CHAPTER 7
POLYMERIC IMPLANT MATERIALS
• Polymers (poly = many, mer = unit): primary covalent bonding in the main chain backbone with C, N, O, Si, etc.

• Polyethylene from ethylene (CH$_2$ = CH$_2$): -CH$_2$-(CH$_2$-CH$_2$)$_n$-CH$_2$-, n: number of repeating units.

• n >> 1,000 giant molecules.

• Other backbone chain elements polymer: polydimethyl siloxane -Si(CH$_3$)$_2$[O-Si(CH$_3$)$_2$]$_n$O-
7.1 Polymerization And Properties

7.1.1 Polymerization

a. Condensation or Step Reaction Polymerization

• During condensation polymerization, small molecule such as water condensed out by chemical reaction:

• \( R\text{-NH}_2 + R'\text{COOH} \Rightarrow R'\text{CONHR} + H_2O \) (7-1)

(amine) (carboxylic acid) (amide) (condensation molecule)
<table>
<thead>
<tr>
<th>Type</th>
<th>Interunit Linkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>-C-O-</td>
</tr>
<tr>
<td>Polyamide</td>
<td>O H</td>
</tr>
<tr>
<td></td>
<td>-C-N-</td>
</tr>
<tr>
<td>Polyurea</td>
<td>H O H</td>
</tr>
<tr>
<td></td>
<td>-N-C-N-</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>O H</td>
</tr>
<tr>
<td></td>
<td>-O-C-N-</td>
</tr>
<tr>
<td>Polysiloxane</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>-Si-O-</td>
</tr>
<tr>
<td></td>
<td>R</td>
</tr>
<tr>
<td>Protein</td>
<td>O H</td>
</tr>
<tr>
<td></td>
<td>-C-N-</td>
</tr>
<tr>
<td>Cellulose</td>
<td>-C-O-C-</td>
</tr>
</tbody>
</table>

TABLE 7-1 TYPICAL CONDENSATION POLYMERS
• **Drawback of condensation polymerization:** short chain lengths by decreased chain mobility.

• **All natural polymers**, made by condensation polymerization.

  – Condensing molecule is always water (H$_2$O).
b. Addition or Free Radical Polymerization

• Addition polymerization: rearranging bonds within each monomer.
• Each 'mer' share at least two covalent electrons
• At least one double bond. Ex: ethylene:

\[
\begin{align*}
\text{H H} & \quad \text{H H H H} \\
\text{n C=C} & \Rightarrow -\text{C-(C-C)}_n\text{-C-} \\
\text{H H} & \quad \text{H H H H}
\end{align*}
\]  

(7-2)
Initiator: Free radical, benzoyl peroxide:

\[ \text{C}_6\text{H}_5\text{COO-OOC}\text{C}_6\text{H}_5 \rightarrow 2\text{C}_6\text{H}_5\text{COO}^{-} \rightarrow 2\text{C}_6\text{H}_5^{-} + 2\text{CO}_2 \]  

(7-3)

(R·)

UV light, heat, other chemicals
• Free radicals (initiators) can react with monomers:

\[
\begin{align*}
R^\cdot + \text{CH}_2=\text{CHX} & \quad \square \quad \text{RCH}_2^\cdot, \\
\text{X} & \\
\end{align*}
\]

(7-4)

• and this free radical can react with another monomer:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{RCH}_2^\cdot + \text{CH}_2=\text{CHX} & \quad \square \quad \text{RCH}_2^\cdot\text{CHX}^\cdot\text{CH}_2-\text{C}^\cdot, \\
\text{X} & \quad \text{X} \\
\end{align*}
\]

(7-5)
• **propagation:**

\[
R' + M \rightarrow RM' \quad \text{M: monomer}
\]

\[
RM' + M \rightarrow RMM'.
\]

(7-6)

• **Terminated:** combining two free radicals, transfer or disproportionate processes,

\[
RM_nM' + R' (or RM') \rightarrow RM_{n+1}R (or RM_{n+2}R)
\]

(7-7)

\[
RM_nM' + RH \rightarrow RM_{n+1}H + R'.
\]

(7-8)

\[
RM_nM' + \cdot MM_nR \rightarrow RM_{n+1} + M_{n+1}R
\]

(7-9)
• An example of the disproportionate termination is given below.

\[
\begin{array}{cccc}
H & H & H & H \\
-\text{CH}_2\text{C}· & + & \cdot\text{C-CH}_2- & \text{[]-CH}_2\text{CH+} & \text{C=CH-} \\
X & X & X & X & X
\end{array}
\]

• Some of the commercially important monomers for addition polymers [Table 7-2].
- **Three more types of initiating species** beside free-radicals; cations, anions & coordination (stereospecific) catalysts.

