CHAPTER 14: POLYMER STRUCTURES

ISSUES TO ADDRESS...

• What are the basic microstructural features?

• How are polymer properties effected by molecular weight?

• How do polymeric crystals accommodate the polymer chain?
Chapter 14 – Polymers

What is a polymer?

Polymer
many repeat unit

Adapted from Fig. 14.2, Callister 7e.

Polyethylene (PE)  Polyvinyl chloride (PVC)  Polypropylene (PP)

repeat unit

Adapted from Fig. 14.2, Callister 7e.
Ancient Polymer History

• Originally natural polymers were used
  – Wood
  – Cotton
  – Leather
  – Rubber
  – Wool
  – Silk

• Oldest known uses
  – Rubber balls used by Incas
  – Noah used pitch (a natural polymer) for the ark
Polymer Composition

Most polymers are hydrocarbons
  – i.e. made up of H and C

- Saturated hydrocarbons
  – Each carbon bonded to four other atoms

\[ \text{C}_n\text{H}_{2n+2} \]
<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Structure</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>H—C—H</td>
<td>-164</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>H—C—C—H</td>
<td>-88.6</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>H—C—C—C—H</td>
<td>-42.1</td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td></td>
<td>-0.5</td>
</tr>
<tr>
<td>Pentane</td>
<td>C₅H₁₂</td>
<td></td>
<td>36.1</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td></td>
<td>69.0</td>
</tr>
</tbody>
</table>

Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: CₙH₂ₙ₊₂
Unsaturated Hydrocarbons

- Double & triple bonds relatively reactive – can form new bonds
  - **Double bond** – ethylene or ethene - $C_nH_{2n}$
    \[
    \begin{array}{c}
    \text{H} \\
    \text{C} = \text{C} \\
    \text{H} \\
    \end{array}
    \]
  - Triple bond – acetylene or ethyne - $C_nH_{2n-2}$
    \[
    \begin{array}{c}
    \text{H} \\
    \text{H} \\
    \text{C} = \text{C} \\
    \text{H} \\
    \end{array}
    \]

- 4-bonds, but only 3 atoms bound to C’s
Chemistry of Polymers

Adapted from Fig. 14.1, Callister 7e.

Note: polyethylene is just a long HC
- paraffin is short polyethylene
# Bulk or Commodity Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>$\text{H} - \text{C} - \text{C} - \text{H}$</td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>$\text{H} - \text{C} - \text{Cl}$</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (PTFE)</td>
<td>$\text{F} - \text{C} - \text{F}$</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>$\text{H} - \text{C} - \text{H}$</td>
</tr>
<tr>
<td>Polymer</td>
<td>Repeat Unit</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td><img src="image1" alt="Polystyrene Repeat Unit" /></td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td><img src="image2" alt="Poly(methyl methacrylate) Repeat Unit" /></td>
</tr>
<tr>
<td>Phenol-formaldehyde (Bakelite)</td>
<td><img src="image3" alt="Phenol-formaldehyde Repeat Unit" /></td>
</tr>
</tbody>
</table>
MOLECULAR WEIGHT

- Molecular weight, $M_i$: Mass of a mole of chains.

$$\bar{M}_n = \frac{\text{total wt of polymer}}{\text{total # of molecules}}$$

Lower $M$  \hspace{2cm} higher $M$

$$\bar{M}_n = \sum x_i M_i$$

$$\bar{M}_w = \sum w_i M_i$$

$\bar{M}_w$ is more sensitive to higher molecular weights

Adapted from Fig. 14.4, Callister 7e.
Molecular Weight Calculation

Example: average mass of a class

<table>
<thead>
<tr>
<th>$N_i$</th>
<th>$M_i$</th>
<th>$x_i$</th>
<th>$w_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td># of students</td>
<td>mass (lb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.1</td>
<td>0.054</td>
</tr>
<tr>
<td>1</td>
<td>120</td>
<td>0.1</td>
<td>0.065</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
<td>0.2</td>
<td>0.151</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>0.3</td>
<td>0.290</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>0.2</td>
<td>0.237</td>
</tr>
<tr>
<td>1</td>
<td>380</td>
<td>0.1</td>
<td>0.204</td>
</tr>
</tbody>
</table>

