</td>
<td>150-450</td>
</tr>
<tr>
<td>PVC-R</td>
<td>1320-1580</td>
<td>81</td>
<td>NA</td>
<td>63-82</td>
<td>41-52</td>
<td>0.07-0.11</td>
<td>40-80</td>
</tr>
<tr>
<td>PMMA</td>
<td>1170-1190</td>
<td>85-105</td>
<td>NA</td>
<td>79-107</td>
<td>48-76</td>
<td>2.2-3.2</td>
<td>2-6</td>
</tr>
<tr>
<td>HI-PMMA</td>
<td>1110-1180</td>
<td>80-100</td>
<td>NA</td>
<td>82-102</td>
<td>55-76</td>
<td>2.4-3.1</td>
<td>2-40</td>
</tr>
</tbody>
</table>
Note: The symbols used in Tables 4 to 6 are:

- \( \rho \) – Density
- \( T_g \) – Glass Transition temperature
- \( T_m \) – Melting Point
- HDT – Heat deflection temperature at 66 psi
- \( \sigma \) – Tensile stress
- E – Tensile modulus
- \( \varepsilon_b \) – Maximum strain at break and
- NA – “Non Applicable”.
Table 5. Typical Properties of Engineering Resins

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\rho$ (kg/m³)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>HDT (°C)</th>
<th>$\sigma$ (MPa)</th>
<th>E (GPa)</th>
<th>$\varepsilon_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-6 (dry)</td>
<td>1130</td>
<td>75</td>
<td>219</td>
<td>&gt;160</td>
<td>80</td>
<td>3.0</td>
<td>50-100</td>
</tr>
<tr>
<td>PA-66 (dry)</td>
<td>1140</td>
<td>57</td>
<td>255</td>
<td>&gt;200</td>
<td>90</td>
<td>3.4</td>
<td>20</td>
</tr>
<tr>
<td>PETG</td>
<td>1270</td>
<td>81</td>
<td>NA</td>
<td>71</td>
<td>50</td>
<td>1.7</td>
<td>180</td>
</tr>
<tr>
<td>PBT</td>
<td>1400</td>
<td>80</td>
<td>245</td>
<td>167</td>
<td>172</td>
<td>4.3</td>
<td>30-300</td>
</tr>
<tr>
<td>PBT</td>
<td>1310</td>
<td>40</td>
<td>225</td>
<td>154</td>
<td>55</td>
<td>2.55</td>
<td>50-300</td>
</tr>
<tr>
<td>PBT+30GF</td>
<td>1520</td>
<td>40</td>
<td>225</td>
<td>221</td>
<td>124</td>
<td>9.65</td>
<td>2</td>
</tr>
<tr>
<td>PC</td>
<td>1200</td>
<td>149</td>
<td>NA</td>
<td>138</td>
<td>62</td>
<td>2.38</td>
<td>110</td>
</tr>
<tr>
<td>POM</td>
<td>1420</td>
<td>-30</td>
<td>175</td>
<td>172</td>
<td>69</td>
<td>3.1</td>
<td>25-75</td>
</tr>
<tr>
<td>POM+GF</td>
<td>1650</td>
<td>-30</td>
<td>165</td>
<td>166</td>
<td>110</td>
<td>8.28</td>
<td>3</td>
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<tr>
<td>PPE</td>
<td>1050-1100</td>
<td>100-150</td>
<td>NA</td>
<td>93-138</td>
<td>41-110</td>
<td>0.2-0.3</td>
<td>2-3</td>
</tr>
<tr>
<td>PPE+GF</td>
<td>1270</td>
<td>165</td>
<td>NA</td>
<td>158</td>
<td>117</td>
<td>8</td>
<td>3-5</td>
</tr>
</tbody>
</table>
Table 6. Typical Properties of Specialty Resins

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

<table>
<thead>
<tr>
<th>No.</th>
<th>Resin Type</th>
<th>Market Share (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Low density polyethylene, LDPE + LLDPE</td>
<td>20</td>
</tr>
<tr>
<td>2.</td>
<td>High density polyethylene, HDPE</td>
<td>12</td>
</tr>
<tr>
<td>3.</td>
<td>Polypropylene, PP</td>
<td>12</td>
</tr>
<tr>
<td>4.</td>
<td>Polystyrene homopolymers and copolymers, PS + ABS</td>
<td>10</td>
</tr>
<tr>
<td>5.</td>
<td>Poly (vinylchloride), PVC</td>
<td>17</td>
</tr>
<tr>
<td>6.</td>
<td>Other thermoplastics, TP</td>
<td>13</td>
</tr>
<tr>
<td>7.</td>
<td>Thermosets, TS</td>
<td>16</td>
</tr>
<tr>
<td>No.</td>
<td>Category</td>
<td>Polymers</td>
</tr>
<tr>
<td>-----</td>
<td>-----------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>Commodity</td>
<td>PE, PP, PS, PVC, PMMA</td>
</tr>
<tr>
<td>2.</td>
<td>Engineering</td>
<td>PA, PEST, PC, POM, PPE</td>
</tr>
<tr>
<td>3.</td>
<td>Speciality</td>
<td>PPS, PSF, PEI, PAI, PEEK, LCP</td>
</tr>
</tbody>
</table>
### Table 7. Competing Engineering and Speciality Resins