**TABLE 7-2  MONOMERS FOR ADDITION POLYMERIZATION AND SUITABLE PROCESSES**

<table>
<thead>
<tr>
<th>Monomer Name</th>
<th>Chemical Formula</th>
<th>Polymerization Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Radical</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>CH$_2$=CH-CN</td>
<td>+</td>
</tr>
<tr>
<td>Ethylene</td>
<td>CH$_2$=CH$_2$</td>
<td>+</td>
</tr>
<tr>
<td>Methacrylate</td>
<td>CH$_2$=CH-COOCH$_3$</td>
<td>+</td>
</tr>
<tr>
<td>Methylmethacrylate</td>
<td>CH$_2$=CCH$_3$ COOCH$_3$</td>
<td>+</td>
</tr>
<tr>
<td>Propylene</td>
<td>CH$_2$=CHCH$_3$</td>
<td>-</td>
</tr>
<tr>
<td>Styrene</td>
<td>CH$_2$=CH-C$_6$H$_5$</td>
<td>+</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>CH$_2$=CHCl</td>
<td>+</td>
</tr>
<tr>
<td>Vinylidene chloride</td>
<td>CH$_2$=CCl$_2$</td>
<td>+</td>
</tr>
</tbody>
</table>

*: high polymer formed.  -: no reaction or oligomers only.
Example 7-1.

Polyethylene has a rhombohedral structure as shown. Calculate its theoretical density.

Answer

From the figure one can see that each unit cell has 2 mers of \(-(C_2H_4)_-\), therefore,

\[
\rho = \frac{2 \text{ mers} \times (28 \text{ g/6} \times 10^{23} \text{mers})}{7.4 \times 4.93 \times 2.53 \times (10^{-8})^3} = 1.01 \text{ g/cm}^3
\]

Figure of the unit cell structure of polyethylene crystal.
7.2. Effect of Structural Modification & Temp on Properties

7.2.1 Effect of Molecular Weight & Composition

- M.W. & its distribution effect on properties due to immobilization or entanglement of the chains. [Fig 7-1].
- Equal in length since if there are short chains they will act as plasticizers.
- Plasticizers: lower T_m, T_g, r, etc.
Figure 7-1. Approximate relations among molecular weight, $T_g$, $T_m$, and polymer properties.
• **Chemical composition**

• Substituting backbone C of a polyethylene with divalent O or S decrease $T_m$, $T_g$ since chain becomes more flexible due to increased rotational freedom.

\[
\begin{array}{ccccccc}
\text{H}_2 & \text{H}_2 & \text{H}_2 & \text{H}_2 & \text{O} & \text{C} & \text{C} & \text{C} & \text{C} & \text{O} & \text{C} \\
\text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{H}_2 & \text{H}_2 & \text{H}_2 & (7-10) \\
\text{H}_2 & \text{H}_2 & \text{H}_2 & \text{H}_2 & \text{S} & \text{C} & \text{C} & \text{C} & \text{C} & \text{S} & \text{C} \\
\text{H}_2 & \text{H}_2 & \text{H}_2 & \text{H}_2 & \text{H}_2 & \text{H}_2 & \text{H}_2
\end{array}
\]
backbone chains can be made more rigid then a stiffer polymer will result as in the case of polyester.

Chemical structure of polyethylene terephthalate (polyester, Dacron®)
7.2.2 Effect of Side Chain Substitution, Cross-Linking, & Branching

- Increasing size of side groups in linear polymers such as polyethylene decrease $T_m$ due to the lesser perfection of molecular packing, i.e. decreased crystallinity [Table 7-3]. Very long side groups can be thought of as being branches.

**TABLE 7-3** EFFECT OF SIDE CHAIN SUBSTITUTION ON MELTING TEMPERATURE IN POLYETHYLENE

<table>
<thead>
<tr>
<th>Side Chain</th>
<th>$T_m (^\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-H</td>
<td>140</td>
</tr>
<tr>
<td>-CH$_3$</td>
<td>165</td>
</tr>
<tr>
<td>-CH$_2$CH$_3$</td>
<td>124</td>
</tr>
<tr>
<td>-CH$_2$CH$_2$CH$_3$</td>
<td>75</td>
</tr>
<tr>
<td>-CH$_2$CH$_2$CH$_2$CH$_3$</td>
<td>-55</td>
</tr>
<tr>
<td>-CH$_2$CH CH$_2$CH$_3$ CH$_3$</td>
<td>196</td>
</tr>
<tr>
<td>-CH$_2$-C-CH$_2$CH$_3$ CH$_3$</td>
<td>350</td>
</tr>
</tbody>
</table>
• Cross-linking of main chains (Fig 2-12) similar to side-chain substitution with a small molecule, decrease $T_m$. Due to interference of cross-linking; lesser mobility of chains; retardation of crystallization rate. Opposite is true with a rubber.
7.2.3 Effect of Temp on Properties

