Deformation of Polymers

- Elastic Behavior
  - Higher crystallinity increases elastic modulus
  - Elastic deformation via stretching and bending of primary covalent bonds
- Plastic Behavior
  - Higher crystallinity greatly increases strength
  - Deformation via complicated processes
  - Produces highly oriented structure

Deformation of Polymers

- Homogeneous Shear Flow
- Shear Banding
  - Localized deformation
  - Orient along directions of principal shear stress
  - Necks form via shear bands
  - Observed in tension and compression
  - Primary mechanism in amorphous glassy polymers

Shear Yielding

**Necking:** reduction in sample cross-sectional area
True stress ≥ Engineering Stress, necked region must be stronger (by a factor of λ) than the un-necked region

**Strain Hardening of Polymers:**
\[
\frac{d\sigma}{d\varepsilon} = \text{entropic subchains, crystal orientation, and crystallization}
\]
Polymeric Behavior by Type

- Large anisotropy of bonding: covalent vs. secondary
- Homogeneous vs. heterogeneous microstructures
- Microstructures: amount, size, shape, orientation, and connectivity-topology
- Large (huge) changes in microstructure with deformation

<table>
<thead>
<tr>
<th>Types of Polymer</th>
<th>Young’s Modulus (N/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel</td>
<td>~10⁵</td>
</tr>
<tr>
<td>Elastomer</td>
<td>~ 10⁶</td>
</tr>
<tr>
<td>Glassy polymer</td>
<td>~ 10⁹</td>
</tr>
<tr>
<td>Polymer crystal (⊥,</td>
<td></td>
</tr>
<tr>
<td>SWCNT (</td>
<td></td>
</tr>
</tbody>
</table>

Polymeric Behavior
- Gels
- Elastomers
- Glasses
- Semicrystalline
- Fibers

Strength/Stiffening Mechanisms

**Stiffening Mechanisms**
- Increase Elastic Modulus
  - Colder temperatures
  - Higher strain rates
  - More crosslinking
  - More secondary bonding
  - Higher crystallinity
  - Aligned polymer chains
- Decrease Ductility
  - Colder temperatures
  - Higher strain rates
  - More crosslinking
  - More secondary bonding
  - Higher crystallinity
  - Longer chains (higher molecular weight)

**Strengthening Mechanisms**
- Drawing of polymers
  - Analogous to cold work in metals, but more dramatic
  - Strength and modulus can have 3x increase in drawing direction
- Heat treatment
  - Prior to drawing, may lead to:
    - Higher modulus and strength
    - Reduced ductility
  - Post drawing
    - Reverse strengthening by undoing chain orientation and strain induced crystallinity
Glass Transition Temperatures

Temperature at which polymers transition from rubbery to rigid (glassy) behavior
- Rubbery above this temperature
- Occurs only in amorphous regions of polymers
- Gibbs free energy exceeds the activation energy for cooperative movement of each element in the polymer
- Molecular chains slide past each other under applied force

Fracture of Polymers

- Fracture strengths of polymers is low relative to metals and ceramics
- Brittle Failure
  - Apply Linear Elastic Fracture Mechanics (LEFM)
  - Thermosetting resins
    - Formation of cracks near stress concentrators
    - Covalent bonds in the network or crosslinked structures are severed during fracture
  - Crazing
    - Proceeds fracture in glassy thermoplastics (localized yielding) small and interconnected microvoids
    - Absorbs fracture energy and effectively increases the fracture toughness
  - Thermoplastic
    - Both ductile and brittle modes are possible (dependent on glass transition temperature)
    - Factors that favor brittle failure: lower temp, increase strain rate, presence of sharp notch, increase specimen thickness
- Amorphous, glassy polymers
- Cavitations
  - Light refraction index changes (stress whitening)
  - Crosslinked, glassy polymers
  - Crystalline thermoplastics
  - Rubbers

![Glass Transition Temperatures Diagram](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>-110</td>
<td>115</td>
</tr>
<tr>
<td>PTFE</td>
<td>-100</td>
<td>330</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>-20</td>
<td>175</td>
</tr>
<tr>
<td>Nylon</td>
<td>50</td>
<td>265</td>
</tr>
<tr>
<td>PVC</td>
<td>90</td>
<td>212</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>100</td>
<td>240</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>150</td>
<td>265</td>
</tr>
</tbody>
</table>


![Fracture of Polymers Diagram](image)

- Brittle fracture surface of a thermosetting resin
- Brittle fracture surface of a thermoplastic
- Fracture surface of a polymer fiber

Features:
- Fracture strengths of polymers is low relative to metals and ceramics
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Craze Yielding