<table>
<thead>
<tr>
<th>No.</th>
<th>Newer Resin</th>
<th>Older Materials</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PAr</td>
<td>PC, PSF, PET/PBT</td>
<td>Appliances, transportation, electrical &amp; electronic, industrial</td>
</tr>
<tr>
<td>2.</td>
<td>PES</td>
<td>PSF, PAI, PPS</td>
<td>Medical, transportation, electrical &amp; electronic</td>
</tr>
<tr>
<td>3.</td>
<td>SMA</td>
<td>ABS, PPE / HIPS</td>
<td>Appliances, transportation, business machines</td>
</tr>
<tr>
<td>4.</td>
<td>PEC</td>
<td>PAr, PC</td>
<td>Appliances, transportation, electrical, industrial, aircraft</td>
</tr>
<tr>
<td>5.</td>
<td>PI</td>
<td>PAI, thermoset PI</td>
<td>Industrial, machinery</td>
</tr>
<tr>
<td>6.</td>
<td>PAI</td>
<td>PI, PPS</td>
<td>Transportation, machinery, industrial</td>
</tr>
<tr>
<td>7.</td>
<td>PE, PEST- elastomers</td>
<td>Elastomers, PU</td>
<td>Electrical, chemical, medical</td>
</tr>
<tr>
<td>8.</td>
<td>PEEK</td>
<td>PSF, PI, PPE/HIPS</td>
<td>Aerospace, automatic, electrical, appliances</td>
</tr>
<tr>
<td>9.</td>
<td>PEI</td>
<td>PC, ABS, PPE/HIPS</td>
<td>Aerospace, automotive, electrical appliances</td>
</tr>
<tr>
<td>10.</td>
<td>PEBA</td>
<td>PC, ABS, PPE/HIPS, PEST</td>
<td>Automotive, electrical, business machines, recreational</td>
</tr>
<tr>
<td>11.</td>
<td>PISU</td>
<td>PC, PSF, PPE/HIPS, PI</td>
<td>Transport, electrical&amp; electronic, Industrial</td>
</tr>
<tr>
<td>12.</td>
<td>PAE</td>
<td>PSF</td>
<td>Structural, aerospace, electrical</td>
</tr>
<tr>
<td>13.</td>
<td>LCP</td>
<td>PPS, thermosets</td>
<td>Automotive, outdoor, electrical &amp; electronic, oil fields</td>
</tr>
<tr>
<td>No.</td>
<td>Newer Resin</td>
<td>Older Materials</td>
<td>Applications</td>
</tr>
<tr>
<td>-----</td>
<td>-------------</td>
<td>----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>14.</td>
<td>PC/LCP</td>
<td>PC/ABS</td>
<td>Economic replacement as thin wall housing for portable telecommunication devices</td>
</tr>
<tr>
<td>15.</td>
<td>PPE/PA</td>
<td>PVC-R</td>
<td>Extruded, power-coated window profiles</td>
</tr>
<tr>
<td>16.</td>
<td>PEI/PPS</td>
<td>LCP</td>
<td>Electronic components for surface mounting</td>
</tr>
<tr>
<td>17.</td>
<td>PA -11</td>
<td>PE</td>
<td>Gas piping applications with excellent quality of connectors and joints</td>
</tr>
<tr>
<td>18.</td>
<td>PPS/Fluoro polymer</td>
<td>PA-46</td>
<td>Injection molded parts for automotive pumps, and electronic office machines</td>
</tr>
<tr>
<td>19.</td>
<td>PA/PPE</td>
<td>PBT/PC or PBT/PET</td>
<td>Automotive exterior parts, electrical equipment and plug &amp; socket connectors</td>
</tr>
<tr>
<td>20.</td>
<td>PET/PE</td>
<td>PET</td>
<td>Hot fill or reusable bottles</td>
</tr>
<tr>
<td>21.</td>
<td>PC/SMA</td>
<td>POM</td>
<td>Scuff plates, camera components, automotive</td>
</tr>
<tr>
<td>22.</td>
<td>SMA/ABS</td>
<td>ABS, PC, PPE/HIPS</td>
<td>Automotive consoles, door trim, instrument panels cowl vents, wheel covers</td>
</tr>
<tr>
<td>23.</td>
<td>PPS/PPS</td>
<td>PPE/HIPS</td>
<td>Electrical &amp; electronic and mechanical parts</td>
</tr>
<tr>
<td>24.</td>
<td>PBT/ABS</td>
<td>PC/ABS; PO/PBT</td>
<td>Automotive instrument panels, cowl vent grill appliances (air conditioner grills, consoles, boxes), electrical &amp; electronic housings, frames parts</td>
</tr>
<tr>
<td>25.</td>
<td>PEI/PC</td>
<td>PSF</td>
<td>Microwave-able cookware, electrical connectors, raceways, headlamps</td>
</tr>
</tbody>
</table>
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 $T_g$ 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 intermolecular 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 up to 200°C.
### Classification of Thermoplastic Polymers

