Chemical Structure and Polymer Properties (Chapter 4 in Stevens)¹

I Introduction - Materials & Fabrication Methods in Antiquity

A) Traditional Materials & Their Modern Analogues

1) Rigid Thermoset Materials

a) Antiquity:

i) Stone

➢ Nature’s Thermoset

ii) Pottery/Ceramics

➢ Made from natural/modified class

➢ Most common & useful materials from antiquity to archeology

iii) Concrete

➢ Coliseum

➢ Pilings

iv) Plaster

b) Modern:

i) Phenol/Urea-Formaldehyde Resins

➢ Bakelite

➢ Plywood, Particle Board, Oriented Strand Board

ii) Epoxy Resins

➢ household

➢ aircraft

¹ The graphics in these notes indicated by “Figure/Table/Equation/Etc., x.x in Stevens” are taken from our lecture text: “Polymer Chemistry: An Introduction - 3rd Edition” Malcolm P. Stevens (Oxford University Press, New York, 2002, 2002, Dr. Allen D. Hunter, Youngstown State University Department of Chemistry
2) Rigid Thermoplastic Materials

a) Antiquity:
   i) Metal
      ➢ much more widely used than once suspected - recycling
   ii) Glass
      ➢ much more widely used than once suspected - recycling
      ➢ natural glass
         ▪ obsidian
      ➢ man-made glass

b) Modern:
   i) Highly crosslinked polymers
   ii) Some high \( T_g \) polymers

3) Flexible Thermoset Materials

a) Antiquity:
   i) Natural & Semi-synthetic materials
      ➢ Bone & Horn
      ➢ Sinew
      ➢ Leather
      ➢ Hair
      ➢ Wood
   ii) Man-made materials
      ➢ Animal glue based composites

b) Modern:
i) Thermoset elastomers (medium and low crosslink density)

4) Flexible Thermoplastic Materials
   a) Antiquity:
      i) True Thermoplastics ????
         ➢ Horn
         ➢ Wood
   b) Modern:
      i) Most commercial thermoplastics

B) Traditional Processing Methods & Their Modern Analogues

1) Molding:
   a) Forging/Hammering/Compression
   b) Injection/Reaction Injection
   c) Blow Molding

2) Extrusion/Drawing:
   a) Wire
   b) Pipe

3) Casting:
   a) Ceramics
   b) Concrete
   c) Reaction Injection

4) Machining of Preformed Objects:

5) Relative Energy, Labor, etc., Costs
II Fabrication Methods

A) Challenges With Polymers

1) Viscosity
   a) back pressure
   b) shear

2) Melting
   a) heat transfer without decomposition at edges

3) Throughput Considerations

B) Compression Molding

1) Figure 4.1 in Stevens

2) Flow induced by applied pressure & heat
   a) may use lower molecular weight pre-polymer (B-Staging)

3) Common Uses
   a) Thermoset polymers
      i) cannot be melted once crosslinked
   b) Composite (Fiber Reinforced) materials
      i) e.g., fiberglass/epoxy & graphite/epoxy resins
C) **Injection Molding**

1) Figure 4.2 in Stevens
2) Thermoplastics
3) Screw Feed
   a) ⇒ pressure
   b) ⇒ heat
   i) heating coils
   ii) friction

D) **Reaction Injection Molding, RIM**

1) Figure 4.3 in Stevens
2) Thermoset Polymers
3) Polymerization-
   Crosslinking occur *in-situ*

E) **Blow Molding**

1) Figure 4.4 in Stevens
2) Thermoplastic
3) Common for both plastic and glass bottles
F) **Foam Production**

1) Foaming Agent
   a) Physical Blowing Agents
      i) Dissolved liquid/gas in early stage
      ii) Gas in later stage
         - temperature change &/or
         - pressure change
      iii) Examples
         - halocarbons
         - hydrocarbons
         - N₂, CO₂, etc.
   b) Chemical Blowing Agents
      i) decompose and give off gas

2) growing gas bubbles
   a) surface tension

3) Hard vs. Soft Foams

4) Open vs. Closed Cells

G) **Filament Production & Winding**

1) **Figure 4.5 in Stevens**

2) Extrusion of fiber
   a) molten
   b) in solution
c) reaction in situ
   i) crosslinks
   ii) fiber formation via monomer pyrolysis
      > graphite

3) Winding ⇒
   a) increased alignment
   b) increased crystallinity
   c) increased strength/stiffness

III Mechanical Properties

A) Dependence of Mechanical Properties on Molecular Weight

1) Figure 4.5 in Stevens
   a) trends in:
      i) Viscosity/Processability
      ii) Properties
      iii) Working Range

