Polymers
Course update

• Room change!!! **Olin 106** (starting Monday)

• Paper distributed today (also available on class website) for simulated LBL next Wednesday
  – Burdick JA, et al. *Biomacromolecules* 2005
  – Discussion questions/terms for paper will be distributed Monday
  – Go over “How to Read the Primary Literature” – adapted from Dr. George Plopper’s “Guide to Critical Reading of Primary Literature”

• Last day to submit groups – if not you will be randomly teamed up!
Polymeric Biomaterials

• Overall...
  – Functional versus structural
    • Better approximate soft tissue characteristics relative to metals or ceramics
    • Viscoelastic – like natural tissues
      – Have properties of both viscous liquids and elastic solids
  – Good optical transmission characteristics
  – Easier to shape at low temperatures
  – Problems
    • Creep – *jeans on a hanger*
    • Biological adsorption
    • Deterioration
Background
What is a polymer?

• A **polymer** is a molecule consisting of many repeating units covalently bonded to one another
  – “poly” meaning **many**, “mer” meaning **monomer**, the individual building block

• You may have heard of bone cement – what’s the formal name of this polymer?

• More on polymer chemistry in a bit...

poly(methyl methacrylate) (PMMA) polymer

methyl methacrylate (MMA) monomer
Polymers as biological building blocks

- There are four classes of biological macromolecules! Which are polymers?

  - **proteins** *(Monday lecture)*
    (polypeptide, amino acid)

  - **carbohydrates**
    (polysaccharide, monosaccharide)

  - **nucleic acids**
    (DNA/RNA, nucleotides)

  - **lipids**
    (not true polymers, though are sometimes referred to as such)
Other polymers of note

• Here are the **most abundant** of each type of biomacromolecule (by mass in the human body)

  - **proteins** (collagen)
  - **carbohydrates** (glycogen)
  - **nucleic acids** (RNA)
History of polymer use by man

- Originally natural polymers were used
  - Wood
  - Rubber
  - Cotton
  - Wool
  - Leather
  - Silk
  - Catgut

- Oldest known uses
  - Rubber balls used by Incas & Maya
  - Noah [used] pitch (a natural polymer) for the ark

- Today
  - Synthetic, petroleum based
    - Hydrocarbon chains
Current polymer use by man

- ...is marked by a huge range of applications!
Polymer Chemistry and Properties
Chemistry of polymers

- What is a polymer?
  - From Greek:
    - *poly* = many
    - *meros* = units

Most basic example:

*Polyethylene*

- **Monomer**
- **Polymer**

**Ethylene**

Polyethylene (PE)

Poly(vinyl chloride) (PVC)

Polypropylene (PP)

Adapted from Fig. 4.2, *Callister & Rethwisch 3e.*
Physical interactions of polymers

“The Olive Garden Effect”
(not a technical term)

- **Structure**
  - “Bowl of spaghetti”
  - Entanglement occurs between chains
  - Coiled between entanglements

- **Complex mechanics**
  - Longer chains $\rightarrow$ greater entanglement
  - Viscoelasticity
  - Mechanical properties vary with time/temp
Molecular shape (or conformation) – chain bending and twisting are possible via rotation of carbon atoms around their chain bonds
– Note: not necessary to break chain bonds to alter molecular shape
– Bond rotation allows chains to slip...viscoelastic response

Effect of side groups or main chain on shape?
Steric and chemical considerations

Adapted from Fig. 4.5, Callister & Rethwisch 3e.
Mechanical properties of polymers

- Fracture strengths of polymers ~10% those of metals
- Plastic deformation strains for some polymers > 1000% (elastomers)
  - For most metals, deformation strains < 10%

But metals and ceramics have a regular 3D structure – what does it mean for linear polymers to have these mechanical properties?