<table>
<thead>
<tr>
<th>Commodity</th>
<th>Volume</th>
<th>Price</th>
<th>Thermal Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET (Unfilled)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polypropylene (vinylchloride)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly (amide-imide)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly (ether ether ketone)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly (etherimide)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly (ether sulfone)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyimide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polysulfone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoro Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modified PPO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly (phenyl en esulfide)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Themoplastics

i) Low Density

ii) Low energy requirement for manufacture

iii) Low product processing cost

\[
\text{H} \quad \text{H}
\]
\[
\text{---(---C-------C--)-----}
\]
\[
\text{H} \quad \text{H}
\]

Polyethylene

\[
\text{H} \quad \text{H}
\]
\[
\text{---(---C-------C--)-----}
\]
\[
\text{H} \quad \text{H}
\]

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.
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
\[ \Delta G = - SdT + VdP \]
\[ \frac{\delta G}{\delta T} = - S \]
\[ \frac{\delta G}{\delta P} = V \]

- \( \frac{\delta^2 G}{\delta T^2} \big|_P = \frac{\delta S}{\delta T} \);
- \( \frac{\delta^2 G}{\delta P^2} \big|_P = \frac{\delta V}{\delta P} \big|_T \)

and \( \left[ \frac{\delta}{\delta T} \left( \frac{\delta G}{\delta T} \right) \big|_T \right] \big|_P = \left( \frac{\delta V}{\delta T} \right) \big|_P \)

\( C_P = T \left( \frac{\delta H}{\delta T} \right) \big|_P \)
\( C_P = T \left( \frac{\delta S}{\delta T} \right) \big|_P \)

i.e. **Second Order Transition** → Discontinuity in Specific Heat

\( \beta = \left( \frac{1}{V} \right) \left( \frac{\Delta v}{\delta P} \right) \big|_T \)

Compressibility coefficient

\( \alpha = \left( \frac{1}{V} \right) \left( \frac{\delta V}{\delta T} \right) \big|_P \)

Thermal expansion coefficient
Characteristics of Glass Transition Temperature ($T_g$)

1. Pendent groups pose restrictions on the Torsion about $\sigma$ 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)

$$T_g = \frac{2 \delta^2}{mR} + C_1$$

$m$ ---- 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.
\[ \frac{T_g}{T_m} = \frac{1}{2} \quad \text{(Symmetrical Polymers)} \]
\[ \frac{T_g}{T_m} = \frac{2}{3} \quad \text{(Asymmetrical Polymers)} \]
\[ \approx 0.5 - 0.8 \]

3. \[ T_g = \frac{C_5 - C_0}{M} \quad \text{(Fox, 1956)} \]

4. \[ T_g \] increases with increasing cross link density
   \[ T_g \approx \frac{C_9 + C_{10}}{M_c} \]
   \[ T_g \approx \frac{C_4 - C_5}{M} + \frac{C_9}{M_c} \]

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

\[ \frac{1}{T_g} = \frac{W_1}{T_g} + \frac{W_2}{T_{g2}} \]

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:

$\left(\frac{dT_g}{dP}\right) = \frac{\Delta\beta}{\Delta\alpha}$

Where $\Delta\beta$ and $\Delta\alpha$ are respectively the changes in compressibility and volume expansion coefficients associated with glass transition.

$\approx 0.2 - 0.8 \text{ KM Pa}^{-1}$

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.
$V_\infty$ = 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°C of T_g, 2nd order transition, 
conformational entropy is zero.

IV. Free Volume Theories
\[ V_{fg} = V_{spg} - V_0 \]
\( V_0 \) is the volume occupied by molecule 
\( V_{fg} \) and \( V_{spg} \) are free and specific volumes 
\[ V_{spg} = V_0 + V_{fg} \]
\( f_g = V_{fg} / V_{spg} = 0.025 \pm 0.003 \)
\( f_g = 0.025 \pm \alpha_s (T - T_g) \)
\( \alpha_s \) – 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 $T_g$

$$T_g = T_{g\infty} - \frac{k}{M}$$
$$\frac{1}{T_g} = \frac{1}{T_{g\infty}} + \frac{k'}{M}$$

$k$ 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 $T_f - T_g$.