- **Amorphous polymers**: substantial change in their properties as a function of temp.
- **Glass transition temp.** \( T_g \) demarcation between glassy region (stiff) & rubbery region (compliant).
- **\( T_g \)**: temp. at which slope of volume change vs temp. has a discontinuity in slope.
- **Alternative definition of \( T_g \)**: temp of the peak in viscoelastic loss tangent [Fig 7-2].
- Hard polymers, such as PMMA, \( T_g > \) room temp.
- Rubbery materials: \( T_g < \) room temp.
- **Cross-links**: serve function of maintaining solidity of polymer when it is subjected to prolonged load (creep).
- Un-cross-linked polymer continued mobility of chains \( \Rightarrow \) decrease of stiffness at low frequency corresponding to flow or creep at long times, **Fig 7-2**.
Figure 7-2. Glass transition temperature obtained from the peak in the loss tangent curve at a given frequency. The stiffness undergoes an abrupt change at the glass transition temperature. An un-cross-linked polymer exhibits continued mobility of chains resulting in a decrease of stiffness at low frequency corresponding to flow or creep at long times.
7.3.1 Polyamides (nylons)

- polymerized by step-reaction (or condensation) & ring-scission polymerization.
- Excellent fiber-forming ability due to interchain H-bonding & a high degree of crystallinity
- Basic chemical structure of repeating unit; two ways,

\[-[\text{NH(CH}_2\text{)}_x\text{NHCO(CH}_2\text{)}_y\text{CO}]_n-\] (7-12)
\[-[\text{NH(CH}_2\text{)}_x\text{CO}]_n-\] (7-13)
• Diamine & diacids such as type 66(x=6, y=4) & 610(x=6, y=8).
• Polyamides made from \[\square\]-acids (caprolactums, Eq (7-13) designated as nylon 6 (x=5), 11 (x=10), & 12 (x=11).
• **Ring-scission polymerization,**

\[
\begin{align*}
\text{NH} & \cdots \text{C}=\text{O} \\
\text{CH}_2 & \quad \text{CH}_2 & \text{Heat} \\
n \text{CH}_2 & \quad \text{CH}_2 & \square & \quad -[\text{NHCO(CH}_2)_5]_n- \\
\text{CH}_2 & \\
(\square\text{-caprolactam}) & \quad (\text{nylon 6})
\end{align*}
\]
-CONH- H-bonding [Fig 7-3]; major role in determining properties. $T_g$ decreased by decreasing number of CONH groups [Table 7-4].

Figure 7-3. Hydrogen bonding in polyamide chains (nylon 6).
• **Aromatic polyamides (aramids):** poly (p-phenylene terephthalate) commonly known as Kevlar®, made by DuPont.
– Readily made into fibers. Specific strength is five times that of steel, suitable for composites.

– Nyons are hygroscopic & lose strength *in vivo*. Water molecules serve as *plasticizers* which attack the amorphous region. *Proteolytic enzymes* hydrolyze by attacking amide group.

**TABLE 7-4 PROPERTIES OF POLYAMIDES**

<table>
<thead>
<tr>
<th>TYPE</th>
<th>( \text{PROPERTIES} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 66 )</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.14</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>76</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>90</td>
</tr>
<tr>
<td>Modulus of Elasticity (GPa)</td>
<td>2.8</td>
</tr>
<tr>
<td>Softening Temperature (°C)</td>
<td>265</td>
</tr>
</tbody>
</table>

*a*: Molded parts, unfilled.

*b*: Kevlar\(^\text{®}\) 49 (duPont) fibers.
7.3.2 Polyethylene

- Polyethylene & polypropylene & their copolymers are called polyolefins.
- Linear thermoplastics.
- Three major grades: low & high density & ultra high molecular weight (UHMWPE).
- Repeating unit structure:

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

(7-16)
– Readily crystallized, because of small H side groups => high mobility of chains.

– First polyethylene was synthesized by reacting ethylene gas at high pressure (100-300 MPa) & a catalyst (peroxide) to initiate polymerization. **Low** density PE. Using **Ziegler catalyst (stereospecific)** at low pressure (10 MPa); **high density PE**, .

– HDPE has no branches better packing of chains increases density & crystallinity.

– **Crystallinity**: 50-70%, LDPE & 70-80% for HDPE

Some important physical properties of polyethylenes, **Table 7-5**.
- **UHMWPE** (m.w. > 2x10^6 g/mol) used in orthopedic implant
- New UHMWPE has been introduced by duPont with DePuy. Longer chain folds length than conventional UHMWPE, increasing crystallinity.
- Folded chains are crystalline => amount of amorphous region is reduced => reducing possibility of environmental attack (usually oxidation).
- Enhanced mechanical properties (higher hardness, modulus of elasticity, tensile yield strength). Creep properties are superior (that is, less creep). Coefficient of friction & wear; improved marginally.
- UHMWPE; no known solvent at room temp; only high temp & pressure sintering to produce desired products. Conventional extrusion or molding processes are difficult to use.
- UHMWPE precoated with PMMA by dissolving in xylene at high temp first then soaked in PMMA.
- Polyethylene, solid or porous form. Biocompatibility tests for nonporous (F981) & porous polyethylene (F639 & 755), ASTM standards.