2) MW Effects
   a) end group concentration
      i) negligible above \( \approx 15,000 \)
   b) interchain forces
      i) increase with MW
      ii) utility of increased chain length drops after total interchain forces are greater than backbone strengths
3) Chemical Structure effects
   a) depend on type(s) of interchain bonding ⇒ required chain length

B) Mechanical Properties

1) Strength & Modulus
   a) Strength (Stress)
      i) a measure of how much force must be applied to get the sample to change
         by the desired amount (Strain)
   b) Modulus
      i) the resistance to deformation (≡ Stress/Strain)

2) Important Mechanical Properties
   a) Tensile Strength & Modulus
   b) Compressive Strength & Modulus
   c) Flexural Strength & Modulus
   d) Impact Resistance
      i) toughness

3) Failure
   a) Graceful vs. Catastrophic Failure
   b) Fatigue
      i) effects of repeated application of stress
C) Tensile Properties

1) Tensile Stress, $\sigma$
   a) a measure of how much force must be applied to get the sample to change by the desired amount (Strain)
   b) Tensile Stress $\equiv$ Applied Force/Cross Sectional Area
   c) $\sigma = F/A$

2) Tensile Strain, $\varepsilon$
   a) a measure of sample stretching
   b) Tensile Strain $\equiv$ Change in Sample Length/Original Length
   c) $\varepsilon = \Delta l/l$

3) Tensile Modulus, $E$
   a) the resistance to deformation
   b) Tensile Modulus $\equiv$ Tensile Stress/Tensile Strain
   c) $E = \sigma/\varepsilon$

4) Stress-Strain Curves
   a) Figure 4.7 & 4.8 in Stevens
   b) Brittle Material
      i) high modulus
         ➢ reversible before breakage
   c) Fiber
      i) lower or high modulus initially
         ➢ depending on
degree of crystallinity
chemical structure
etc.

⇒ elongation
reversible

ii) critical stress

⇒ flow of polymer chains & untangling of chains
⇒ rapid lengthening
∴ drop in applied stress felt
irreversible

iii) highly crystalline fiber

Figure 4.7 in Stevens

often yields breakage soon after yield point

iv) induced crystallinity in previously amorphous or low crystalline fiber

⇒ increased modulus
as in fiber drawing
often yields breakage soon after yield point

d) Elastomer

i) typically lower modulus overall

ii) reversible flow

iii) yield point

iv) irreversible flow
5) Temperature Dependence of Modulus

a) Amorphous Thermoplastic
   i) **Figure 4.9 in Stevens**
   ii) $T_g$ 
      ➢ rapid decrease of modulus
   iii) mp 
      ➢ rapid decrease of modulus

b) Other Materials
   i) **Figure 4.10 in Stevens**
   ii) Regions of Curves
      ➢ Brittle-Glassy region 
      ➢ Rubbery/Plastic region 
      ➢ Liquid Region 
   iii) Effects on Curves
      ➢ MW Effects 
      ➢ Crosslink Density Effects 
      ➢ Crystallinity Effects

D) Time Dependent properties

1) Creep
   a) cold flow
2) stress relaxation

E) Influences of Polymer Structure

1) Tables 4.1 & 4.2 in Stevens

<table>
<thead>
<tr>
<th>TABLE 4.1. Mechanical Properties of Common Homopolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
</tr>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Polyethylene, low density</td>
</tr>
<tr>
<td>Polyethylene, high density</td>
</tr>
<tr>
<td>Polypropylene</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
</tr>
<tr>
<td>Polystyrene</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>Polytertrafluoroethylene</td>
</tr>
<tr>
<td>Nylon 66</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>Polycarbonate</td>
</tr>
</tbody>
</table>

a) Values taken from Agranoff,11a converted to SI units, and rounded off.

b) To convert megapascals to pounds per square inch, multiply by 145.

c) Izod notched impact test (see Chap. 5). To convert newtons per centimeter to foot pounds per inch, multiply by 1.75.

<table>
<thead>
<tr>
<th>TABLE 4.2. Fiber Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Type</td>
</tr>
<tr>
<td>Natural</td>
</tr>
<tr>
<td>Cotton</td>
</tr>
<tr>
<td>Wool</td>
</tr>
<tr>
<td>Synthetic</td>
</tr>
<tr>
<td>Polyester</td>
</tr>
<tr>
<td>Nylon</td>
</tr>
<tr>
<td>Aromatic polyamide (aramid)</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>Polypropylene</td>
</tr>
<tr>
<td>Polyethylene (high strength)</td>
</tr>
<tr>
<td>Inorganic</td>
</tr>
<tr>
<td>Glass</td>
</tr>
<tr>
<td>Steel</td>
</tr>
</tbody>
</table>


b) To convert newtons per tex to grams per denier, multiply by 1.13.

c) Izod (see Chap. 2, structure 58).