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

PIB ; $M \approx 1000$

PS ; $M \approx 40,000$
VI. Effect of Molecular Flexibility and Geometry

i) Polymers with low hindrance potentials to internal rotation show very low $T_g$.
PE – $T_g = -120^0\text{C}$
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 ; $T_g = -18^0\text{C}$  PS; $T_g = 100^0\text{C}$

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

iv) Molecular Symmetry tends to lower $T_g$
PVC; $T_g = 87^0\text{C}$  PVDF; $T_g = -10^0\text{C}$
PP; $T_g = -18^0\text{C}$  PIB = -65 $^0\text{C}$
VII. Intermolecular Forces

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

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

Polyacrylic Acid $T_g > 100^0C$

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

\[ T_m^0 - \frac{(\Delta H_m)_p}{(\Delta S_m)_p} \]

\( \Delta H_m \) and \( \Delta S_m \), 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 \( T_m^0 \).

\[ \left( \frac{1}{T_m} \right) \left( \frac{1}{T_m^0} \right) = \frac{R}{\Delta H_m} \left( \frac{1}{XW_a} + \frac{1}{X-Z} +1 \right) \]

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

\( \Delta H_m \) 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.
\( T_m \propto \frac{1}{d} \)

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

\( T_m \propto T_X \)

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 $\Delta S_m$. 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 $\Delta H_m$, hence they have high $T_m$.

3) The rigid (stiffer) and less mobile chains randomize less upon heating and therefore have a low $\Delta S_m$ 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.
Stereo Isomerism (Tacticity) in Thermoplastics

1) Atactic: The pendent CH\(_3\) randomly arranged on either side of the main carbon chain.
2) Isotactic: CH\(_3\) on the same side of the main chain.
3) Syndiotactic: CH\(_3\) alternates regularity on either side of the main chain.

Isomers: The substituent groups on the carbon atoms linked by double bonds can in reality be on the same side of the chain. This is the CIS isomer. Alternatively, they may be on opposite sides. This is the Trans isomer.
Diene Polymers

1, 3 butadiene

1,4 poly (1,3 butadiene)

Trans 1-4
1,2- poly (1,3 butadiene)
Crystallisation in Polymers

1) Fringed Micelle Model
2) Folded Chain Model

Lamella → Super Molecular Structures → Spherulite

\[ T_g \]

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>-110</td>
</tr>
<tr>
<td>PP</td>
<td>-18</td>
</tr>
<tr>
<td>PVAC</td>
<td>29</td>
</tr>
<tr>
<td>PVC</td>
<td>80</td>
</tr>
<tr>
<td>PS</td>
<td>75 – 100</td>
</tr>
<tr>
<td>PMMA</td>
<td>72</td>
</tr>
</tbody>
</table>
Singh crystal of polymers Lamellae
Thickness ≈ 100 nm lateral dimensions ≈ several μm 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

<table>
<thead>
<tr>
<th>Crystalline Properties</th>
<th>Amorphous Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent chemical resistance</td>
<td>Dimensional stability and Warpage resistance</td>
</tr>
<tr>
<td>Sharp melting point</td>
<td>Maintenance of properties at elevated temperatures</td>
</tr>
<tr>
<td>Low viscosity</td>
<td>Clarity</td>
</tr>
<tr>
<td>Significant tensile flexural and heat distortion improvement with reinforcement</td>
<td>Generally good impact strength</td>
</tr>
<tr>
<td>Melting range</td>
<td>Melting range</td>
</tr>
<tr>
<td>Polymers</td>
<td>Polymers</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>ABS</td>
</tr>
<tr>
<td>Polyacetal</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>Polysulfure</td>
</tr>
<tr>
<td>Polybutylene terephthalate (PBT)</td>
<td>Polyarylate</td>
</tr>
</tbody>
</table>
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.
a) Repeat unit of dyadic polyamide and
b) Monoadic polyamide

\[
\begin{align*}
\text{Polyethylene} & : \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{Polypropylene} & : \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Property</th>
<th>PTFE</th>
<th>PTFE / 30% Glass Fibre</th>
<th>PCTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.1.2.2</td>
<td>2.22.2.35</td>
<td>2.1.2.15</td>
</tr>
<tr>
<td>Tensile strength / MNm(^{-2}) (yield)</td>
<td>19.20</td>
<td>16.20</td>
<td>24.25</td>
</tr>
<tr>
<td>Elongation –to-break %</td>
<td>250-400</td>
<td>250-300</td>
<td>125-175</td>
</tr>
<tr>
<td>Tensile modulus / GN m(^{-2})</td>
<td>0.27-0.6</td>
<td>1.6</td>
<td>1.3.2.0</td>
</tr>
<tr>
<td>Flexural modulus / GN (^{-2})</td>
<td>0.6</td>
<td>1.3.1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Continuous service Temperature / °C</td>
<td>288</td>
<td>288</td>
<td>199</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length R</th>
<th>Dissociation energy Kcal mol⁻¹</th>
<th>kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>1.32</td>
<td>35</td>
<td>146</td>
</tr>
<tr>
<td>Si-Si</td>
<td>2.35</td>
<td>42.5</td>
<td>178</td>
</tr>
<tr>
<td>S-S</td>
<td>1.92.1</td>
<td>64</td>
<td>268</td>
</tr>
<tr>
<td>C-N</td>
<td>1.47</td>
<td>73</td>
<td>305</td>
</tr>
<tr>
<td>C-Cl</td>
<td>1.77</td>
<td>81</td>
<td>339</td>
</tr>
<tr>
<td>C-C</td>
<td>1.54</td>
<td>83</td>
<td>347</td>
</tr>
<tr>
<td>C-O</td>
<td>1.46</td>
<td>86</td>
<td>359</td>
</tr>
<tr>
<td>N-H</td>
<td>1.01</td>
<td>93</td>
<td>389</td>
</tr>
<tr>
<td>C-H</td>
<td>1.10</td>
<td>99</td>
<td>414</td>
</tr>
<tr>
<td>C-F</td>
<td>1.32 1.39</td>
<td>103.123</td>
<td>431.514</td>
</tr>
<tr>
<td>O-H</td>
<td>0.96</td>
<td>111</td>
<td>464</td>
</tr>
<tr>
<td>C=C</td>
<td>1.34</td>
<td>146</td>
<td>610</td>
</tr>
<tr>
<td>C=O</td>
<td>1.21</td>
<td>179</td>
<td>748</td>
</tr>
<tr>
<td>C=N</td>
<td>1.15</td>
<td>213</td>
<td>890</td>
</tr>
</tbody>
</table>
CH$_3$ by replacing CH$_3$ groups by phenyl groups

