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?
Temperature influence

Strain rate influence: slow => High T
Mechanical Properties

- i.e. stress-strain behavior of polymers

Strains – deformations > 1000% possible
(for metals, maximum strain ca. 10% or less)
Elastic behavior \((\sigma = E\varepsilon)\)

Viscoelastic behavior

Viscous behavior
Viscoelastic relaxation modulus

\[ E_r(t) = \frac{\sigma(t)}{\varepsilon_0} \]

constant strain \( \varepsilon_0 \)

Creep modulus

\[ E_c(t) = \frac{\sigma_0}{\varepsilon(t)} \]

constant stress \( \sigma_0 \)
A: highly crystallized
B: Rubber or elastomeric
C: amorphous
Polymer Fracture

Crazing

– spherulites plastically deform to fibrillar structure
– microvoids and fibrillar bridges form

Adapted from Fig. 15.9, Callister 7e.
Tensile Response: Brittle & Plastic

\[ \sigma(\text{MPa}) \]

brittle failure

plastic failure

onset of necking

unload/reload

Initial

aligned, cross-linked case

networked case

Near Failure

crystalline regions slide

semi-crystalline case

amorphous regions elongate

crystalline regions align

fibrillar structure

near failure

Chapter 15 - 8
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 (~ 3 times)
  -- increases the tensile strength \( (TS) \) in the stretching direction (~2-5 times)
  -- 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.)
Other factors that influence the mechanical properties of semicrystalline polymers

• **Molecular Weight**…

\[ TS = TS_\infty - \frac{A}{M_n} \]

*TS*\(_\infty\)* tensile strength with infinite molecular weight

*A* a constant; *M*\(_n\)* number - average molecular weight

• **Degree of Crystallinity**

closely packed in an ordered and parallel arrangement…

Increase tensile modulius, strength, brittleness

• **Heat treating** for undrawn polymers…

  increase in the percent crystallinity, crystal size and perfection

  increase in tensile modulus, yield strength and brittleness
Chapter 15 - 11

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

Tensile Response: Elastomer Case

- Amorphous, not easily crystallize
- Chain bonds easily rotate in responding to applied force
- Delayed plastic deformation

\[ \sigma \text{(MPa)} \]

- initial: amorphous chains are kinked, cross-linked.
- Deformation is reversible!
- final: chains are straight, still cross-linked.

\[ \varepsilon \]

- brittle failure
- plastic failure

Tensile Response: Elastomer Case

- • Amorphous, not easily crystallize
- • Chain bonds easily rotate in responding to applied force
- • Delayed plastic deformation

Initial: amorphous chains are kinked, cross-linked. Deformation is reversible! Final: chains are straight, still cross-linked.
Thermoplastics vs. Thermosets

- **Thermoplastics:**
  - little crosslinking
  - ductile
  - soften w/heat
  - polyethylene
  - polypropylene
  - polycarbonate
  - polystyrene

- **Thermosets:**
  - large crosslinking (10 to 50%)
  - hard and brittle
  - do NOT soften w/heat
  - rubber, epoxies,
    - polyester resin, phenolic resin
Crystallization, melting and glass transition in polymers

- **Crystallization:**
  -- Nucleation and growth
  -- follow Avrami Equation
    \[ y = 1 - \exp\left(-kt^n\right) \]
  -- polyethylene
  -- polypropylene
  -- polycarbonate
  -- polystyrene

- **Melting:**
  -- melting over a range of T
  -- \( T_m \) depends on history of the polymer, crystallization P/T
  -- \( T_m \) depends on heating rate, higher rate \( \Rightarrow \) higher \( T_m \)

- **Glass transition:**
  -- transition from rubbery to rigid state
  -- reversible at \( T_g \)
Melting vs. Glass Transition Temp.

