Principle Characteristics of Polymers

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Early History

**Stone Age** (Paleolithic, ~2.5 Million BC)
Flint: cutting edge easily formed by chipping

**Copper Age** (~8000 – 5000 BC)
Pottery kilns hot enough to melt Cu from ore (Cu $T_m = 1085^\circ C$)
strength $\sigma_y = 70$ MPa (10,000 lb/in$^2$)

**Bronze Age** (~3500 BC)
“Alloying”: add tin to copper (Sn $T_m = 232^\circ C$)
strength $\sigma_y = 125$ MPa (18,000 lb/in$^2$)

**Iron Age** (~1500 BC)
Reduce Fe ore at high T with charcoal to capture $O_2$, release Fe metal
(Fe $T_m = 1538^\circ C$)
strength $\sigma_y = 275$ MPa (40,000 lb/in$^2$)

Add carbon to Fe $\Rightarrow$ Steel! $\sigma_y \rightarrow > 1500$ MPa (200,000 lb/in$^2$)
# MATERIAL CLASSIFICATIONS

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<th>Applications/Trends:</th>
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<td><strong>3. Polymers</strong></td>
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The essence of MATERIALS SCIENCE & ENGINEERING

- Structure
- Performance
- Properties
- Processing
POLMER MOLECULAR STRUCTURE

- Polymer = many mers
  - Polyethylene (PE)
  - Polyvinyl chloride (PVC)
  - Polypropylene (PP)

- Zig-zag structure ⇒ easily kinked

Adapted from Figs. 14.1, 14.2, Cailley 5e.
Polymers are giant molecules. They are important chemicals in our bodies (proteins, poly(nucleic acids)), in plants (starch, cellulose), and in our everyday lives (fibers, plastics, elastomers). Every polymer has its own characteristics, but most polymers have the following general properties:

- Polymers can be very resistant to chemicals
- Polymers can be both thermal and electrical insulators
- Generally, polymers are light in weight with varying degrees of strength
- Polymers can be processed in various ways to produce thin fibers or intricate parts.
Several key parameters determine the properties of a polymer

- Chemical Composition
- Molecular Weight and Distribution
- Chain Structure (Topology)
- Morphology
Topics:

- Classification of Polymer
  Thermoplastics and thermomets
  Classification based upon polymerization
  Classification based on polymer structure

- Structure of polymer
  Copolymers
  Isomerism (Structural Isomerism, Sequence Isomerism, Tacticity)
  Chain arrangement (Topology)

- Molecular weight in polymers

- Thermal transitions
  glass transition and melting

- Mechanical properties of polymer
**Thermoplastics Thermosets and Elastomers**

**Polymers**
- **Thermoplastics**
  - Crystalline
  - Amorphous
- **Thermosets**
- **Elastomers**

**Thermoplastics**
Molecules in a thermoplastic are held together by relatively weak intermolecular forces so that the material softens when exposed to heat and then returns to its original condition when cooled.

**Thermosets**
A thermosetting plastic, or thermoset, solidifies or "sets" irreversibly when heated.

**Elastomers**
Elastomers are rubbery polymers that can be stretched easily to several times their unstretched length and which rapidly return to their original dimensions when the applied stress is released.
Classification of Polymer

**Block copolymer, example:**
Poly(styrene)-block-poly(butadiene)

**Random copolymer, example:**
Poly(styrene-ran-butadiene)

**Alternating copolymer, example:**
Poly(styrene-al-butadiene)

**Graft copolymer, example:**
Poly(styrene)-graft-poly(butadiene)
Double bonds in the polymer chain can show *cis-* or *trans-*isomerism. When a monomer with two conjugated double bonds, such as isoprene, undergoes chain polymerization one double bond can remain in the chain.

The difference between the properties of the cis- and trans-isomers is apparent for naturally-occurring *polyisoprenes*.

*Gutta Percha (trans-1,4-polyisoprene)*  *Natural Rubber (cis-1,4-polyisoprene)*
In chain polymerization monomers with pendant groups can attach in two ways:

- **Head-to-Tail**: The pendant groups are on every other carbon atom in the chain.
- **Head-to-Head**: The pendant groups are not on every other carbon atom.

The usual arrangement is head-to-tail with the pendant groups on every other carbon atom in the chain.
When a chiral center is present in a polymer molecule, different configurations or optical isomers are possible. Three of them are shown below for a Mono substituted vinyl polymer.

**isotactic**

**syndiotactic**

**atactic**

Stereochemistry can have an important effect on chain packing. Isotactic polypropylene (PP), for instance, is highly **crystalline** because the regular chains can pack closely together. Isotactic PP has a melting point of 160°C. Atactic PP, on the other hand is a soft **noncrystalline** polymer with a melting point of only 75°C.
Polymers are very large molecules with unusual physical properties that depend on the interactions between its chains. An important factor in these interactions is the shape of the chain making up the backbone of the molecule.

Some polymer molecules are linear, similar to a normal alkane such as n-decane. An example is high density polyethylene (HDPE), which can contain more than 1000 CH₂ groups.