\[
\text{Si} \quad \text{O} \quad T_g = -123^\circ C
\]
Figure 4. The repeat unit of poly (dimethylsiloxane) (PDMS)
<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Gravity (g/cm³)</th>
<th>Modulus (GN/m²)</th>
<th>Specific Modulus (MN/m/kg)</th>
<th>Strength (MN/m²)</th>
<th>Specific Strength (MN/m⁻¹/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>2.7</td>
<td>71</td>
<td>26</td>
<td>80</td>
<td>30</td>
</tr>
<tr>
<td>Brass (70Cu/30Zn)</td>
<td>8.5</td>
<td>100</td>
<td>12</td>
<td>550</td>
<td>65</td>
</tr>
<tr>
<td>Mild steel</td>
<td>7.86</td>
<td>210</td>
<td>27</td>
<td>460</td>
<td>59</td>
</tr>
<tr>
<td>Polyamide 66</td>
<td>1.41</td>
<td>3</td>
<td>2.6</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>1.24</td>
<td>2.3</td>
<td>1.9</td>
<td>60</td>
<td>48</td>
</tr>
<tr>
<td>Polyamide 66 /30% glass</td>
<td>1.38</td>
<td>8</td>
<td>5.8</td>
<td>160</td>
<td>116</td>
</tr>
<tr>
<td>Poly(phenylens sulphide) / glass</td>
<td>1.72</td>
<td>14.0</td>
<td>8.1</td>
<td>131</td>
<td>76</td>
</tr>
<tr>
<td>Poly(etherether ketone)</td>
<td>1.4</td>
<td>13.7</td>
<td>9.8</td>
<td>240</td>
<td>171</td>
</tr>
<tr>
<td>Liquid crystal polymer</td>
<td>1.38</td>
<td>12.9</td>
<td>9.3</td>
<td>230</td>
<td>164</td>
</tr>
</tbody>
</table>
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)
<table>
<thead>
<tr>
<th>Material</th>
<th>Energy (KJ / Kg⁻¹)</th>
<th>Energy (KJ / m³/10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottle glass</td>
<td>18</td>
<td>41</td>
</tr>
<tr>
<td>Low-density polyethylene</td>
<td>69</td>
<td>64</td>
</tr>
<tr>
<td>High-density polyethylene</td>
<td>70</td>
<td>67</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>73</td>
<td>68</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>53</td>
<td>69</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>80</td>
<td>84</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>130</td>
<td>100</td>
</tr>
<tr>
<td>Polypropylene / 30% glass fibre</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Polyester / 30% glass fibre</td>
<td>90</td>
<td>150</td>
</tr>
<tr>
<td>Phenoplast</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Steel</td>
<td>45</td>
<td>350</td>
</tr>
<tr>
<td>Aluminium</td>
<td>&gt;200</td>
<td>&gt;540</td>
</tr>
<tr>
<td>Brass</td>
<td>95</td>
<td>600</td>
</tr>
</tbody>
</table>
Cyclic units in Backbone….
3) Partially Aromatic Thermoplastic Polyesters and Polyacrylates

a) Repeat Units of Polyarylate

b) Aromatic Polyesters (UST 85-115°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

