Structure and Properties of Engineering Polymers

Lecture: Polymeric Materials: Molecular Viewpoint

Nikolai V. Priezjev

Polymeric Materials: Molecular Viewpoint

• Periodic table of elements, number of protons, electrons, neutrons; atomic weight, electron orbitals, and octet rule

• Covalent bonding, bond energy, carbon atom bonding, hybridization

• Secondary Bonding: dipole hydrogen bonds, van der Waals forces

• Ionic and Metallic bonding

• Functional groups, formation of polymers

• Thermoplastics and thermosets

• Copolymers

**Reading:** Chapter 2 of *Plastics: Materials and Processing* by A. Brent Strong

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Dmitri Mendeleev published the first periodic table in 1869.

Neutron = $1.6749286 \times 10^{-27}$ kg
Proton = $1.6726231 \times 10^{-27}$ kg
Electron = $9.1093897 \times 10^{-31}$ kg
M proton = $1837$ M electron
Electron Configuration: Electron Orbitals

(a) The lone $s$ orbital is spherical in distribution. (b) The three $p$ orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five $d$ orbitals are rosette in shape, except for the $d_{z^2}$ orbital, which is a “dumbbell + torus” combination. They are all oriented in different directions.
Heisenberg and Schrödinger get pulled over for speeding.

The cop asks Heisenberg "Do you know how fast you were going?"

Heisenberg replies, "No, but we know exactly where we are!"

The officer looks at him confused and says "you were going 108 miles per hour!"

Heisenberg throws his arms up and cries, "Great! Now we're lost!"

The officer looks over the car and asks Schrödinger if the two men have anything in the trunk.


The cop opens the trunk and yells "Hey! This cat is dead."

Schrödinger angrily replies, "Well he is now."
**Octet Rule** = atoms tend to gain, lose or share electrons so as to have 8 electrons

- C would like to gain 4 electrons
- N would like to gain 3 electrons
- O would like to gain 2 electrons

Each noble gas has a **fully filled** valence shell.
What is chemical bonding?

Chemical Bonding is the way in which atoms join together with each other.

sodium metal + chlorine gas → table salt
Formation of Covalent Bonds (between non-metals)

Consider hydrogen, H₂, the simplest molecule. A hydrogen atom has a single valence electron. A single covalent bond is formed when a pair of electrons is shared between two, usually nonmetal, atoms.

Bond strength = 
Amount of energy needed to break the bond

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The diagram shows the energy for two hydrogen atoms. There is a clear minimum at 74 pm (0.74 Å). Therefore one can say that the bond length is 74 pm. The bond strength is the depth of this "well" which is 436 kJ mol⁻¹. That is the amount of energy the H₂ molecule would need to gain to break the bond and end up as two separate H atoms.

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Bond Formation Process

- It is an **exothermic process** (energy released in a form of heat)

- Strong, STABLE bonds require lots of energy to be formed or broken
- Weak bonds require little energy

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**Bond Breaking Process**

- **Endothermic reaction**
  - energy must be put into the bond in order to break it

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Secondary Bonding: Electric Dipoles

An electric dipole is basically a pair of equal positive and negative charges separated by a small distance.

These dipoles will arise, for example, in a molecule, where atoms share an electron, but the electron spends more time with one atom, because it is bigger, and less time with the smaller atom.

The effective charge separation may be only a fraction (perhaps a tenth) of the electron's charge.

Bonding between dipoles happens when the positive end of one dipole is attracted to the negative end of another.

Since the effective charges are small compared with those involved in primary bonding, secondary bonding is about one tenth of primary bond strengths.

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Secondary Bonding: dipole hydrogen bonds

A special type of dipole-dipole attraction bonds form due to the polarity of water.