- Both $T_m$ and $T_g$ increase with increasing molecular weight
- Both $T_m$ and $T_g$ increase with increasing chain stiffness
- Chain stiffness increased by
  1. Bulky sidegroups
  2. Polar groups (e.g. Cl)
  3. Double bonds chain groups
- Normally $0.5T_m < T_g < 0.8T_m$
<table>
<thead>
<tr>
<th>Material</th>
<th>Glass Transition Temperature [°C (°F)]</th>
<th>Melting Temperature [°C (°F)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (low density)</td>
<td>−110 (−165)</td>
<td>115 (240)</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>−97 (−140)</td>
<td>327 (620)</td>
</tr>
<tr>
<td>Polyethylene (high density)</td>
<td>−90 (−130)</td>
<td>137 (279)</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>−18 (0)</td>
<td>175 (347)</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>57 (135)</td>
<td>265 (510)</td>
</tr>
<tr>
<td>Polyester (PET)</td>
<td>69 (155)</td>
<td>265 (510)</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>87 (190)</td>
<td>212 (415)</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>100 (212)</td>
<td>240 (465)</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>150 (300)</td>
<td>265 (510)</td>
</tr>
</tbody>
</table>
Polymer types

Plastics

Relative
Rigid

Any degree of crystallinity
All molecular structures and configurations
Work below $T_m$ or $T_g$, crosslinked
  e.g. polyamide (nylon), polystyrene

Elastomers

Rubbery

amorphous
Highly twisted kinked and coiled crosslinked molecular chains
  e.g. Natural polyisoprene (rubber), chloroprene

Highly crystallinity and high molecular weight
  e.g. polyamide (nylon), polyester

Fibers

High TS
Addition (Chain) Polymerization

- **Initiation**
  \[
  R\cdot + \text{C=C} \rightarrow R-C-C\cdot
  \]

- **Propagation**
  \[
  R-C-C\cdot + \text{C=C} \rightarrow R-C-C-C-C\cdot
  \]

- **Termination**
  \[
  R-C-C-C-C\cdot + \cdot-C-C-C-C-R \rightarrow
  \]
  \[
  \text{Disproportionation: } R-C-C-C-C\cdot + \cdot-C-C-C-C-R \rightarrow
  \]
  \[
  \text{Combination: } R-C-C-C-C-C-C-C-C-R
  \]

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Condensation (Step) Polymerization

\[
\text{hexamethylene diamine} \quad \text{adipic acid}
\]

\[
\begin{align*}
\text{H}_2\text{N(}\text{CH}_2\text{)}_6\text{N}-\text{H} & + \text{HO-C(}\text{CH}_2\text{)}_4\text{C-OH} \\
\text{H}_2\text{N(}\text{CH}_2\text{)}_6\text{N-C(}\text{CH}_2\text{)}_4\text{C-OH} & + \text{H}_2\text{O}
\end{align*}
\]

nylon-6,6
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 (small molecules between large chains weaken binding)
  - Added to improve flexibility, ductility and toughness
  - reduce the glass transition temperature $T_g$
  - commonly added to PVC - otherwise it is brittle

- Stabilizers
  - Antioxidants
  - UV protectants
  - 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 (linear polymer) then allow further reaction (curing with heating or catalysts) to form crosslinked or network structures.
  - ex: urethane, epoxy
Processing Plastics - Molding

- Compression and transfer molding
  - thermoplastic or thermoset

Adapted from Fig. 15.23, *Callister 7e*. (Fig. 15.23 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley & Sons, 1984.)
Processing Plastics - Molding

- **Injection molding**
  - thermoplastic & some thermosets

Adapted from Fig. 15.24, *Callister 7e*. (Fig. 15.24 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd edition, John Wiley & Sons, 1971.)
Processing Plastics – Extrusion

Adapted from Fig. 15.25, Callister 7e. (Fig. 15.25 is from Encyclopædia Britannica, 1997.)
Fabrication of fibers (spinning)

Melt spinning: molten

Dry spinning: dissolved in volatile solvent which will be evaporated

Wet spinning: precipitate solvent with second solvent

www.madehow.com/Volume-1/Rayon.html
Blown-Film Extrusion

Adapted from Fig. 15.26, Callister 7e.
(Fig. 15.26 is from Encyclopædia Britannica, 1997.)
Summary

• General drawbacks to polymers:
  -- $E$, $\sigma_y$, $T_{\text{application}}$ are generally small.
  -- Deformation is often $T$ and time dependent.

• Thermoplastics (PE, PS, PP, PC):
  -- Smaller $E$, $\sigma_y$, $T_{\text{application}}$
  -- Larger $K_c$ (fracture strength)
  -- 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.