<table>
<thead>
<tr>
<th>Property</th>
<th>PET</th>
<th>PBT</th>
<th>‘Ardel’ Polyarylate</th>
<th>PBT /30% glass fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.34-1.39</td>
<td>1.31</td>
<td>1.21-1.26</td>
<td>1.71</td>
</tr>
<tr>
<td>Tensile strength/MNm(^{-2})</td>
<td>58-71</td>
<td>52</td>
<td>69</td>
<td>1.80</td>
</tr>
<tr>
<td>Elongation-to-break %</td>
<td>3-300</td>
<td>250</td>
<td>50-100</td>
<td>2</td>
</tr>
<tr>
<td>Tensile modulus/GN m(^{-2})</td>
<td>2.7-4.0</td>
<td>2.7</td>
<td>2.07-2.28</td>
<td>16.0</td>
</tr>
<tr>
<td>Flexural modulus/GN m(^{-2})</td>
<td>2.4-3.1</td>
<td>2.1</td>
<td>2.14-2.23</td>
<td>9.0</td>
</tr>
<tr>
<td>Heat deflection temperature at 1.82 MN m(^{-2})/(^{0})C</td>
<td>37-40</td>
<td>50-85</td>
<td>110-170</td>
<td>200</td>
</tr>
<tr>
<td>Continuous service temperature/(^{0})C</td>
<td>85-115</td>
<td>120</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>Property</td>
<td>PC</td>
<td>PPC</td>
<td>PC/40% glass fibre</td>
<td>PC/PBT/ modifier</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>------</td>
<td>------</td>
<td>--------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.2</td>
<td>-</td>
<td>1.52</td>
<td>1.22</td>
</tr>
<tr>
<td>Tensile strength/MNm$^{-2}$</td>
<td>70</td>
<td>70</td>
<td>120</td>
<td>.50</td>
</tr>
<tr>
<td>Elongation-to-break / %</td>
<td>100</td>
<td>80</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>Tensile modulus/GN m$^{-2}$</td>
<td>2.3</td>
<td>2.1</td>
<td>10.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Flexural modulus/GN m$^{-2}$</td>
<td>2.5</td>
<td>2.2</td>
<td>100</td>
<td>1.9</td>
</tr>
<tr>
<td>Heat deflection temperature at 1.82 MN m$^{-2}$/°C</td>
<td>135-140</td>
<td>163</td>
<td>150</td>
<td>95</td>
</tr>
<tr>
<td>Continuous service temperature/°C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
2. Polycarbonate and Polyphthalate Carbonate

\[
\begin{array}{c}
\text{CH}_3 \\
\text{C} \text{O} \text{C} \text{O} \\
\text{CH}_3
\end{array}
\]

Carbonate linkage

\[
\begin{array}{c}
\text{O} \\
\text{O} \text{C} \text{O} \text{C} \text{O} \\
\text{O}
\end{array}
\]

Ester linkage

\[
\begin{array}{c}
\text{C} \text{O} \text{O} \\
\text{CH}_3 \\
\text{C} \text{O} \text{C} \text{O} \\
\text{CH}_3
\end{array}
\]
<table>
<thead>
<tr>
<th>Property</th>
<th>Trogamid T</th>
<th>Grilamid TR55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.12</td>
<td>1.06</td>
</tr>
<tr>
<td>Tensile strength/MNm(^{-2})</td>
<td>68</td>
<td>75</td>
</tr>
<tr>
<td>Elongation-to-break / %</td>
<td>132</td>
<td>-</td>
</tr>
<tr>
<td>Tensile modulus/GN m(^{-2})</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>Heat deflection temperature at 1.82 MN m(^{-2})/(^{0})C</td>
<td>124</td>
<td>124</td>
</tr>
<tr>
<td>Continuous service temperature/(^{0})C</td>
<td>130</td>
<td>140</td>
</tr>
</tbody>
</table>
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; $T_g = 215^\circ C$

<table>
<thead>
<tr>
<th></th>
<th>PPS glass fibre</th>
<th>PPS mineral</th>
<th>PAS 2</th>
<th>PAS2 glass fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.57-1.72</td>
<td>1.9-2.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tensile strength/MNm$^{-2}$</td>
<td>110-131</td>
<td>72-96</td>
<td>96</td>
<td>117</td>
</tr>
<tr>
<td>Elongation-to-break / %</td>
<td>1.0-0.8</td>
<td>0.5-0.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tensile modulus/GN m$^{-2}$</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
<td>10.2</td>
</tr>
<tr>
<td>Flexural modulus/GN m$^{-2}$</td>
<td>9.6-14.0</td>
<td>14.0-17.0</td>
<td>3.4</td>
<td>9.6</td>
</tr>
<tr>
<td>Heat deflection temperature at 1.82 MN m$^{-2}/^\circ C$</td>
<td>240</td>
<td>-</td>
<td>198</td>
<td>200</td>
</tr>
<tr>
<td>Continuous service temperature/$^\circ C$</td>
<td>220-220</td>
<td>200-240</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 13. Property data for some of the polysulphones