Hydrogen bonds keep water in the liquid phase over a wider range of temperatures than is found for any other molecule of its size. Permanent dipole is created due to asymmetrical arrangement of hydrogen atoms.
Secondary Bonding: van der Waals forces

- Fluctuation-induced dipole bonds
  - Charge on atom in motion being re-distributed
  - Electric dipole
  - Induced electric dipole
- Polar molecule induced dipole bonds
  - Neutral atoms form dipole
- Permanent dipole bonds: HCl

Van der Waal bonds

\[ U_N = -\frac{A}{r^6} + \frac{B}{r^n} \quad n \approx 12 \]

Linear chains

**Attraction Energy**  **Repulsion Energy**
Ionic bonds are formed when an atom that has a strong tendency to give up electrons (a metal) is in close proximity to an atom that has a strong tendency to accept electrons (a nonmetal). This nearness of the atoms allows a transfer of one or more electrons.

(a) Formation of a metal (Na\(^+\)) ion and a nonmetal (Cl\(^-\)) ion as a metal atom and a nonmetal atom approach each other

(b) Many metal (Na\(^+\)) ions and nonmetal (Cl\(^-\)) ions in a crystal structure showing attractive forces between oppositely charged ions

**Figure 2.4** Ionic bonding and the resulting crystal structure.
Metallic Bonding: Me in the sea of electrons

(a) Formation of metal (Fe^{++}) ions and sea of electrons as metal atoms approach each other

(b) Many metal (Fe^{++}) ions in a crystal structure surrounded with a sea of electrons

Figure 2.5 Metallic bonding of iron and the resulting crystal structure.
Covalent Bonding

Figure 2.6 Covalent bonding between one carbon (C) and four hydrogens (H) to form methane (CH₄).

One bond = 2 shared electrons

(a) Formation of covalent bonds between nonmetal atoms (one C and four H atoms)

(b) Representation of the resulting CH₄ molecule using conventional chemistry notation

Three dimensional structure?
Carbon Atom Bonding

- The number of valence electrons attempts to satisfy the octet rule.
- Each bond has two electrons.
- Each bonding orbital moves as far away from all other orbitals as possible. Repulsion between orbitals containing electrons.

**Hybridization:** Formation of $sp^3$ orbitals

**Lewis dot structures:**

(a) Methane ($CH_4$)

(b) Chloromethane ($CH_3Cl$)
FIGURE 1.10  The structure of ethane. The carbon–carbon bond is formed by sigma overlap of two carbon $sp^3$ hybrid orbitals.
Carbon-Carbon Molecular Orbitals: Structure of Ethylene

(b) Unstable configuration

(c) Ethene or ethylene ($C_2H_4$)

(a) Prior to overlap of $p_y$ orbitals

(b) After overlap of $p_y$ orbitals to form a $\pi$-bond

Figure 2.13 Types of bonding in double bonds (ethylene).
Hydrocarbon Molecules

Examples of *saturated* (all bonds are single ones) hydrocarbon molecules:

- **Methane, CH₄**
- **Ethane, C₂H₆**
- **Propane, C₃H₈**

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Hydrocarbon Molecules

In table below R represents a **radical**, an organic group of atoms that remains as a unit and maintains their identity during chemical reactions (e.g. CH$_3$, C$_2$H$_5$, C$_6$H$_5$).

<table>
<thead>
<tr>
<th>Family</th>
<th>Characteristic Unit</th>
<th>Representative Compound</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohols</td>
<td>R—OH</td>
<td>Methyl alcohol</td>
<td>Methanol, “wood alcohol” toxic, chemical manufacturing, fuel</td>
</tr>
<tr>
<td>Ethers</td>
<td>R—O—R′</td>
<td>Dimethyl ether</td>
<td></td>
</tr>
<tr>
<td>Acids</td>
<td>R—COH</td>
<td>Acetic acid</td>
<td>Vinegar smell</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>R—C=O</td>
<td>Formalddehyde</td>
<td></td>
</tr>
<tr>
<td>Aromatic hydrocarbons</td>
<td>R—OH</td>
<td>Phenol</td>
<td></td>
</tr>
</tbody>
</table>
**Functional Groups:**

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Name</th>
<th>Functional Group</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{R} - \text{C} = \text{C} - \text{R'}$</td>
<td>Alkene</td>
<td>$\text{R} - \text{C} - \text{N} - \text{R'}$</td>
<td>Amide</td>
</tr>
<tr>
<td>$\text{R} - \text{C} = \text{O} - \text{H}$</td>
<td>Alcohol</td>
<td>$\text{R} - \text{C} - \text{C} - \text{R'}$</td>
<td>Ether</td>
</tr>
<tr>
<td>$\text{R} - \text{N} - \text{H}$</td>
<td>Amine</td>
<td>$\text{R} - \text{N} = \text{C} = \text{O}$</td>
<td>Isocyanate</td>
</tr>
<tr>
<td>$\text{R} - \text{C} = \text{O} - \text{H}$</td>
<td>Acid</td>
<td>$\text{R} - \text{C} = \text{C} - \text{C} - \text{C} - \text{C} - \text{C}$</td>
<td>Aromatic</td>
</tr>
<tr>
<td>$\text{R} - \text{C} = \text{R}'$</td>
<td>Ketone</td>
<td>$\text{R} - \text{C} = \text{C} - \text{H}$</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>$\text{R} - \text{C} - \text{O} - \text{H}$</td>
<td>Acid</td>
<td>$\text{R} - \text{C} = \text{C} - \text{C} - \text{C} - \text{H}$</td>
<td>Aromatic</td>
</tr>
<tr>
<td>$\text{R} - \text{C} = \text{O} - \text{C} - \text{R'}$</td>
<td>Ester</td>
<td>$\text{R} - \text{C} = \text{C} - \text{C} - \text{H}$</td>
<td>Aromatic</td>
</tr>
</tbody>
</table>

**Figure 2.14** Functional groups in organic chemistry. (Some hydrogen atoms have been omitted for simplicity and ease of focusing on key atoms in the functional group. The R can be any organic group.)
Chemistry of Polymer Molecules

When all mers are the same, the molecule is called a **homopolymer**

When there is more than one type of mer present, the molecule is a **copolymer**

Mer units that have 2 active bonds to connect with other mers are called **bifunctional**

Mer units that have 3 active bonds to connect with other mers are called **trifunctional**. They form three-dimensional molecular network structures

Polyethylene (bifunctional)  
Phenol-formaldehyde (trifunctional)

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Isomers are molecules that have the same composition (contain the same atoms) but have different atomic arrangement. An example is butane and isobutane:

Butane → $\text{C}_4\text{H}_{10}$ ← Isobutane

Butane is suited for use as a fuel for cigarette lighters and torches, whereas isobutane is best used as a refrigerant and a propellant in spray cans.
Isomers (cont.)

- **Isomerism**
  - two compounds with same chemical formula can have quite different structures

  **Ex: C$_8$H$_{18}$**
  - n-octane

  \[
  \text{H-C-C-C-C-C-C-C-H} = \text{H}_3\text{C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3
  \]

  \[
  \downarrow \quad \text{H}_3\text{C}\langle\text{CH}_2\rangle_6\text{CH}_3
  \]

  - 2-methyl-4-ethyl pentane (isooctane)

\[\text{CH}_3\]

\[\begin{array}{c}
\text{H}_3\text{C-CH-CH}_2\text{-CH-CH}_3 \\
\text{CH}_2 \\
\text{CH}_3
\end{array}\]

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Isomers are molecules that have the same composition (contain the same atoms) but have different atomic arrangement. Geometrical isomerism: consider two carbon atoms bonded by a double bond in a chain. H atom or radical R bonded to these two atoms can be on the same side of the chain (cis structure) or on opposite sides of the chain (trans structure).

\[
\text{ cis-2-butene } \\
\text{ trans-2-butene } \\
\]

The same molecule!

Trans/cis structure

restricted rotation (often involving a carbon-carbon double bond)
**Stereoisomerism**

**Stereoisomerism:** atoms are linked together in the same order, but can have different spatial arrangement.

- **Isotactic configuration:** all side groups R are on the same side of the chain.

- **Syndiotactic configuration:** side groups R alternate sides of the chain.

