Lecture 26, Mar 28, 2022

Tacticity

- Polyethylene crystallizes readily, giving it higher density
- *Isotactic*: The functional group in the mer unit is always on the same side
- *Syndiotactic*: The functional groups alternate on both sides
- *Atatic*: Random placement of the functional groups
- In general isotactic is the easiest to crystallize, followed by syndiotactic and then atactic
- e.g. atactic polypropylene is amorphous (linear low density PP, clear and flexible, used in soda bottles), vs isotactic PP which is more crystalline, stronger and more rigid, used in detergent bottles

Side Chains

- PE chains are never perfect single chains; they always have side chains coming out
- HDPE has shorter side chains, making it easier for chains to line up and crystallize; LDPE has longer side chains, making it harder to crystallize, more flexible and less strong
  - The actual densities are not very different, but the crystallinity creates large differences in material properties

Changing Mer Units (Composition)

- Different mer units have different intermolecular bonding
- Example: PVC (changing one of the hydrogens on PE to chlorine)
  - Chlorine is much more electronegative and forms a dipole, creating a polar molecule
  - Since intermolecular forces are dipole-dipole interactions, the stronger polarization creates a stronger intermolecular bond

Cross Linking

- Creating covalent bonds between polymer chains (primary bonding between chains)
- Since primary bonds are much stronger than secondary bonds this makes the polymer stronger
- Cross linking also prevents plastic flow, i.e. plastic deformation
- Example: Vulcanization of rubber
  - Sulfur compounds build cross links between raw rubber chains
  - Raw rubber from the tree is a fluid, but after vulcanization the new bonds hold the rubber together
- Elastomer: A polymer with large elasticity (i.e. it can be stretched a lot without plastic deformation)
  - Elastomers can be created with cross linking, since the primary bonds pull the chains back to their original position
  - However too much cross linking makes the polymer brittle
- Hysteresis: The return curve upon unloading is not the same as the original loading curve
  - When some materials are loaded and then unloaded, the return path on unloading is different, even though there is full elastic recovery
  - Since the area under the stress-strain curve represents energy, loading and then unloading takes energy (converts to heat)
  - This can be used for shock absorption as the elastomer absorbs energy

Temperature Dependence

- Intermolecular bonds have much lower energy than covalent or ionic bonds
- Energy in intermolecular bonds is comparable to thermal energy, meaning relatively small variations in temperature near room temperature can have large impacts on a polymer
- At colder temperatures polymers are brittle and behave almost like ceramics; at warmer temperatures they are much more flexible and can be deformed a lot