**TABLE 7-5 PROPERTIES OF POLYETHYLENE**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Low Density</th>
<th>High Density</th>
<th>UHMWPE&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Enhanced UHMWPE&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>3~4x10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>5x10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>2x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>same</td>
</tr>
<tr>
<td>Density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>0.90-0.92</td>
<td>0.92-0.96</td>
<td>0.93-0.94</td>
<td>same</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>7.6</td>
<td>23-40</td>
<td>27 min.</td>
<td>higher</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>150</td>
<td>400-500</td>
<td>200-250</td>
<td>same</td>
</tr>
<tr>
<td>Modulus of Elasticity (MPa)</td>
<td>96-260</td>
<td>410-1,240</td>
<td>c</td>
<td>2,200</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>50-70</td>
<td>70-80 d</td>
<td>d e</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>: Data from ASTM F 648, also 2% deformation after 90 minutes recovery subjected to 7 MPa for 24 hours (D621).
<sup>b</sup>: Same as the conventional UHMWPE (ASTM F648) Data from "A new enhanced UHMWPE for orthopaedic applications: A technical brief," DePuy, Warsaw, IN, 1989.
<sup>c</sup>: Close to 2,200 Mpa. <sup>d</sup>: Higher than high density polyethylene <sup>e</sup>: Equal or slightly higher than d.
7.3.3 Polypropylene

- Synthesized by using a Ziegler catalyst.

\[
\begin{align*}
\text{H CH}_3 \\
-(\text{C-C})_n- \\
\text{H H}
\end{align*}
\]

\( (7-17) \)

- Three types of structure can exist, depending on position of methyl \((\text{CH}_3)\) group.
- **Atactic**: amorphous polypropylene,
- **Isotactic & syndiotactic**: usually crystallize rarely exceeds 50-70% for material with isotacticity over 95%.
- Exceptionally high flex life; integrally molded hinges for finger joint prostheses.
- Excellent environmental stress-cracking resistance.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>0.90-0.91</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>28-36</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>400-900</td>
</tr>
<tr>
<td>Modulus of Elasticity (GPa)</td>
<td>1.1-1.55</td>
</tr>
<tr>
<td>Softening Temperature (°C)</td>
<td>150</td>
</tr>
</tbody>
</table>
Example 7-2.

Calculate the percent crystallinity of UHMWPE assuming the non-crystalline and 100% crystalline polyethylene have densities of 0.85 and 1.01 g/cm³ respectively.

Answer

From Table 7-5, the density of UHMWPE is 0.93~0.94, therefore,

\[
\%\text{Crystallinity} = \frac{0.94}{1.01} \times \frac{0.85}{0.85} = 0.56(56\%).
\]

This value is lower than that of the low and high density polyethylene as given in Table 7-5. The tabulated crystallinities were based on x-ray diffraction measurement technique instead of the density method.
7.3.4 Polyacrylates

a. Structure & Properties of Acrylics & Hydrogels

– Basic chemical structure of repeating units of acrylcs,

\[ \mathbf{R_1} \]

\[-(\mathbf{CH_2-C-})_n \quad (7-18)\]

\[ \mathbf{COOR_2} \]
<table>
<thead>
<tr>
<th>Polymer</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Tensile Strength (MPa)</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymethyl acrylate (PMA):</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>7</td>
<td>33</td>
</tr>
<tr>
<td>Polymethyl methacrylate (PMMA)</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>60</td>
<td>125</td>
</tr>
</tbody>
</table>
– Clear amorphous state.
– Excellent light transparency (92% transmission), high index of refraction (1.49), & excellent weathering properties.
– Can be cast, molded, or machined with conventional tools.
– Excellent chemical resistivity & highly biocompatible in pure form.
– Hard & brittle in comparison with other polymers.
– First hydrogel polymer developed is the poly(hydroxyethyl methacrylate) or polyHEMA, Absorb water > 30% of its weight. Useful for soft lens.

\[
\begin{align*}
\text{CH}_3 \\
-(\text{CH}_2\text{-C-})_n \\
\text{COOCH}_2\text{CH}_2\text{OH}
\end{align*}
\]
– OH group; **hydrophilic** group responsible for hydration of the polymer.