Adapted from Fig. 7.22, Callister & Rethwisch 3e.
Commodity Polymers (also biomedical uses)

Table 4.3  A Listing of Repeat Units for 10 of the More Common Polymeric Materials

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
<th>Use</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>H H</td>
<td>Tubing, acetabular cup in hips, knee articulating surface</td>
<td>Tough, oil/fat resistant, cheap</td>
</tr>
<tr>
<td>~200-800 MPa</td>
<td>H H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>H H Cl</td>
<td>Tubing for blood/feeding/dialysis</td>
<td>Hard &amp; brittle – plasticizers added</td>
</tr>
<tr>
<td></td>
<td>F F F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polytetrafluoroethylene (PTFE)</td>
<td>F F</td>
<td>GoreTex (microporous) vascular grafts</td>
<td>Stable (thermally/chemically), hydrophobic, excellent lubricity</td>
</tr>
<tr>
<td></td>
<td>C C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>H H</td>
<td>Similar to PE</td>
<td>Similar to PE (more crack resistant)</td>
</tr>
<tr>
<td>~2 – 3 GPa</td>
<td>H H CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>H H</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
**Commodity Polymers (also biomedical uses) (cont.)**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td><img src="image" alt="PMMA Repeat Unit" /></td>
</tr>
<tr>
<td>Poly(hexamethylene adipamide) (nylon 6,6)</td>
<td><img src="image" alt="Hexamethylene Adipamide Repeat Unit" /></td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) (PET, a polyester)</td>
<td><img src="image" alt="PET Repeat Unit" /></td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td><img src="image" alt="Polycarbonate Repeat Unit" /></td>
</tr>
</tbody>
</table>

Common: Plexiglas® ...

Uses: Intraocular & hard contact lenses, bone cement, dental,
Characteristics: hydrophobic, tough, hard

Fibers/clothing/textiles, surgical sutures

Coke™ bottles, Dacron tubing vascular grafts, sutures

Lexan®

Used in nalgene® bottles (no longer),
Eyeglasses (safety glass)

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*Adapted from Table 4.3, Callister & Rethwisch 3e.*
The polymer parameters

- Chemical composition
- Molecular weight distribution
- Stereochemistry
- Topology
- Morphology
Molecular weight of polymers

• The molecular weight (M) of a polymer is the **average** mass of **one mole of chains** (6.02 x 10^{23} molecules) of the polymer
  – We say *average* because a given batch of polymer can be very monodisperse or polydisperse

  ![Diagram showing monodisperse and polydisperse polymers](image)

  **Low M**

  **High M**

  **monodisperse** (all similar molecular weight)

  **polydisperse** (variation in chain molecular weight)

• Can use a frequency distribution of the MW:

  ![Frequency distribution graph](image)

 Think back to the physical entanglement point – for the same mass and polymer, which solution would be more viscous – a M = 10^9 \text{ g/mol} or a M = 10^6 \text{ g/mol} solution?
Molecular weight of polymers

Many polymer properties affected by length of polymer chains

- Tensile Strength
- Elastic Modulus
- Relaxation Times
- Melt Viscosity
- Hardness
- Flex Life
- Biological Activity
- Softening Temperature
- Elongation at Break
- Tear Strength
- Low Temperature Toughness
- Resistance to Environmental Stress Cracking
- Drawability
- Coefficient of Friction
- Spinability
- Permeability
### Molecular weight of polymers – effect on properties

#### Properties of the alkane/alkene series

<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></td>
<td>-164</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td></td>
<td>-88.6</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td></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

- **Boiling Point (°C):**
  - Methane: -164
  - Ethane: -88.6
  - Propane: -42.1
  - Butane: -0.5
  - Pentane: 36.1
  - Hexane: 69.0