- **Atactic configuration:** random orientations of groups R along the chain. Can’t Crystallize
Quiz

1. Every covalent bond is made up of how many electrons?
   a) one  
   b) two  
   c) three  
   d) eight  

   b) two  

2. Most polymers in use today are molecules with a backbone consisting primarily of which basic element?

   (a) carbon  

3. When naming organic compounds, the prefix but- (or buta-) is used to indicate which quantity?
   a) four  
   b) five  
   c) six  
   d) seven  

   a) four  

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Polymer chains: how to assemble?

4 bonds for each carbon atom

\[ \begin{align*}
&\text{(c) Semiabbreviated notation} \\
&\text{Figure 2.16 Three-dimensional perspective representation of ethylene monomers built into a polymer chain (polyethylene).}
\end{align*} \]

(a) Electron-dot notation

(b) Full notation
Formation of polymers: **Chain-Growth polymerization**

**Step-growth polymerization** or **condensation polymerization**

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Formation of polymers: **Chain-Growth polymerization**

**Peroxide initiator** $\text{R-O} \cdot \cdot \cdot \text{O} \cdot \rightarrow \text{R} \cdot \cdot \cdot \rightarrow 2\text{R} \cdot \cdot \cdot \cdot \cdot$

**Free radical**

**Heat**

**Monomer** $\text{C}_2\text{H}_4$

**Additional polymerization:**

**Initiators:** part of the chain end

**Catalysts** are not “used up”, Me

**New bond**

**Growing chain**

**New bond**

**Growing chain**

**New free radical**

**Monomer free radical**

**New monomer**

**Carbon free radical**

**Free radical**

**pi (\(\pi\)) bond**

**Pi (\(\pi\)) bond in new monomer**

**Several thousand units in a chain!**
Formation of polymers: Chain-Growth polymerization

**Addition** in which one “mer” is added to the structure at a time.

This process is begun by an ***initiator*** that "opens up" a C=C double bond, attaches itself to one of the resulting single bonds, & leaves the second one dangling to repeat the process.

**Termination** when two active chain ends meet each other or active chain end meet with initiator or other species with single active bond.

Rapid propagation ~1000 mer units in 1-10 ms:
Formation of polymers: **Chain-Growth polymerization** (cont.)

**How to end the polymer chain?**

*Another radical* at the chain end

*Two half-chains* meet and form one chain

**Additional polymerization:**

*Initiators*: part of the chain end

*Catalysts* are not “used up”, Me

**Branching process:**

[Diagram of branching process showing carbon free radical, new bond, hydrogen free radical, and molecular structures.]
Formation of polymers: Chain-Growth polymerization (cont.)

Several thousand units in a chain!

Monomer

Polymers

Ethylene

Polyethylene

Propylene

Polypropylene

Vinyl chloride

Polyvinylchloride

Methyl methacrylate

Polymethylmethacrylate

Styrene

Polystyrene

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Step-growth polymerization or condensation polymerization

**Figure 2.23** Reaction between dissimilar functional groups, which is the basis of condensation or step-growth polymerization reactions.

(a) Reaction of an alcohol and an acid to make an ester and water

(b) Reaction of an amine and an acid to make an amide and water
Step-growth polymerization or condensation polymerization

Condensation reaction steps to form a polyamide

No initiator or catalyst just heat and stir

Cool down or end-caps
## Comparison of Addition and Condensation Polymers

<table>
<thead>
<tr>
<th></th>
<th>Addition or Chain-Growth Polymerization</th>
<th>Condensation or Step-Growth Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer growth mechanism</td>
<td>Chain reaction</td>
<td>Step-by-step reactions</td>
</tr>
<tr>
<td>Dependence on previous step</td>
<td>Yes—sequential dependent events</td>
<td>No—-independent events</td>
</tr>
<tr>
<td>Initiator needed</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Type of monomer</td>
<td>Contains carbon-carbon double bond</td>
<td>Bifunctional (has reacting functional groups on the ends)</td>
</tr>
<tr>
<td>Number of active sites (functional groups) per monomer</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Number of different types of monomers needed to form polymer</td>
<td>1</td>
<td>2 (usually)</td>
</tr>
<tr>
<td>By-product formed</td>
<td>No</td>
<td>Yes (usually)</td>
</tr>
<tr>
<td>New type of bond formed</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Basic representation (polymer repeat unit)</td>
<td>Monomer without the double bond and with bonds on either side</td>
<td>Two monomers joined together</td>
</tr>
<tr>
<td>Polymer chain characteristics</td>
<td>A few, long chains</td>
<td>Many, not very long chains</td>
</tr>
<tr>
<td>Branching</td>
<td>Possible</td>
<td>Unlikely</td>
</tr>
<tr>
<td>Name of polymer</td>
<td>Poly + name of monomer</td>
<td>Poly + name of new bond</td>
</tr>
</tbody>
</table>
Thermoplastics and Thermosets