Simulated Structure

Simulated Skeletal Structure

Linear Polymer

High Density Polyethylene (HDPE)
Some polymers, such as low density polyethylene (LDPE), have branches of different sizes irregularly spaced along the chain. Such polymers are said to be nonlinear.

Simulated Structure

Simulated Skeletal Structure

Low Density Polyethylene (LDPE)
Some polymers have cross-links between polymer chains creating three-dimensional networks. A high density of cross-linking restricts the motion of the chains and leads to a rigid material.
The threshold molecular weight is a lower limit for the molecular weight required for a given commercial application.

**Molecular weight in polymers**

**Number-Average Molecular Weight**

\[
\bar{M}_n = \frac{\sum_{i=0}^{\infty} \frac{N_i}{\sum_j N_j} M_i}{\sum_j N_j}
\]

**Weight-Average Molecular Weight**

\[
\bar{M}_w = \frac{\sum_{i=0}^{\infty} \frac{N_i M_i}{\sum_j N_j M_j}}{\sum_j N_j M_j}
\]

**Properties vs. Molecular Weight**

- Melt Viscosity
- Tensile Strength
- Impact Resistance
- Commercial Polymer Range
Semi-crystalline solids have both amorphous and crystalline regions. According to the temperature, the amorphous regions can be either in the glassy or rubbery state. The temperature at which the transition in the amorphous regions between the glassy and rubbery state occurs is called the glass transition temperature.

At a low temperature the amorphous regions of a polymer are in the glassy state. In this state the molecules are frozen on place. They may be able to vibrate slightly, but do not have any segmental motion in which portions of the molecule wiggle around. When the amorphous regions of a polymer are in the glassy state, it generally will be hard, rigid, and brittle.
If the polymer is heated it eventually will reach its **glass transition temperature**. At this temperature portions of the molecules can start to wiggle around as is illustrated by the red molecule in the diagram above. The polymer now is in its **rubbery state**. The rubbery state lends softness and flexibility to a polymer.
**MOLECULAR WEIGHT & CRYSTALLINITY**

- **Molecular weight, $M_w$:** Mass of a mole of chains.  
  - smaller $M_w$  
  - larger $M_w$

- **Tensile strength (TS):**  
  -- often increases with $M_w$.  
  -- Why? Longer chains are entangled (anchored) better.

- **% Crystallinity:** % of material that is crystalline.  
  -- TS and E often increase with % crystallinity.  
  -- Annealing causes crystalline regions to grow. % crystallinity increases.

Adapted from Fig. 14.11, *Callister 6e.*  
**Topic:** Principle Characteristics of Polymers

**Comparison of glass and melting transition**

**Property of the amorphous region**
- Below $T_g$: Disordered amorphous solid with immobile molecules
- Above $T_g$: Disordered amorphous solid in which portions of molecules can wiggle around
- A second-order transition (see below)

**Property of the crystalline region**
- Below $T_m$: Ordered crystalline solid
- Above $T_m$: Disordered melt
- A first-order transition (see below)
DSC thermograms of PLLA samples irradiated to (a) 0, (b) 10, (c) 25 and (d) 80 kGy (b) in vacuum.
A given polymer sample does not have a unique value of $T_g$ because the glass phase is not at equilibrium. The measured value of $T_g$ will depend on:

- The molecular weight of the polymer
- Thermal history
- Age
- Measurement method
- The rate of heating or cooling

### Tg values of some polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (LDPE)</td>
<td>-125</td>
</tr>
<tr>
<td>Polypropylene (atactic)</td>
<td>-20</td>
</tr>
<tr>
<td>Poly(vinyl acetate) (PVAc)</td>
<td>28</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) (PET)</td>
<td>69</td>
</tr>
<tr>
<td>Poly(vinyl alcohol) (PVA)</td>
<td>85</td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>81</td>
</tr>
<tr>
<td>Polypropylene (isotactic)</td>
<td>100</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>100</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (atactic)</td>
<td>105</td>
</tr>
</tbody>
</table>
The value of $T_g$ depends on the mobility of the polymer chain – the more immobile the chain, the higher the value of $T_g$. In particular, anything that restricts rotational motion within the chain should raise $T_g$.

**Factors Influencing $T_g$**

- Chain Stiffness
- Intermolecular Forces
- Pendant Groups
- Cross-Linking
- Plasticizers
Glass transition and Chain Stiffness

Stiffening groups in the polymer chain reduce the flexibility of the chain and raise the value of $T_g$.

- Poly(ethylene terephthalate) $T_g = 78-84^\circ C$
- Poly(ethylene adipate) $T_g = 69^\circ C$
- Nylon 3 $T_g = 111^\circ C$
- Nylon 6 $T_g = 53^\circ C$
- Nylon 6,6 $T_g = 58^\circ C$
Stronger intermolecular forces lead to a higher Tg. PVC has stronger intermolecular forces than polypropylene because of the dipole-dipole forces from the C-Cl bond.