– Hydrogels made by polymerization of certain hydrophilic monomers with small amounts of cross-linking agent, ethylene glycol dimethacrylate (EGDM),

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2=\text{C-COOCH}_2 \\
\text{CH}_2=\text{C-COOCH}_2 \\
\text{CH}_3
\end{align*}
\]

(7-20)
Polyacrylamide hydrogel developed in the U.S.,

\[
\text{H} \quad \text{CH}_2=\text{CCONH}_2 \quad (7-21)
\]

- Water content of the copolymer to over 60%, normal water content for polyHEMA is 40%.
- Hydrogels have a relatively low oxygen permeability in comparison with silicone rubber (see Table 7-7).
- Silicone rubber is not a hydrophilic material but its high oxygen permeability and transparency makes it an attractive lens material. It is usually used after coating with hydrophilic hydrogels by grafting.
<table>
<thead>
<tr>
<th>Polymers</th>
<th>$P_g \times 10^4$ (ml cm/cm$^2$h kPa)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methylmethacrylate)</td>
<td>0.27</td>
<td>hard contact lens</td>
</tr>
<tr>
<td>Poly(dimethylsiloxane)</td>
<td>1750</td>
<td>flexible</td>
</tr>
<tr>
<td>Poly(hydroxyethylmethacrylate)</td>
<td>24</td>
<td>39% H$_2$O, soft contact lens</td>
</tr>
</tbody>
</table>

at STP to convert ml cm/cm$^2$h kPa to ml cm/cm$^2$h mmHg divide by 7.5.
b. Bone Cement (PMMA)

- Poly (methylmethacrylate) powder & monomer methylmethacrylate liquid [Table 7-8].
- Hydroquinone: prevent premature polymerization
- N, N-dimethyl-p-toluidine: promote or accelerate (cold) curing finished compound.
- **Cold curing** to distinguish it from high temp. & pressure (hot) molding technique.
- Liquid monomer; sterilized by membrane filtration.
- Solid component; finely ground white powder (mixture of polymethyl methacrylate, methyl methacrylate-stryrene-copolymer, barium sulfate, & benzoyl peroxide).
Table 7-8  COMPOSITION OF BONE CEMENT*

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid component (20 ml)</strong></td>
<td></td>
</tr>
<tr>
<td>Methyl methacrylate (monomer)</td>
<td>97.4 v/o (volume %)</td>
</tr>
<tr>
<td>N, N, -dimethyl-p-toluidine</td>
<td>2.6 v/o</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>75 ± 15 ppm</td>
</tr>
<tr>
<td><strong>Solid powder component (40g)</strong></td>
<td></td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>15.0 w/o (weight %)</td>
</tr>
<tr>
<td>Methyl methacrylate-styrene-copolymer</td>
<td>75.0 w/o</td>
</tr>
<tr>
<td>Barium sulfate (BaSO$_4$), USP</td>
<td>10.0 w/o</td>
</tr>
<tr>
<td>Dibenzoyl peroxide</td>
<td>not available</td>
</tr>
</tbody>
</table>

*Surgical Simplex® P Radiopaque Bone Cement (Howmedicall, Inc. Rutherford, NJ)(3)
– Powder & liquid mixed together, monomer liquid is polymerized by free radical (addition) polymerization process.

– Dibenzoyl peroxide: activator or initiator react w/ monomer monomer radical dimer radical. Monomer liquid wet polymer powder particle surfaces link them [Fig 7-4].

---

Figure 7-4. Two-dimensional representation of bone cement structure after curing. The monomer liquid will be polymerized and become solid.
**TABLE 7-9 REQUIREMENTS FOR POWDER LIQUID MIXTURE**

<table>
<thead>
<tr>
<th>Maximum Dough Time (min)</th>
<th>Setting Time Range (min)</th>
<th>Maximum Exotherm (°C)</th>
<th>Minimum Intrusion (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>5-15</td>
<td>90</td>
<td>2.0</td>
</tr>
</tbody>
</table>

From ASTM F451.
**TABLE 7-10 REQUIREMENTS FOR CURED POLYMER AFTER SETTING**

<table>
<thead>
<tr>
<th>Minimum Compressive Strength (MPa)</th>
<th>Maximum Indentation (mm)</th>
<th>Minimum Recovery (%)</th>
<th>Maximum Water Sorption (mg/cm²)</th>
<th>Maximum Water Solubility (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.14</td>
<td>60</td>
<td>0.7</td>
<td>0.05</td>
</tr>
</tbody>
</table>

From ASTM F451.
Polymerization during curing obviously increases degree of polymerization => increase in molecular weight [Table 7-11].

Molecular weight distribution does not change significantly after curing [Fig 7-5].

– Bone cement properties affected by intrinsic & extrinsic factors [Table 7-13].

– Porosity developed during curing.

– Reduce porosity by vacuum & by centrifugation during mixing. Depletion of monomer, difficulty of mixing while under vacuum, segregation of constituents by centrifuging, etc.

– Mixing inside a plastic bag after puncturing a partition is a good method of containing monomer vapor & keeping out air during mixing.
### TABLE 7-11 MOLECULAR WEIGHT OF BONE CEMENT (4)

<table>
<thead>
<tr>
<th>TYPES OF M.W. (g/mol)</th>
<th>MONOMER</th>
<th>POWDER</th>
<th>CURED</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$ (number average)</td>
<td>100</td>
<td>44,000</td>
<td>51,000</td>
</tr>
<tr>
<td>$M_w$ (weight average)</td>
<td>100</td>
<td>198,000</td>
<td>242,000</td>
</tr>
<tr>
<td>PROPERTIES</td>
<td>RADIOPAQUE</td>
<td>COMMERCIAL</td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>28.9 ± 1.6</td>
<td>55-76</td>
<td></td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>91.7 ± 2.5</td>
<td>76-131</td>
<td></td>
</tr>
<tr>
<td>Young's Modulus (Compressive Load, MPa)</td>
<td>2,200 ± 60</td>
<td>2,960-3,280</td>
<td></td>
</tr>
<tr>
<td>Endurance limit$^c$</td>
<td>0.3 uts$^d$</td>
<td>0.3 uts</td>
<td></td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.10-1.23</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>Water Sorption (%)</td>
<td>0.5</td>
<td>0.3-0.4</td>
<td></td>
</tr>
<tr>
<td>Shrinkage after setting (%)</td>
<td>2.75 - 5</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 7-13 FACTORS AFFECTING BONE CEMENT PROPERTIES

<table>
<thead>
<tr>
<th><strong>Intrinsic Factors</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>- Composition of monomer and</td>
<td>- Powder particle size, shape, and distribution: degree of</td>
</tr>
<tr>
<td>powder.</td>
<td>polymerization.</td>
</tr>
<tr>
<td>- Liquid/powder ratio.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Extrinsic Factors</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>- Mixing environment:</td>
<td>temperature, humidity, type of container.</td>
</tr>
<tr>
<td>- Mixing technique:</td>
<td>rate and number of beating with spatula</td>
</tr>
<tr>
<td>- Curing environment:</td>
<td>temperature, humidity, pressure, contacting surface (tissue,</td>
</tr>
<tr>
<td></td>
<td>air, water, etc.)</td>
</tr>
</tbody>
</table>
7.3.5 Fluorocarbon Polymers

– Polytetrafluoroethylene (PTFE), Teflon® (DuPont).
– Polytrifluorochloroethylene (PTFCE), polyvinylfluoride (PVF), & fluorinated ethylene propylene (FEP) have rather inferior chemical & physical properties & not for implant.
– Made from tetrafluoroethylene under pressure with a peroxide catalyst in presence of excess water for removal of heat.

\[ \text{F} \quad \text{F} \]
\[-(\text{C}-\text{C})_n-\quad (7-22)\]
\[ \text{F} \quad \text{F} \]
– Highly crystalline (> 94%); average m.w. 0.5~5x10^6 amu
– High density (2.15~2.2 g/cm^3)
– Low modulus of elasticity (0.5GPa) & tensile strength (14 MPa).
– Low surface tension (18.5 erg/cm^2) & friction coefficient (0.1).
– Implantable PTFE, ASTM F754.
– Being able to expand on a microscopic scale into a microporous material => excellent thermal insulator.
– PTFE not injection molded or extruded, high melt viscosity & it cannot be plasticized.
– Powders sintered to above 327°C under pressure
7.3.6. Rubbers

- Silicone, natural, & synthetic rubbers
- **Rubbers or elastomers**, stretchable because of kinks of individual chains such as seen in *cis*-1,4 polyisoprene.
- **Repeated stretchability due cross-links** between chains. Amount of cross-linking the flexibility of rubber: 2-3% sulfur => flexible rubber; 30% sulfur, hard rubber.
- **Antioxidants**: improve aging properties.
- **Fillers**: carbon black or silica powders to improve physical properties.
– **Natural rubber**: latex of *Hevea brasiliensis* tree and the chemical formula is the same as that of *cis*-1,4 polyisoprene.

– Cross-linking by x-ray & organic peroxides produces rubber with superior blood compatibility compared with rubbers made by conventional sulfur vulcanization.

– **Synthetic rubbers**: Natta and Ziegler types of *stereospecific* polymerization. *Neoprene* (polychloroprene, (-CH\(_2\)-C(\(\text{Cl}\))=CH-CH\(_2\)-))
**TABLE 7-14 PROPERTIES OF RUBBERS**

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>NATURAL</th>
<th>NEOPRENE</th>
<th>SILICONE</th>
<th>URETHANE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>7-30</td>
<td>20</td>
<td>6-7</td>
<td>35</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>100-700</td>
<td>--</td>
<td>350-600</td>
<td>650</td>
</tr>
<tr>
<td>Hardness (Shore A Durometer)</td>
<td>30-90</td>
<td>40-95</td>
<td>--</td>
<td>65</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.92</td>
<td>1.23</td>
<td>1.12-1.23</td>
<td>1.1-1.23</td>
</tr>
</tbody>
</table>

See also ASTM standards F604, F881 (silicone rubber) and F624 (urethane).
• **Silicone rubber**, by Dow Corning, developed for medical use. Polymerized by a condensation polymerization. Reaction product is unstable and condenses, resulting in polymers:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
n \text{HO-Si-OH} & \Rightarrow -(\text{Si-O-})_n + n\text{H}_2\text{O} (7-23) \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]
• Low m.w. polymers have low viscosity & can be cross-linked to make a higher m.w. rubber-like material.

• Medical grade silicone rubbers contain stannous octate as catalyst

• Contain silica (SiO₂) powder as fillers to improve their mechanical properties.

• Filled rubber is a particle reinforced composite.
– Polyurethanes: thermosetting polymers; to coat implants.
– Reacting a prepared prepolymer chain A with an aromatic diisocyanate to make very long chains possessing active isocyanate groups for cross-linking.
– Polyurethane rubber is quite strong & has good resistance to oil & chemicals [Table 7-14].
– Polymethylsiloxane rubber, (block) copolymerized with urethanes, carbonates, etc. to improve its properties. Copolymers tailor made to meet a particular need, contact lenses[Figure 7-6].
– Oxygen permeability, most important for contact lens
Figure 7-6. Oxygen permeability of contact lenses made of various materials versus thickness. From B. Arkles and P. Redinger, “Silicones in Biomedical Applications,” in *Biocompatible Polymers, Metals and Composites*, M. Szycher (ed.), Technomic Publ., Westport, Conn., 1983, Chapter 32.
7.4 High Strength Thermoplastics

- Developed to match properties of light metals.
- Excellent mechanical, thermal & chemical properties due to stiffened main backbone chains.
- Polyacetals & polysulfones; tested as implant materials, polycarbonates found their applications in heart/lung assist devices, food packaging, etc.
• **Polyacetals** are produced by reacting formaldehyde,

\[
\begin{align*}
\text{H} & \quad \text{CH}_2 \quad \text{CH}_2 \\
n \text{C}=\text{O} & \Rightarrow \quad \text{O} \quad \text{O} \quad \text{O}( \text{O}) \quad \text{n} \ (7-24) \\
\text{H} & 
\end{align*}
\]

• Polyformaldehyde, polyoxymethylene (POM) [Delrin® (DuPont)].

• High m.w. (> 20,000 g/mol) & excellent mechanical properties.

• Excellent resistance to most chemicals & to water
- **Polysulfones**: by Union Carbide 1960's,

\[
\left(\begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\text{CH}_3
\end{array}\right)_n
\]

- High thermal stability due to bulky side groups (amorphous) & rigid main backbone chains.
- Stable to chemicals, not so stable in the presence of polar organic solvents such as ketones & chlorinated hydrocarbons.
• **Polycarbonates**: tough, amorphous, & transparent, reacting bisphenol A & diphenyl carbonate,

\[ \text{CH}_3\text{C}_n\text{O} \]

• Best known Lexan® (General Electric Co.).
- Excellent mechanical & thermal properties. Table 7-15.

**TABLE 7-15 PROPERTIES OF POLYACETAL, POLYSULFONES, AND POLYCARBONATES**

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>POLYACETAL (Delrin®)</th>
<th>POLYSULFONE (UDEL®)</th>
<th>POLYCARBONATE (Lexan®)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.425</td>
<td>1.24</td>
<td>1.20</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>70</td>
<td>70</td>
<td>63</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>15-75</td>
<td>50-100</td>
<td>60-100</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>3.65</td>
<td>2.52</td>
<td>2.45</td>
</tr>
<tr>
<td>Water Adsorption (%, 24h)</td>
<td>0.25</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Example 7-3

- Silica flour (finely ground SiO$_2$, $\rho = 2.65$ g/cm$^3$) is used as a filler for a polydimethyl siloxane.

(a) What volume fraction of SiO$_2$ is required to make a silastic rubber with density of 1.25 g/cm$^3$?

(b) What is the weight percent of SiO$_2$?
Answer

(a) \[ \square = \square_1 V_1 + \square_2 V_2 + \ldots \]

\[ \square_{rubber} = 1.25 = 2.65 \times V_1 + 0.90 \times V_2 \]

\[ V_1 + V_2 = 1 \]

\[ 1.25 = 2.65 \times V_1 + 0.90 \times (1-V_1) \]

\[ = 1.75 \times V_1 + 0.90 \]

\[ V_1 = 0.20 \text{ (20 v/o)} \]

(b) Since the weight of 1 cm\(^3\) of rubber is 1.25 g and the volume fraction is 0.2 (or 0.2 cm\(^3\)/1 cm\(^3\)), therefore,

\[ W_1 = \frac{0.2 \times 2.65}{1.25} = 0.42 \text{ (42 w/o)} \]
7.5 Deterioration of Polymers

7.5.1 Chemical Effects

• Linear polymer: main chains randomly scissioned (cut). *Depolymerization* occurs, process is inverse of chain termination of addition polymerization (c.f. Equ 7-8 & 9).