IV  *Thermal Stability*

A) **Origins of Decomposition**

1) Bond breakage
   
   a)  $\Rightarrow$ decreased materials properties
   
   b)  $\Rightarrow$ depolymerization with many polymers
      
      i)  this is especially true with vinyl polymers

2) Aromatization upon heating

3) **Thermal Stability Criterion**
   
   a)  decompose at $\geq 400 \, ^\circ \text{C}$
   
   b)  retain useful properties near this temperature

B) **Thermally Stable Polymers**

1) **Table 4.3 in Stevens**
   
   a)  Inert atmosphere values

2) Primarily a function of bond energy
   
   a)  i.e., increased bond vibration $\Rightarrow$ bond rupture
   
   b)  aromatics have advantage in that breaking one bond does not disrupt structure
   
   c)  this is especially true with ladder type polymers where there are no single atom-atom interactions that solely hold together the polymer backbone

3) **Thermooxidative Stability values**
a) initial onset may be lower than those in inert atmospheres and the TGA curve will typically be different

b) initial decomposition is still via bond rupture then new mechanism involving oxidation may come into play

V  Flammability and Flame Resistance

A) Flammability Issues

1) Mechanical Failure

2) Heat Induced Damage

   a) direct heat effects on skin

   b) high temperature gasses

   c) hot “molten” materials on skin

3) Toxicity

   a) evolved gasses

   b) particulates

4) Relative Importance Varies for

   a) Structural Components

   b) Coatings

   c) Fabrics

   d) etc.

5) Terminology

   a) Nonflammable

      i) e.g., PVC
b) Self-Extinguishing
   i) e.g., polycarbonates

c) Flammable

B) **Mechanism of Flames**

1) **Figure 4.11 in Stevens**

2) Flame Components
   a) Pyrolysis Zone
   b) Diffusion Zone
   c) Combustion Zone

3) Kinetic & Thermodynamic Processes
   a) Heat Transfer/Loss
      i) generated by ignition source
      ii) generated by combustion
      iii) causes pyrolysis
      iv) heating of gasses
      v) radiative loss
   b) Mass Transfer
      i) diffusion of fuel molecules
         - CO
         - C₂H₂
         - H₂
         - etc.
ii) diffusion of oxygen molecules

iii) diffusion of combustion products

- CO₂
- H₂O
- etc.

4) Flame resistance/retardent strategies

a) starve flame for fuel

i) decrease pyrolysis

ii) insulating/impermeable crusts

- char formation
- phosphorous containing materials in cellulosic fibers

iii) cool pyrolysis zone

- Al₂O₃.3H₂O
- NaHCO₃

b) inhibit heat flow to pyrolysis zone

i) must slow combustion

ii) Free Radical Scavengers (Radical Traps)

- halogens
  - toxicity
- phosphorous compounds

iii) increased amounts of spectator gasses

- their heat capacity lowers flame temperature
VI  Chemical Resistance

A) Morphology Influence

1) For most reactions, chemical reagents must diffuse into bulk polymer
   a) ∴ deduced diffusion ⇒ reduced reactivity
   b) decrease pore size/volume
   c) make polymer and chemical incompatible so that they repel each other
      i) e.g.,
         ➢ hydrophobic polymers
         ➢ fluoropolymers

2) Chemical Reactivity
   a) Polymers react similarly to their discrete molecule analogues
      i) albeit often slower
      ii) ∴ choose polymers that chemically are expected to be unreactive
   b) e.g.,
      i) Ozone converts C=C into carbonyls

VII  Electrical Conductivity

A) Band Structure & Conductivity

1) Relationship of Molecular Orbitals to Bands
   a) Hückel Orbitals for Aromatics
      i) Benzene
      ii) Naphthalene
      iii) Anthracene
iv) Graphite

b) Structural Isomers of PAHs
   i) Anthracene & Phenanthrene
   ii) changes to HOMO-LUMO Gap
   iii) Nature of HOMO
   iv) etc.