$\bar{M}_n = \sum x_i M_i$

$\bar{M}_w = \sum w_i M_i$

$\bar{M}_n = 186 \text{ lb}$

$\bar{M}_w = 216 \text{ lb}$
Degree of Polymerization, $n$

$n = \text{number of repeat units per chain}$

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

$n_i = 6$

\[
\begin{align*}
  n_n &= \sum x_i n_i = \frac{\bar{M}_n}{m} \\
  n_w &= \sum w_i n_i = \frac{\bar{M}_w}{m}
\end{align*}
\]

where $\bar{m} = \text{average molecular weight of repeat unit}$

\[
\bar{m} = \sum f_i m_i
\]

Chain fraction \quad mol. wt of repeat unit $i$
Molecular Structures

- Covalent **chain** configurations and strength:

  - Linear
  - Branched
  - Cross-Linked
  - Network

Direction of increasing strength

Adapted from Fig. 14.7, *Callister 7e.*
Polymers – Molecular Shape

Conformation – Molecular orientation can be changed by rotation around the bonds – note: no bond breaking needed

Adapted from Fig. 14.5, Callister 7e.
Copolymers

two or more monomers polymerized together

- **random** – A and B randomly vary in chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A alternate with large blocks of B
- **graft** – chains of B grafted on to A backbone

\[ A \quad B \]
Polymer Crystallinity

Ex: polyethylene unit cell

- Crystals must contain the polymer chains in some way
  - Chain folded structure

Adapted from Fig. 14.10, Callister 7e.

Adapted from Fig. 14.12, Callister 7e.
Polymer Crystallinity

Polymers rarely 100% crystalline

- Too difficult to get all those chains aligned

- % **Crystallinity**: % of material that is crystalline.
  - \(TS\) and \(E\) often increase with % crystallinity.
  - Annealing causes crystalline regions to grow. % crystallinity increases.

Adapted from Fig. 14.11, *Callister 6e.*
Polymer Crystal Forms

- **Single crystals** – only if slow careful growth

Adapted from Fig. 14.11, *Callister 7e.*
Polymer Crystal Forms

- **Spherulites** – fast growth – forms lamellar (layered) structures

Adapted from Fig. 14.13, Callister 7e.
Spherulites – crossed polarizers

Maltese cross

Adapted from Fig. 14.14, *Callister 7e.*
Characteristics, Applications & Processing of Polymers

ISSUES TO ADDRESS...

• What are the tensile properties of polymers and how are they affected by basic microstructural features?

• Hardening, anisotropy, and annealing in polymers.

• How does the elevated temperature mechanical response of polymers compare to ceramics and metals?

• What are the primary polymer processing methods?
Mechanical Properties

- i.e. stress-strain behavior of polymers

Strains – deformations > 1000% possible
(for metals, maximum strain ca. 10% or less)

Adapted from Fig. 15.1, Callister 7e.
Tensile Response: Brittle & Plastic

Stress-strain curves adapted from Fig. 15.1, *Callister 7e*. Inset figures along plastic response curve adapted from Figs. 15.12 & 15.13, *Callister 7e*. (Figs. 15.12 & 15.13 are from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)
Predeformation by Drawing

- **Drawing** (ex: monofilament fishline)
  - stretches the polymer prior to use
  - aligns chains in the stretching direction
- **Results of drawing:**
  - increases the elastic modulus ($E$) in the stretching direction
  - increases the tensile strength ($TS$) in the stretching direction
  - decreases ductility (%$EL$)
- **Annealing** after drawing...
  - decreases alignment
  - reverses effects of drawing.
- Compare to **cold working** in metals!

