

- **Chapter 8: POLYMERS**

- Polymers are large molecules built by linking 50 or more smaller molecules called monomers
- It is a collection of very long molecules intertwined with one another
- