Polymers as engineering materials

• Becoming more and more important in many engineering fields
  – Aerospace, transport, sporting, medical.

• Comparing to metal
  – Light, less stiff, less strong, less tough
  – New polymers and polymer composites can be as stiff and strong
  – Very large elastic strain (rubber)
  – More temperature sensitive
Polymers in nature

- Almost all biological systems are built of polymers (bio-engineering)
  - Cellulose, lignin (wood)
  - Natural rubber
  - Protein
  - DNA/RNA

From using natural polymers to making polymers!
Polymer molecules

- Long, chain-like molecules
- The backbone of the chain is usually carbon atoms linked by covalent bonds.

Polyethylene:
Polymerization

• Addition polymerization
  – Polyethylene (PE)

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

• Condensation polymerization
  – Epoxy:

\[
\text{R-OH} + \text{HOOC-R}’ \rightarrow \text{R-OOC-R}’ + \text{H}_2\text{O}
\]
Degree of polymerization

• DP = the number of monomer units in a chain, normally $10^3$ – $10^5$.

• Molecular weight = DP times the molecular weight of the monomer.

• Not all chains are of the same length. Take the average for DP and molecular weight.
Polymer properties depend on DP

Strength vs. DP

Softening temperature vs. DP
Molecular structures

Figure 14.7  Schematic representations of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures. Circles designate individual mer units.
Polymer crystallinity

- Polymers can be amorphous or partly crystalline.
Polymer crystals

- **Lamellae:** molecular chains fold into a thin plate.

- **Spherulites:** a spherical shaped aggregate of lamellae
Degree of crystallinity

- Range from 0 (completely amorphous) up to about 95%.
- Density: more crystalline leads to higher density

\[
\%\text{crystallinity} = \frac{\rho_c (\rho_s - \rho_a)}{\rho_s (\rho_c - \rho_a)} \times 100\%
\]
Volume vs temperature

Perfect crystal

Glass (amorphous)

Imperfect crystal

Sharper transition means more crystallinity.
Glass transition temperature

- $T_g = $ the temperature when the secondary bonds start to melt.
- Below $T_g$, the polymer is a glass.
- Above $T_g$, the polymer becomes first leathery, then rubbery, capable of large elastic deformation without fracture.

- Typical values (-40°C - 200°C)
  - PMMA: ~ 100°C
  - Low-density PE: ~ -20°C
  - Rubber: ~ -40°C

$T_g$ or $T_m$ sets the temperature limits for applications of polymers.
Generic Polymers

• Thermoplastics (polyethylene, PMMA)
  – Linear polymers, no cross-links

• Thermosets (epoxy, heavily cross-linked)
  – Network polymers, heavily cross-linked, amorphous

• Elastomers (rubber, lightly cross-linked)
  – Almost linear polymers, occasional cross-links

• Natural polymers (cellulose, protein, etc.)
Molecular structure of polymers

- Molecular weight/chain length/degree of polymerization
- Cross-linking
- Degree of crystallinity
- All affect mechanical properties of polymers.
Elastic modulus of polymers

- Covalent bonds (C-C): $E \sim 200-1000\text{GPa}$
- Secondary bonds: $E \sim 2-4\text{ GPa}$

- Polymers: partly covalent and partly secondary bonds.
  - At low temperature, $E \sim 2-4\text{ GPa}$
  - At high temperature, $E \sim 0.01\text{ GPa}$ (secondary bonds melt)

Cross-linking increases the fraction of covalent bonds and thus the modulus.
Time-dependent behavior

- Polymers creep at the room temperature.

- Viscoelastic behavior: combination of elastic solid and viscous fluid.

\[ \varepsilon = f(\sigma, t, T) \quad \text{or} \quad \sigma = g(\varepsilon, t, T) \]
Summary

- Molecular structure of polymers
  - Polymerization
  - Cross-linking
  - Crystallinity (density, $T_m$ and $T_g$)

- Elastic modulus

- Viscoelastic behavior (more to come!)