Adapted from Table 14.3, *Callister & Rethwisch 3e.*

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#### Properties

<table>
<thead>
<tr>
<th>Number of Carbons in Chain</th>
<th>State and Properties of Material</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Simple gas</td>
<td>Bottled gas for cooking</td>
</tr>
<tr>
<td>5-11</td>
<td>Simple liquid</td>
<td>Gasoline</td>
</tr>
<tr>
<td>9-16</td>
<td>Medium-viscosity liquid</td>
<td>Kerosene</td>
</tr>
<tr>
<td>16-25</td>
<td>High-viscosity liquid</td>
<td>Oil and grease</td>
</tr>
<tr>
<td>25-50</td>
<td>Crystalline solid</td>
<td>Paraffin wax candles</td>
</tr>
<tr>
<td>50-1000</td>
<td>Semicrystalline solid</td>
<td>Milk carton adhesives and coatings</td>
</tr>
<tr>
<td>1000-5000</td>
<td>Tough plastic solid</td>
<td>Polyethylene bottles and containers</td>
</tr>
<tr>
<td>3-6 x 10⁵</td>
<td>Fibers</td>
<td>Surgical gloves, bullet-proof vests</td>
</tr>
</tbody>
</table>

[Adapted from Table. 14.3, *Callister & Rethwisch 3e.*]
Do cis/trans isomers exist? Can there be stereoisomers (tacticity)?

- **Isomers** – molecules with the same chemical formula, but different structural formulas

**Configurations** – to change, must break bonds

- **Stereoisomerism**

Stereoisomers are mirror images – can’t superimpose without breaking a bond

Mirror plane
Cis/trans isomerism

The cis isomer has the H atom and CH$_3$ group on the same side of the chain, while the trans isomer has them on opposite sides.

- **cis**
  - cis-isoprene (natural rubber)
  - H atom and CH$_3$ group on same side of chain

- **trans**
  - trans-isoprene (gutta percha)
  - H atom and CH$_3$ group on opposite sides of chain
Polymer topology

Are the chains linear, branched, or crosslinked?

• Linear – two ends
• Branched – more than two ends
  – Stars, combs, random
• Crosslinked...
  – Crosslinked – primary bonds between chains
  – Network – primary bonds between chains
    • one enormous molecule, insoluble, x-linker
    • Vulcanization in rubber
Polymer morphology

What is the actual **structure** of the solid?

- **Crystalline**
- **Semicrystalline**
- **Amorphous** “rubbery”

**Melting @ T_m**
- Heat of fusion
- Stronger forces
- Correlated structure

**Glass transition**
- No heat of fusion
- Free volume
- Amorphous form
Polymer crystallinity

Polymers rarely 100% crystalline
• Difficult for all regions of all chains to become aligned

• Degree of crystallinity expressed as % crystallinity.
  -- Some physical properties depend on % crystallinity
  -- Amorphous material “melts” at a low temperature
  -- Crystalline material “melts” at a higher temperature
  -- Use temperature determines properties

Adapted from Fig. 14.11, Callister 6e.
(Fig. 14.11 is from H.W. Hayden, W.G. Moffatt, and J. Wulff, The Structure and Properties of Materials, Vol. III, Mechanical Behavior, John Wiley and Sons, Inc., 1965.)
Expanded classes of polymers

- Thermoplastic homopolymers & copolymers
- Thermosets
- Hydrogels
- Resorbable Polymers

**Y. Kanekiyo, H. Tao, and B. Sellergren,** *Stimuli-Responsive Guest Binding and Releasing by Dendritic Polymer-Based Hydrogels, Polymer Journal,* 684-687, 40 (8), 2008

These are water swollen, so mechanical properties are much lower (in the <1 MPa range).

(PCL-PEG example)
Examples of Biomedical Applications
Polyethylene (PE) – articulating surfaces

• Varieties
  – Low density PE (LDPE); ~200 Mpa
  – High density PE (HDPE); ~800 MPa
  – UHMWPE

• Advantages
  – Solvent resistance
    • Ease of processing
    • Infection resistance

• Applications
  – Weight bearing & articulating surfaces for knee/hip
  – Sutures
  – Tubing

UHMWPE Insert, access date 1/6/2011
http://www.uhmwpe.org/pub_reports/view/2126
Complications/problems for PE

- Sterilization methods
  - Autoclave
    - High temperatures
  - EtO gas sterilization
    - Toxicity
  - $\gamma$ – irradiation
    - Degradation & chain scission
      - Broken chain = free radicals
    - Shelf-life
    - Surface vs. bulk
- Creep
- Wear

