Chapter 15: 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 of Polymers – Stress-Strain Behavior

- Fracture strengths of polymers ~ 10% of those for metals
- Deformation strains for polymers > 1000%
  - for most metals, deformation strains < 10%

Adapted from Fig. 15.1, Callister & Rethwisch 8e.
Mechanisms of Deformation — Semicrystalline (Plastic) Polymers

Stress-strain curves adapted from Fig. 15.1, Callister & Rethwisch 8e. Inset figures along plastic response curve adapted from Figs. 15.12 & 15.13, Callister & Rethwisch 8e. (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 chain alignment
  -- reverses effects of drawing (reduces $E$ and $TS$, enhances $%EL$)
- Contrast to effects of **cold working** in metals!

Adapted from Fig. 15.13, *Callister & Rethwisch 8e*. (Fig. 15.13 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)
Mechanisms of Deformation—Elastomers

Stress-strain curves adapted from Fig. 15.1, Callister & Rethwisch 8e. Inset figures along elastomer curve (green) adapted from Fig. 15.15, Callister & Rethwisch 8e. (Fig. 15.15 is from Z.D. Jastrzebski, The Nature and Properties of Engineering Materials, 3rd ed., John Wiley and Sons, 1987.)

• Compare elastic behavior of elastomers with the:
  -- brittle behavior (of aligned, crosslinked & network polymers), and
  -- plastic behavior (of semicrystalline polymers)
  (as shown on previous slides)
**Thermoplastics vs. Thermosets**

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

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

Adapted from Fig. 15.19, *Callister & Rethwisch 8e.* (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science,* 3rd ed., John Wiley and Sons, Inc., 1984.)
Influence of $T$ and Strain Rate on Thermoplastics

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

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

Adapted from Fig. 15.3, Callister & Rethwisch 8e. (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.)
Melting & Glass Transition Temps.

What factors affect $T_m$ and $T_g$?

- Both $T_m$ and $T_g$ increase with increasing chain stiffness.
- Chain stiffness increased by presence of:
  1. Bulky sidegroups
  2. Polar groups or sidegroups
  3. Chain double bonds and aromatic chain groups
- Regularity of repeat unit arrangements – affects $T_m$ only

Adapted from Fig. 15.18, Callister & Rethwisch 8e.
Chapter 15

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

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

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

- There is a large decrease in \( E_r \) for \( T > T_g \).

Adapted from Fig. 15.7, *Callister & Rethwisch 8e*. (Fig. 15.7 is from A.V. Tobolsky, *Properties and Structures of Polymers*, John Wiley and Sons, Inc., 1960.)

- Time-Dependent Deformation

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**Note:** The diagram represents the stress relaxation behavior of materials, showing the change in stress over time at different temperatures. The graph illustrates the transition region where materials change from a rigid solid to a viscous liquid, indicating the point of critical interest for engineering applications. The representative \( T_g \) values are listed for various polymers, showing the temperature at which the material transitions from a rigid to a more flexible state.
Crazing During Fracture of Thermoplastic Polymers

Craze formation prior to cracking

– during crazing, plastic deformation of spherulites
– and formation of microvoids and fibrillar bridges

Adapted from Fig. 15.9, Callister & Rethwisch 8e.
Polymer Formation

• There are two types of polymerization
  – Addition (or chain) polymerization
  – Condensation (step) polymerization
Addition (Chain) Polymerization

– Initiation

\[ R\cdot + C=\overset{\circ}{C}H \rightarrow R-C-C\cdot \]

– Propagation

\[ R-C-C\cdot + C=\overset{\circ}{C}H \rightarrow R-C-C-C-C\cdot \]

– Termination

\[ R-C-C-C-C\cdot + \cdot-C-C-C-C-R \rightarrow \]

Disproportionation

\[ R-C-C-C-C-H + \cdot-C-C-C-C-R \rightarrow \]

Combination

\[ R-C-C-C-C-C-C-R \]
Condensation (Step) Polymerization

\[
\begin{align*}
\text{Hexamethylene diamine} & \quad + \quad \text{Adipic acid} \\
\text{Nylon-6,6} & \quad + \quad \text{H}_2\text{O}
\end{align*}
\]
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 $T_g$ below room temperature
  – Presence of plasticizer transforms brittle polymer to a ductile one
  – Commonly added to PVC - otherwise it is brittle
Polymer Additives (cont.)