Like candy caramels: soften and melt when heated, then put in mold and cooled to take its shape; repeat many times. Solid at room T.

Thermosets cannot be reshaped; curing process.

**Thermoplastics** - materials become fluid and processible upon heating, allowing them to be transformed into desired shapes that are stabilized by cooling.

- polyethylene
- polypropylene
- polycarbonate
- polystyrene

**Thermosets** - initial mixture of reactive, low molar mass compounds reacts upon heating in the mold to form an insoluble, infusible network

- vulcanized rubber
- epoxies
- polyester resin
- phenolic resin
Thermoplastics and Thermosetting Polymers

- **Thermoplastics:**
  - little cross-linking
  - ductile
  - soften w/heating
  
  Ex: grocery bags, bottles

- **Thermosets:**
  - large cross-linking
    (10 to 50% of mers)
  - hard and brittle
  - do NOT soften w/heating
  - vulcanized rubber, epoxies, polyester resin, phenolic resin
  
  Ex: car tires, structural plastics

Phenol-formaldehyde (trifunctional)
**Thermoplastics and Thermosets**

**Thermoplastics:**
- little crosslinking
- ductile
- soften w/ heating
- polyethylene
- polypropylene
- polycarbonate
- polystyrene

**Thermosets:**
- large crosslinking (10 to 50% of mers)
- hard and brittle
- do NOT soften w/ heating
- vulcanized rubber, epoxies, polyester resin, phenolic resin

Adapted from Fig. 15.19, *Callister 7e*. (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

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Vulcanization

In thermoset, the network is inter-connected in a non-regular fashion. *Polyisoprene*, the hydrocarbon that constitutes raw natural rubber, is an example. It contains unsaturated C=C bonds, and when vulcanizing rubber, sulfur is added to promote crosslinks. Two S atoms are required to fully saturate a pair of –C=C— bonds and link a pair of adjacent molecules (mers) as indicated in the reaction.

Without vulcanization, rubber is soft and sticky and flows viscously even at room temperature. By crosslinking about 10% of the sites, the rubber attains mechanical stability while preserving its flexibility. Hard rubber materials contain even greater sulfur additions.
Vulcanization (cont.)

Two adjacent polyisoprene molecules...

Isoprene mer

can be joined together by a sulfur atom

Isoprene mer

or by a series of S atoms (vulcanization).
Copolymers

two or more monomers polymerized together

- **random** – A and B randomly vary in chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A alternate with large blocks of B
- **graft** – chains of B grafted on to A backbone

A – \[\text{Structure of A}\]

B – \[\text{Structure of B}\]

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Block Copolymer Microstructures

- **Linear**
  - diblock copolymers
  - triblock copolymers
    - **ABA type**
    - **ABC type** (ABCD, ...)

- **Lamella structure.**
- **Double gyroid (bicontinuous) structure.**
- **Cylindrical dispersion structure.**
- **Spherical dispersion structure.**
Summary

- Periodic table of elements, number of protons, electrons, neutrons; atomic weight, electron orbitals, and octet rule
- Covalent bonding, bond energy, carbon atom bonding, hybridization
- Secondary Bonding: dipole hydrogen bonds, van der Waals forces
- Ionic and Metallic bonding
- Functional groups, formation of polymers
- Thermoplastics and thermosets
- Copolymers

Reading: Chapter 2 of Plastics: Materials and Processing by A. Brent Strong