Dr. Fraser Buchanan, *Accelerated Ageing and Characterisation of UHMWPE used in Orthopaedic Implants*, access date 1/6/2011
http://www.azom.com/Details.asp?ArticleID=q09
TKA Revision – 11 years post-op. BioHexagon Ltd. access date 1/6/2011.
Suture materials

• Materials
  – Thermoplastic fibers
    • Spectra (UHMWPE fiber)
    • Polypropylene
    • Polyethylene terephthalate (PET)
  – Alternative: Resorbable sutures
    • Poly (lactic acid) PLA
    • Poly (glycolic acid) PGA -> PLA/PGA copolymers
    • How do they breakdown?
    • Can also be used for drug delivery
      – Carrier could be polymeric micro/nanoparticles, hydrogels, etc.

Sigma-Aldrich, access date 1/6/2011
Ophthalmic polymer biomaterials

• These are hydrogels
• Intraocular lenses (internal) or contact lenses
  – PMMA (hard) vs. PHEMA (soft)
• Advantages
  – Index of refraction/optical absorption
• Issues
  – Breathability/permeability
    • Oxygen to surface of eye
  – Protein adsorption
    • cleaning
• Preference?
  – PHEMA – why? (hint: look at difference in chemistry and remember that hydrogels are water swollen)

http://www.clinicaomegalanzarote.com/en/eyesover60.htm
Soft tissue polymers

- Polyurethanes, silicones, etc.
  - Rubbery in nature (crosslinks in structure retain resilience)
  - Uses
    - Anything flexible
      - catheters
    - Vascular grafts
    - Pacemaker leads
    - Cosmetic/space filling/contour
    - Burn sites/artificial skin
  - Polymerization catalysts
    - Could remain as impurities
    - Hardware store silicone caulk vs. medical grade
  - Encapsulation (internal)
    - Encapsulate with fibrous tissue
    - Hardening in area with time
## A sampling of polymeric biomaterials

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Application</th>
<th>Areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylates (acrylics)</td>
<td>Orthopaedics, Dentistry, Surgery, General, Ophthalmology</td>
<td>Cement, Composites, Bandages, Contact Lenses</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Orthopaedics</td>
<td>Joint Bearings, Joints, Floss</td>
</tr>
<tr>
<td></td>
<td>Dentistry</td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td>Surgery</td>
<td>Sutures, Patches, Vascular grafts</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Orthopaedics</td>
<td>Disk Bearings</td>
</tr>
<tr>
<td></td>
<td>Dentistry</td>
<td>Ligatures</td>
</tr>
<tr>
<td></td>
<td>Cardiology</td>
<td>Lead Insulation</td>
</tr>
<tr>
<td>Silicones</td>
<td>General</td>
<td>Soft Tissues, Leads, Artificial Skin, Other space-filling implants, Lung</td>
</tr>
<tr>
<td>Nylons</td>
<td>Surgery</td>
<td>Sutures and patch materials</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Biochemistry</td>
<td>Assay Dishes</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>General Surgery, Cardiovascular</td>
<td>Grafts, Sutures</td>
</tr>
<tr>
<td>PTFE (Teflon)</td>
<td>Cardiovascular</td>
<td>Grafts</td>
</tr>
<tr>
<td>Polyvinyl Alcohol</td>
<td>Burns</td>
<td>Wound dressings</td>
</tr>
<tr>
<td>Poly α hydroxy acids</td>
<td>General</td>
<td>Biodegradable sutures and devices, drug delivery</td>
</tr>
<tr>
<td>Polyanhydrides, PCL</td>
<td></td>
<td>Drug delivery</td>
</tr>
</tbody>
</table>
Final thoughts…

A word cloud that shows the 222 words that appeared at least 10 times in all the titles published in the journal, with the size of each word proportional to its frequency.

BNG-XXX: Polymeric Biomaterials – coming to a classroom near you Winter 2014!