- **Stabilizers**
  - Antioxidants
  - UV protectants
- **Lubricants**
  - Added to allow easier processing
  - polymer “slides” through dies easier
  - ex: sodium stearate
- **Colorants**
  - Dyes and pigments
- **Flame Retardants**
  - Substances containing chlorine, fluorine, and boron
Processing of Plastics

- **Thermoplastic**
  - can be reversibly cooled & reheated, i.e. recycled
  - heat until soft, shape as desired, then cool
  - ex: polyethylene, polypropylene, polystyrene.

- **Thermoset**
  - when heated forms a molecular network (chemical reaction)
  - degrades (doesn’t melt) when heated
  - a prepolymer molded into desired shape, then chemical reaction occurs
  - ex: urethane, epoxy
Processing Plastics – Compression Molding

Thermoplastics and thermosets

- polymer and additives placed in mold cavity
- mold heated and pressure applied
- fluid polymer assumes shape of mold

Fig. 15.23, Callister & Rethwisch 8e. (Fig. 15.23 is from F.W. Billmeyer, Jr., Textbook of Polymer Science, 3rd ed., John Wiley & Sons, 1984.)
Processing Plastics – Injection Molding

Thermoplastics and some thermosets

- when ram retracts, plastic pellets drop from hopper into barrel
- ram forces plastic into the heating chamber (around the spreader) where the plastic melts as it moves forward
- molten plastic is forced under pressure (injected) into the mold cavity where it assumes the shape of the mold

Fig. 15.24, Callister & Rethwisch 8e. (Fig. 15.24 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd edition, John Wiley & Sons, 1971.)
Processing Plastics – Extrusion

thermoplastics

• plastic pellets drop from hopper onto the turning screw
• plastic pellets melt as the turning screw pushes them forward by the heaters
• molten polymer is forced under pressure through the shaping die to form the final product (extrudate)

Fig. 15.25, Callister & Rethwisch 8e. 
(Fig. 15.25 is from Encyclopædia Britannica, 1997.)
Processing Plastics – Blown-Film Extrusion

Fig. 15.26, Callister & Rethwisch 8e.
(Fig. 15.26 is from Encyclopædia Britannica, 1997.)
Polymer Types – Fibers

Fibers - length/diameter >100
- Primary use is in textiles.
- Fiber characteristics:
  - high tensile strengths
  - high degrees of crystallinity
  - structures containing polar groups
- Formed by spinning
  - extrude polymer through a spinneret (a die containing many small orifices)
  - the spun fibers are drawn under tension
  - leads to highly aligned chains - fibrillar structure
Polymer Types – Miscellaneous

- **Coatings** – thin polymer films applied to surfaces – i.e., paints, varnishes
  - protects from corrosion/degradation
  - decorative – improves appearance
  - can provide electrical insulation

- **Adhesives** – bonds two solid materials *(adherands)*
  - bonding types:
    1. Secondary – van der Waals forces
    2. Mechanical – penetration into pores/crevices

- **Films** – produced by blown film extrusion

- **Foams** – gas bubbles incorporated into plastic
Advanced Polymers

Ultrahigh Molecular Weight Polyethylene (UHMWPE)

- Molecular weight ca. $4 \times 10^6$ g/mol
- Outstanding properties
  - high impact strength
  - resistance to wear/abrasion
  - low coefficient of friction
  - self-lubricating surface
- Important applications
  - bullet-proof vests
  - golf ball covers
  - hip implants (acetabular cup)

Adapted from chapter-opening photograph, Chapter 22, Callister 7e.
Advanced Polymers
Thermoplastic Elastomers

Styrene-butadiene block copolymer

Fig. 15.22, Callister & Rethwisch 8e. (Fig. 15.22 adapted from the Science and Engineering of Materials, 5th Ed., D.R. Askeland and P.P. Phule, Thomson Learning, 2006.)
Summary

• Limitations of polymers:
  -- $E$, $\sigma_y$, $K_c$, $T_{\text{application}}$ are generally small.
  -- Deformation is often time and temperature dependent.

• 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 & Rethwisch 8e:
Good overview of applications and trade names of polymers.
Summary

• Polymer Processing
  -- compression and injection molding, extrusion, blown film extrusion

• Polymer melting and glass transition temperatures

• Polymer applications
  -- elastomers
  -- coatings
  -- films
  -- advanced polymeric materials
  -- fibers
  -- adhesives
  -- foams