Adapted from Fig. 15.13, *Callister 7e*. (Fig. 15.13 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)
Tensile Response: Elastomer Case

- Compare to responses of other polymers:
  -- brittle response (aligned, crosslinked & networked polymer)
  -- plastic response (semi-crystalline polymers)

Stress-strain curves adapted from Fig. 15.1, *Callister 7e*. Inset figures along elastomer curve (green) adapted from Fig. 15.15, *Callister 7e*. (Fig. 15.15 is from Z.D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd ed., John Wiley and Sons, 1987.)
Thermoplastics vs. Thermosets

- **Thermoplastics:**
  -- little crosslinking
  -- ductile
  -- soften with heating
  -- polyethylene
  -- polypropylene
  -- polycarbonate
  -- polystyrene

- **Thermosets:**
  -- large crosslinking
    (10 to 50% of mers)
  -- hard and brittle
  -- do NOT soften with heating
  -- vulcanized rubber, epoxies,
    polyester resin, phenolic resin

Molecular weight

Adapted from Fig. 15.19, Callister 7e. (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)
### $T$ and Strain Rate: Thermoplastics

- **Decreasing $T$...**
  - increases $E$
  - increases $TS$
  - decreases $\%EL$

- **Increasing strain rate...**
  - same effects as decreasing $T$.

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Adapted from Fig. 15.3, *Callister 7e*. (Fig. 15.3 is from T.S. Carswell and J.K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics", *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)
Time Dependent Deformation

- **Stress relaxation test:**
  - strain to \( \varepsilon_0 \) and hold.
  - observe decrease in stress with time.

- **Relaxation modulus:**
  \[ E_r(t) = \frac{\sigma(t)}{\varepsilon_0} \]

- **Data:** Large drop in \( E_r \) for \( T > T_g \).
  (amorphous polystyrene)

- **Sample \( T_g(\degree C) \) values:**
  - PE (low density) - 110
  - PE (high density) - 90
  - PVC + 87
  - PS +100
  - PC +150

Adapted from Fig. 15.7, *Callister 7e.*
(Fig. 15.7 is from A.V. Tobolsky, *Properties and Structures of Polymers,* John Wiley and Sons, Inc., 1960.)
Polymer Additives

Improve mechanical properties, processability, durability, etc.

- **Fillers**
  - Added to improve tensile strength & abrasion resistance, toughness & decrease cost
  - ex: carbon black, silica gel, wood flour, glass, limestone, talc, etc.

- **Plasticizers**
  - Added to reduce the glass transition temperature $T_g$
  - commonly added to PVC - otherwise it is brittle
Polymer Additives

- **Stabilizers**
  - Antioxidants
  - UV protectants
- **Lubricants**
  - Added to allow easier processing
  - “slides” through dies easier – ex: Na stearate
- **Colorants**
  - Dyes or pigments
- **Flame Retardants**
  - Cl/F & B
Processing of Plastics

• Thermoplastic –
  – can be reversibly cooled & reheated, i.e. recycled
  – heat till soft, shape as desired, then cool
  – ex: polyethylene, polypropylene, polystyrene, etc.

• Thermoset
  – when heated forms a network
  – degrades (not melts) when heated
  – mold the prepolymer then allow further reaction
  – ex: urethane, epoxy
Summary

• General drawbacks to polymers:
  -- $E$, $\sigma_y$, $K_c$, $T_{\text{application}}$ are generally small.
  -- Deformation is often $T$ and time dependent.
  -- Result: polymers benefit from composite reinforcement.
• **Thermoplastics** (PE, PS, PP, PC):
  -- Smaller $E$, $\sigma_y$, $T_{\text{application}}$
  -- Larger $K_c$
  -- Easier to form and recycle
• **Elastomers** (rubber):
  -- Large reversible strains!
• **Thermosets** (epoxies, polyesters):
  -- Larger $E$, $\sigma_y$, $T_{\text{application}}$
  -- Smaller $K_c$

Table 15.3 *Callister 7e*:
Good overview of applications and trade names of polymers.