<table>
<thead>
<tr>
<th></th>
<th>PSO</th>
<th>PES</th>
<th>PES/30% glass fibre</th>
<th>PES HTA</th>
<th>PSO/ABS Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.24</td>
<td>1.37</td>
<td>1.67</td>
<td>1.36</td>
<td>1.14</td>
</tr>
<tr>
<td>Tensile strength/MNm²</td>
<td>70</td>
<td>83</td>
<td>156</td>
<td>86</td>
<td>51</td>
</tr>
<tr>
<td>Elongation-to-break / %</td>
<td>50-100</td>
<td>30-80</td>
<td>3.0</td>
<td>19</td>
<td>3.7</td>
</tr>
<tr>
<td>Tensile modulus/GN m⁻²</td>
<td>2.48</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
</tr>
<tr>
<td>Flexural modulus/GN m⁻²</td>
<td>2.65</td>
<td>2.55</td>
<td>8.0</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Heat deflection temperature at 1.82 MN m⁻²/°C</td>
<td>174</td>
<td>202</td>
<td>216</td>
<td>234</td>
<td>150</td>
</tr>
<tr>
<td>Continuous service temperature/°C</td>
<td>160</td>
<td>180</td>
<td>180</td>
<td>200</td>
<td>125</td>
</tr>
</tbody>
</table>
Table 14. Property data for thermoplastic polyimides

<table>
<thead>
<tr>
<th></th>
<th>Polyimide</th>
<th>Polyimide glass fibre</th>
<th>Polyamide-imide</th>
<th>Polyetherimide</th>
<th>Polyetherimide/40% glass fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.4</td>
<td>1.9</td>
<td>1.4-1.45</td>
<td>1.27</td>
<td>1.51</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>118</td>
<td>186</td>
<td>83-110</td>
<td>105</td>
<td>186</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>-</td>
<td>-</td>
<td>4.9-6.7</td>
<td>3.0</td>
<td>11.7</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>3.3</td>
<td>16.5</td>
<td>4.58</td>
<td>3.3</td>
<td>11.7</td>
</tr>
<tr>
<td>Heat deflection</td>
<td>270-280</td>
<td>348</td>
<td>260</td>
<td>200</td>
<td>210</td>
</tr>
<tr>
<td>Continuous service</td>
<td>260</td>
<td>260</td>
<td>250</td>
<td>170</td>
<td>170</td>
</tr>
</tbody>
</table>
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:

<table>
<thead>
<tr>
<th>Component</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>Fatty Acid</td>
<td>1 – 4</td>
</tr>
<tr>
<td>Zine Oxide</td>
<td>2 – 10</td>
</tr>
<tr>
<td>Accelerator</td>
<td>0.5 – 2</td>
</tr>
</tbody>
</table>

(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.
The vulcanization is the chemical process by which unsaturated elastomer polymers are joined together by crosslinking using sulfur 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
(3) \[ \text{COOH} + \text{ZnO} \]

\[ \begin{array}{c}
\text{---CH}_2\text{---CH=CH---CH}_2\text{---CH}_2\text{---CH}----- \\
\text{---CH}_2\text{---CH=CH---CH}_2\text{---CH}_2\text{---CH}----- \\
\text{---CH}_2\text{---CH=CH---CH}_2\text{---CH}_2\text{---CH}----- \\
\end{array} \]

\[ \begin{array}{c}
\text{Zn} \\
\text{COO} \\
\text{COO} \\
\end{array} \]
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\quad & \quad & \quad & \\
\text{----Si----O----Si----O----Si----O----Si----O----} \\
\quad & \quad & \quad & \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\quad & \quad & \quad & \\
\text{CH}_3 & \quad \text{CH}_3 \\
\quad & \quad & \\
\text{----Si----O----Si----} \\
\quad & \quad & \\
\text{CH}_3 & \quad \text{CH}_3 \\
\quad & \quad & \\
\text{CH}_2 & \quad \text{CH}_3 \\
\quad & \quad & \\
\text{----Si----O----Si----O----} \\
\quad & \quad & \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
Elastomers or Rubbers

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

Thermosets or Elastomers

**Elastomers:**
Polymers that have limited or no crystallinity, have low glass transition temperature (-50 - -70°C) 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.

\[
\begin{align*}
\text{H} & \quad R \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{C} & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{R} & \\
\text{H}_2\text{C} & \quad = \quad \text{C} \quad \text{C} & \quad \text{CH} = \text{CH}_2
\end{align*}
\]

\[R = \text{H}\quad \text{PB}\]
\[= \text{Cl}\quad \text{PCP}\]
\[= \text{CH}_3\quad \text{PIP}\]

Polymerization \(\text{Single double bond in repeat unit}\rightarrow\text{site for subsequent crosslinking (Vulcanization)}\)
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 O₂, 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

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} \\
\text{C} & \quad \text{=} & \quad \text{C} & \quad \text{=} & \quad \text{C} \\
\text{H} & & \text{H} \\
\end{align*}
\]

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

2. Chloroprene or Neoprene

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} \\
\text{C} & \quad \text{=} & \quad \text{C} & \quad \text{=} & \quad \text{C} \\
\text{H} & & \text{H} \\
\end{align*}
\]