• **Cross-linking** of a linear polymer may result in deterioration. Ex: LDPE, cross-linking interferes with regular orderly arrangement of chains => lower crystallinity => decreases mechanical properties. If cross-linking is broken by oxygen or ozone attack on (poly-) isoprene rubber, rubber becomes brittle.
• Change nature of bonds, as in case of polyvinylchloride;

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \Rightarrow & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad + & \quad \text{HCl} \\
\text{H} & \quad \text{Cl} & \quad \text{H} & \quad \text{Cl} & \quad \text{H} & \quad \text{H} & \quad \text{Cl} & \quad \text{H}
\end{align*}
\]  
(7-27)

• By-products of degradation (HCl) irritable to tissues since they are acids.
7.5.2 Sterilization Effects

- **Dry heat sterilization**: 160-190°C. Above Tm, Tg of linear polymers like PE & PMMA. Polyamide (nylon): oxidation. Safely dry sterilized: PTFE (Teflon®), silicone rubber.

- **Steam sterilization (autoclaving)**: high steam pressure, low temperature (120-135°C). PVC, polyacetals, PE (low density variety), and polyamides (nylons) cannot be used.
• **Chemical agents** (ethylene & propylene oxide gases, & phenolic & hypochloride solutions) at low temp. longer time & more costly. most polymeric implants can be sterilized by this method.

• **Radiation** sterilization: isotope Co\(^{60}\) can deteriorate polymers: PE > 10\(^6\) Gy brittle, hard. Combination of random chain scission & cross-linking.
7.5.3 Mechano-Chemical Effects

– Cyclic or constant loading deteriorates polymers. [Fig 7-7].
– Plasticizing effect of water molecules at higher temp. Decrease strength [Fig. 7-8].

![Graph 1: Ultimate tensile strength versus time for polymethyl methacrylate in saline solution at 37°C. Note the large decrease in tensile strengths for both solid and porous bone cement. Unpublished data of T. Parchinski, G. Cipoletti, and F. W. Cooke, Clemson University, 1977.]

![Graph 2: Fatigue test of solid polymethyl methacrylate. Note the S-N curve is the same for both untreated samples and samples soaked in saline solution at 37°C. After T. Parchinski and F. W. Cooke, Clemson University, 1977.]

Figure 7-7. Ultimate tensile strength versus time for polymethyl methacrylate in saline solution at 37°C. Note the large decrease in tensile strengths for both solid and porous bone cement. Unpublished data of T. Parchinski, G. Cipoletti, and F. W. Cooke, Clemson University, 1977.

Figure 7-8. Fatigue test of solid polymethyl methacrylate. Note the S-N curve is the same for both untreated samples and samples soaked in saline solution at 37°C. After T. Parchinski and F. W. Cooke, Clemson University, 1977.
7.5.4 *In Vivo* Environmental Effects

- **All polymers** start to deteriorate soon they implanted.
- Ionic attack (especially hydroxyl, OH-) & dissolved oxygen.
- Enzymatic degradation if implant is made from natural polymeric materials like reconstituted collagen.
• Most hydrophilic polymers such as polyamides and polyvinyl alcohol undergo a rapid deterioration.
• Hydrophobic polymers like polytetrafluoroethylene (Teflon®) & polypropylene less prone to deteriorate in vivo.
• Deterioration products => tissue reactions.
<table>
<thead>
<tr>
<th>POLYMERS</th>
<th>EFFECTS OF IMPLANTATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>Low density ones absorb some lipids and lose tensile strength. High density ones are inert and no deterioration occurs.</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Generally no deterioration.</td>
</tr>
<tr>
<td>Polyvinylchloride (rigid)</td>
<td>Tissue reaction, plasticizers may leach out and become brittle.</td>
</tr>
<tr>
<td>Polyethyleneterephthalate</td>
<td>Susceptible to hydrolysis and loss of tensile strength.</td>
</tr>
<tr>
<td>Polyamides (nylon)</td>
<td>Absorb water and irritate tissue, lose tensile strength rapidly.</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>No tissue reaction, very little deterioration.</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>Solid specimens are inert. If it is fragmented into pieces, irritation will occur.</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>Rigid form: crazing, abrasion, and loss of strength by heat sterilization. Cement form: High heat generation, unreacted monomers during and after polymerization may damage tissues.</td>
</tr>
</tbody>
</table>
The End