2) Classes of Conductors
   a) Metallic Conductors
   b) Semiconductors
      i) thermal population
      ii) photoconductors
      iii) n-type & p-type doped semiconductors
   c) Insulators

B) Polymeric Conductors/Semiconductors

1) Structural Features for Conductivity
   a) Delocalization usually required
      i) conjugation of $\pi$ system
         ➢ Molecules 20-23 in Stevens
            ▪ poly(sulfur nitride)
            ▪ polyacetylene
      ii) exceptions via charge transfer between pendant groups
         ➢ poly(N-vinyl-cabazole), 19
2) Mechanism of Conductivity
   a) Interchain Electron Transfer!
   b) Valence & Conduction band populations
   c) Solitons
      i) Figure 4.14 in Stevens
   d) Doping
      i) Molecules 23a in Stevens
         ➢ p-type doping
         ➢ n-type doping
      ii) Property Changes on Doping
         ➢ thermal stability
         ➢ oxidative stability
         ➢ processability
3) Measuring Conductivity
   a) Units of conductivity, \( \sigma \)
      i) siemens (S)/cm
      ii) siemen = 1/ohm
   b) Classes
      i) Insulators
         ➢ \( \sigma < 10^{-9} \text{ S/cm} \)
ii) Semiconductors
   - $10^{-8} < \sigma < 10^2 \text{ S/cm}$

iii) Conductors
   - $\sigma \cdot 10^2 \text{ S/cm}$

c) Examples
   i) poly(sulfur nitride), 20
      - 100 S/cm
      - superconductive at about 0.3 K
   ii) polyacetylene (undoped)
      - $1.7 \times 10^{-9} \text{ S/cm for cis}$, 22
      - $4.4 \times 10^{-5} \text{ S/cm for trans}$, 23
      - doped materials are conductive in metallic range
        - Molecules 23a in Stevens
        - doping converts cis to trans isomers

C) Conjugated Organic Polymeric Conductors

1) Examples of Conjugated Organics
   a) Molecules 24-28 in Stevens
   b) polyaniline, 24
   c) polypyrrole, 25
   d) polythiophene, 26
   e) poly(para-phenylene), 27
   f) poly(para-phenylenevinylene), 28
2) Experimental Conductivities
   a) **Table 4.5 in Stevens**
   b) Typically less than those of polyacetylene
      i) sufficient for commercial application
      ii) better stabilities

3) Applications
   a) anti-static materials
   b) light weight batteries
   c) thin film transistors
   d) light-emitting diodes
   e) molecular electronics

4) Ionic Conductors/Electrolytes
   a) **Molecules 29 & 30 in Stevens**
   b) poly(ethylene oxide), **29**
   c) polyphosphazenes, **30**
   d) Key properties
      i) highly amorphous
      ii) low $T_g$
      iii) $\Rightarrow$ highly mobile ions
         e.g., $\text{Li}^+$
VIII Nonlinear Optical, NLO, Properties

A) Non-Linear Optical Behavior

1) 1\textsuperscript{st} Order (linear) behavior
   a) refraction, etc., typically see in our lives

2) 2\textsuperscript{nd} Order behavior, $\chi_2$
   a) frequency doubling
   b) requires molecular dipoles on Chromophores
      i) increases with
         ➢ extended conjugation
         ➢ $\pi$ donor/acceptor strength
      ii) called $\beta$ values in solution
   c) requires that they be aligned
      i) Poling of polymeric solids
      ii) non-centrosymmetric single crystals
      iii) host-guest complexes

3) 3\textsuperscript{rd} Order behavior, $\chi_3$
   a) frequency tripling
   b) requires polarizable materials on Chromophores

4) 2\textsuperscript{nd} & 3\textsuperscript{rd} order effects
   a) interaction of electric fields of light with those of sample
   b) $\Rightarrow$ electro-optic interactions
      i) $\Rightarrow$ electrical-light signal converters
   c) $\Rightarrow$ optical-optical interactions
ix) => all optical device elements

IX Additives

A) Turn Polymers into Plastics

1) Found in almost all commercial plastics

2) Purposes
   a) Alter polymer properties
      i) pigments
      ii) odorants
      iii) stability
      iv) mechanical property modification
      v) crosslinking agents
      vi) etc.
   b) Improve processability
      i) lubricants

3) Interactions with Polymers
   a) Miscible
   b) Immiscible

B) Commercial Additives

1) $10^9$ kg used per year in US

2) Classes
   a) Table 4.6 in Stevens
3) Examples

a) Table 4.7 in Stevens

b) Plasticizers
   i) permanence
      ➢ “new car smell”
      ➢ solubility parameters
   ii) toxicity
   iii) di-2-ethylhexyl phthalate, 33