Atactic Polypropylene \( T_g = -20^\circ C \)

Atactic Poly(vinyl chloride) \( T_g = 81^\circ C \)
Glass transition and Pendant Groups

The influence of pendant groups on the glass transition temperature is somewhat more complicated.

*Bulky pendant groups*, such as a benzene ring, can catch on neighboring chains like a "fish hook" and restrict rotational freedom. This increases $T_g$.

Atactic Polypropylene $T_g = -20^\circ C$

Atactic Polystyrene $T_g = 100^\circ C$
The influence of pendant groups on the glass transition temperature is somewhat more complicated.

Flexible pendant groups, such as aliphatic chains, tend to limit how close chains can pack. This increases rotational motion and lowers $T_g$.

- Poly(methylmethacrylate) $T_g = 105^\circ C$
- Poly(butyl methacrylate) $T_g = 20^\circ C$
The presence of cross-links between chains restricts rotational motion and raises $T_g$.

Plasticizers are low molecular weight compounds added to plastics to increase their flexibility and workability. They weaken the intermolecular forces between the polymer chains and decrease $T_g$. Plasticizers often are added to semi-crystalline polymers to lower the value of $T_g$ below room temperature.
The mechanical properties of a polymer involve its behavior under stress. These properties tell a polymer scientist or engineer many of the things he or she needs to know when considering how a polymer can be used:

- How strong is the polymer? *How much can you stretch it before it breaks?*
- How stiff is it? *How much does it bend when you push on it?*
- Is it brittle? *Does it break easily if you hit it hard?*
- Is it hard or soft?
- Does it hold up well under repeated stress?

The mechanical properties of polymers are one of the features that distinguishes them from small molecules.
Topic: Principle Characteristics of Polymers

- **Tensile Strength**
  - Graph showing stress vs. strain with label "Sample breaks".
  - Tensile Strength is indicated by the vertical axis.

- **% Elongation to Break**
  - Graph showing stress vs. strain with label "Sample breaks".
  - Elongation-to-Break is indicated by the horizontal axis.

- **Young's Modulus**
  - Graph showing stress vs. strain with label "Slope = Young's Modulus".
  - The area under the curve represents Young's Modulus.

- **Toughness**
  - Graph showing stress vs. strain with label "Sample breaks".
  - The area under the curve represents Toughness.
A material that is strong but not tough is said to be brittle. Brittle substances are strong, but cannot deform very much. Polystyrene (PS) is brittle, for example. High impact polystyrene (HIPS), a blend of polystyrene and polybutadiene (a rubbery polymer above its glass transition temperature) is said to be rubber-toughened.
## Mechanical Properties of some materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength (MPa)</th>
<th>% Elongation-to-Break</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel Balls</td>
<td>2,000</td>
<td>Very small</td>
<td>200</td>
</tr>
<tr>
<td>Cellophane Film</td>
<td>50 - 120</td>
<td>10 - 50</td>
<td>3</td>
</tr>
<tr>
<td>Nitrile Rubber Sheet</td>
<td>20 - 30</td>
<td>250 - 500</td>
<td>Very low</td>
</tr>
<tr>
<td>Fiberglass Yarn</td>
<td>1400 - 2000</td>
<td>3 - 4</td>
<td>72</td>
</tr>
<tr>
<td>Nylon</td>
<td>50</td>
<td>150</td>
<td>2</td>
</tr>
</tbody>
</table>
**TENSILE RESPONSE: BRITTLE & PLASTIC**

Stress-strain curves adapted from Fig. 15.1, *Callister 6e*. Inset figures along plastic response curve (purple) adapted from Fig. 15.12, *Callister 6e*. (Fig. 15.12 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)

Chapter 14/15-4
Figure 11.29. Steps in the Deformation of Semicrystalline Polymers.
Figure 11.20. Schematic Stress-Strain Curves for a Semicrystalline Polymer. The shape of tensile specimens at several stages is indicated.
TENSILE RESPONSE: ELASTOMER CASE

- Compare to responses of other polymers:
  -- brittle response (aligned, cross linked & networked case)
  -- plastic response (semi-crystalline case)
**T AND STRAIN RATE: THERMOPLASTICS**

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

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

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Adapted from Fig. 15.3, *Callister 6e*. (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.)
Generally speaking, polymers are insulators. However there is a special class of polymers – the intrinsically conductive polymers – that have conductivity levels between those of semiconductors and metals (up to $10^2$ - $10^3$ S/cm) The combination of metallic and polymeric properties opens completely new opportunities in numerous applications, particularly in the electronics industry, which were previously not possible. The first generation of conductive polymers like polyacetylene or polypyrrole were not suitable for practical applications due to low long term stability of the conductivity and/or low processability.

H.C. Starck has developed the latest generation of conductive polymers which are characterized by outstanding properties:

- High conductivity
- High transparency
- High stability
- Easy processing

poly(3,4-ethylenedioxythiophene) or briefly named PEDT or PEDOT – available under the trade name BAYTRON®