- Crazing in tension only, not in compression
- $\Delta V > 0$ dilatation/cavitations – void formation under tension
- Nucleation at flaws – usually at surface
- Crazing only occurs for (+) hydrostatic tensile stress state
- Craze plane forms perpendicular to max principal tensile stress
- Voids form at advancing craze tip due to dilatational stresses
- Craze tip growth is by Taylor meniscus instability of fingering and fibril pinch-off
- As bridges elongate and break, causing microvoids to grow and coalesce, which leads to the formation of cracks
- Voids grow and fibrils elongate as polymer chains orient, become drawn into the craze and work harden
- Craze thickens by drawing in new material as well as by further elongation of the fibril (decrease in diameter)

Craze Microstructure

- Elongated fibril/void network
- Typical void content, ~50%
- Fibril diameter, ~5nm
- Fibril spacing, ~20nm
- Draw ratio of fibrils is $1/(\text{void volume fraction})$, ~2
- Heating above $T_g$ leads to healing and recovery (entanglement network of subchains)
- Crazes with high void content and a large fibril draw ratio are prone to easy breakdown (crack propagation and brittle fracture)
- The draw ratio ($\lambda$) of a fibril depends on the contour length ($l$) between entanglements and the distance between entanglements ($d$):

$$\lambda \approx \frac{l}{\sqrt{d}} = \frac{M_w}{\sqrt{M_w}} = \sqrt{M_w}$$

where $M_w$ is the molecular weight of the polymer

Crazing

Crazed material in this figure has a residual strain of ~60% and results in permanent deformation.

Temperature and strain rate dependence on craze initiation.

Craze Yielding Criterion

\[ \sigma_{\text{max}} - \sigma_{\text{min}} \geq \Lambda(T) + \frac{\Omega_1(T)}{\sigma_{\text{H}}} \]

Material Constants (temperature dependent)

- Principal Stresses
- Hydrostatic Stress

Criterion for the nucleation of a craze in a 3d stress state

Yield Loci for Biaxial Tension, Crazing dominates in region 1 and part of 2 and 4

Yield Loci where \(\sigma_3<0\) and shear yielding is preferred

Expanded view of second quadrant where \(\sigma_1<0\) and \(\sigma_2>0\)

Crazing vs. Shear Banding

Both result in localized deformation in polymers

1. Shear banding
   - Constant volume deformation
   - Oriented along directions of principal shear stress
   - Occurs in compression and tension
   - More prevalent in semicrystalline polymers

2. Crazing
   - Dilatational deformation
   - Oriented perpendicular to principal tensile stress
   - Occurs only in tension
   - More prevalent in amorphous and glassy polymers

• Shear banding occurs if the number of entanglements per chain is large so that the crazing stress is higher than the yield stress.
• Crazing occurs if the yield stress is lower, for example if the molecular weight is low (few entanglements). In general, lower temperatures favors crazing.
• In many cases, heterogeneous deformation is a competition between crazing and shear banding in polymers, but the two mechanisms are not mutually exclusive.

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Crazing vs. Shear Banding

Role of drawing:
- Strengthening Mechanism
- Orient the polymer chains
- Increasing strength and modulus

Impact Strength

- Test type: Izod, Charpy, Plate Impact, etc.
- Some polymers have brittle to ductile transition
- Impact strength generally increases as thermal softening occurs due to greater ductility

Tear Strength

- Ability to resist tearing
- Energy required to tear apart a cut specimen that has a standard geometry
- Related to tensile strength
- Energy balance concepts of Griffith (brittle glasses)
  - Strain energy release rate, G:
    \[ G_{\text{brittle}} = \frac{1}{t} \frac{d}{da} (W_{\text{ext}} - U_{\text{elastic}}) \]
    where a is the crack length, t is the thickness, W is the external work on the system, U is the elastic energy
- Four energy sinks operative during crack propagation of crazed materials, in order of importance:
  1. Plastic work of craze formation
  2. Viscoelastic work of craze extension under stress
  3. Surface energy of the holes of the craze
  4. Breaking of chemical bonds
- Griffith theory extended to tearing of rubbers by Rivlin & Thomas – 1952, at crack growth:
  \[ G_{\text{rubber}} = -2 \left( \frac{\partial \Omega}{\partial a} \right)_{\text{fracture}} \]
  \( G_{\text{rubber}} \) = strain energy release rate; tear strength related to energy required to produce unit area of crack, \( \Omega \) = total energy of the system
- Tearing of Rubbers ideally are ‘non-linear elastic’; little energy dissipation from the crack tip