---- C ---- C = C ------ C ------
3. Butadiene

\[
\begin{align*}
&\text{H } \text{H } \text{H } \text{H } \text{H} \\
&\text{C } = \text{C } - \text{C } = \text{C} \\
&\text{H } \text{H} \\
&\text{---- C } \text{---- C } = \text{C } \text{---- C } \text{----}
\end{align*}
\]

4. Styrene butadiene

\[
\begin{align*}
&\text{H } \text{H } \text{H } \text{H } \text{H } \text{H } \text{H} \\
&\text{C } \text{---C } \text{---C } \text{--- C } = \text{C } \text{---C } \text{---} \\
&\text{H } \text{H } \text{H } \text{H } \text{n}
\end{align*}
\]
5. Nitrile Rubber

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} \\
\text{H} & \quad \text{CN} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

6. Silicon Rubber

\[
\begin{align*}
\text{X} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} \\
\text{X'} & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

(-100 -250°C)
<table>
<thead>
<tr>
<th>Common Name</th>
<th>Chemical Name</th>
<th>Tensile strength, psi</th>
<th>Percent Elongation</th>
<th>Resistance to Oil, Gas</th>
<th>Useful Temperature Range °F (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber</td>
<td>Cis-Polyisoprene</td>
<td>3,000</td>
<td>800</td>
<td>Poor</td>
<td>-60 to 180 (-51 to 82)</td>
</tr>
<tr>
<td>GR-S or Buna S</td>
<td>Butadiene styrene copolymer</td>
<td>250</td>
<td>3,000</td>
<td>Poor</td>
<td>(-60 to 180) (-51 to 82)</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Polyisoprene</td>
<td>3,000</td>
<td>400</td>
<td>Poor</td>
<td>(-60 to 180) (-51 to 82)</td>
</tr>
<tr>
<td>Nitrile or Buna N</td>
<td>Butadiene-acrylonitrile copolymer</td>
<td>700</td>
<td>400</td>
<td>Excellent</td>
<td>(-60 to 300) (-51 to 149)</td>
</tr>
<tr>
<td>Neoprene [GR-M]</td>
<td>Polychloroprene</td>
<td>3,500</td>
<td>800</td>
<td>Good</td>
<td>(-40 to 200) (-40 to 93)</td>
</tr>
<tr>
<td>Silicon</td>
<td>Polysiloxane</td>
<td>700</td>
<td>300</td>
<td>Poor</td>
<td>(-178 to 600) (-117 to 315)</td>
</tr>
<tr>
<td>Urethane</td>
<td>Diisocyanate polyester</td>
<td>5,000</td>
<td>600</td>
<td>Excellent</td>
<td>(-65 to 240) (-54 to 115)</td>
</tr>
</tbody>
</table>
Polydispersity

Number Average Molecular Weight
\[
\overline{M}_n = \frac{\sum N_i m_i}{\sum N_i}
\]

Weight Average Molecular Weight
\[
M_n = \frac{\sum W_i m_i}{\sum W_i}; W_i = N_i M_i
\]

\[
= \frac{\sum N_i M_i^2}{\sum N_i M_i}
\]

\[
\langle \rangle = K M_v^a
\]

For rigid molecular \(a = 2\)

\(\theta\) solvent, \(a = 0.5\), common \(a = 0.5 - 0.8\)
Viscosity Average Molecular Weight

$$\bar{M}_v = \left[ \frac{\sum N_i m_i^{1+a}}{\sum N_i m_i} \right]^{1/a}$$

a – measure of polymer – solution interaction

Polydispersity Index (PDI):
Measure of breadth of the molecular weight distribution and is given by:

$$\frac{\bar{M}_w}{\bar{M}_n}$$

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

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{-----C-----C} & = \text{C---C--} & \quad \text{-----C-----C} & = \text{C---C--} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

+ 2S →

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{-----C-----C} & = \text{C---C--} & \quad \text{-----C-----C} & = \text{C---C--} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]
Polymer Additives

1. Fillers: Wood Flour, SiO$_2$, glass, clay, tale, limestone, carbon black, ZnO.

2. Plasticizers: To improve flexibility, ductility and toughness ---- DOP; DEHP; DBP; DEP.


4. Flame retardants: Halides

5. Colorants
Contour Length – Full contour length \( (l_{\text{count}}) \) is obtained by multiplying the length of the segments \( (1) \) by number of segments \((N)\) i.e.
\[
l_{\text{count}} = N \cdot 1
\]

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 \( \theta \) 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.
\[
< L^2 > = N \cdot 1^2
\]

For a definite valence angle, which occur in real macromolecular chains.
\[
l_{\text{max}} = N \cdot 1 \sin (0.5 \theta)
\]
\( l_{\text{max}} \) = 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:

\[
<R_G^2>^{1/2} = \left[ \sum m_i R_i^2 / m_i \right]^{1/2}
\]

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.

\[
<L^2> = 6 <R_G^2>
\]
Text Books

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