Environmental Degradations

- Polymers
  - Degrades due to solubility in certain liquids or absorbs solvent and swells
  - Crazing leads to microvoids, which increases susceptibility of polymer degradation from liquids, including water!
  - Degradation due to alterations in molecular structure caused by radiation, heat, or light source
- Polymeric degradation is physiochemical
- Polymers may deteriorate when exposed to liquids (water) by swelling and dissolution
  - Swelling
    - The liquid or solute diffuses into and is absorbed within the polymer forcing the macromolecules apart and causes the swelling
    - Secondary intermolecular bonding forces are reduced making the material softer and more ductile
  - Dissolution
    - Polymer is completely soluble in the liquid
    - Both are affected by molecular structure and temperature
- Mechanical integrity can also be compromised via covalent bond scission which results in a reduction in molecular weight
  - Radiation
  - Chemical reaction
  - Thermal
Case Study: Bone Cement

- Also known as poly(methyl methacrylate) or PMMA, which is a thermoplastic
- Affixes orthopedic implants and remodels lost bone
- Benefits:
  - Biologically compatible
  - Bone cement has a Young’s modulus between cancellous and cortical bone
    - Promotes load sharing
    - Avoids stress shielding and bone resorption
  - Bone cement acts like a grout and not so much like a glue in arthroplasty

Mechanical failure of bone cement is linked to failure of cemented total joint prostheses!

Application of Bone Cement

- Supplied to the surgeon as a powder and liquid (MMA) and mixed together at the time of surgery
- Surgical procedure:
  - Remove disease tissue
  - Drill out marrow cavity and fit implant
  - Mix together bone cement powder and liquid
  - Inject cement
  - Insert implant and remove excess cement
  - Allow cement to harden or cure without motion
Hardening of Bone Cement

• Mixed cement is liquid-like and doughy for 5-10 minutes prior to hardening
• Hardening reaction is due to conversion of monomer to polymer (ie in-situ free radical polymerization – initiation and propagation of polymer chain)
• Bonding is mechanical, not chemical (although sticky, it does not bond to either the bone or the implant, it primarily fills the spaces between the prosthesis and the bone preventing motion)

Porosity in Bone Cement

• Formation of bubbles
  – Bone cement heats to quite a high temperature while setting and because of this it can kill bone cells in the surrounding area
  – Vaporized monomer may end up in blood stream or cause bubbles leading to voids
• Polymerization shrinkage
  – Density in liquid and solid state are 1.18 g/cc and 0.94 g/cc
  – Full conversion of monomer to polymer results in 21% volume shrinkage
  – Forms pores or retraction from cement/implant or cement/bone interface
  – This is why commercial bone cements are not made entirely of monomer (other reasons include temperature rise and poor handling properties), and have polymerization shrinkage ~7%
• Effect of porosity on bone cement properties
  – Pores significantly weaken bone cement
  – % porosity dependent on surgical technique
  – Conventional mixing of powder and liquid results in many pores
  – Centrifugation and vacuum mixing result in lower porosity and significantly improved properties
Microstructural Pathway of Fracture in Bone Cement

Overview (20x) of crack and pore field

Damage zone

Crack

Microcracks

Expanded damage zone

Crack

Pores

Microcracks

Leading crack and pore field

Short and thin microcracks emanating from pores (360x)

Leading crack and microcrack from pore (640x)

Open leading crack face displaying damage zone


Fracture Properties of Bone Cement

The Effects of Mixing Method and Molecular Weight

Fracture Toughness vs. Mixing Method

Fatigue vs. Mixing Method

Fracture Toughness vs. Molecular Weight

Vacuum Mixed – Less Pores

Hand Mixed

Self healing polymers

- Synthetic material design to mimic healing response of nature
- Also known as autonomous or smart materials
- Invented at UIUC by co-creates Prof Nancy Sottos (MatSE) and Scott White (AeroE)
- Tiny capsules containing a healing agent are embedded in the polymer. When the material is damaged, the capsules rupture and release the healing agent, which repairs the cracks.
- A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent (Figure 1).
  - (i) Cracks form in the matrix wherever damage occurs.
  - (ii) The crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action.
  - (iii) The healing agent contacts the catalyst triggering polymerization that bonds the crack faces closed.
- SEM image of the fracture plane of a self-healing epoxy with a ruptured microcapsule (Figure 2).
- Applications include: Adhesives, Coatings, Biomaterials, Microelectronics, Aeronautical Structural Components, Nanodevices, etc.

Self Healing Polymers

Movie from:
http://autonomic.beckman.illinois.edu/gallery.html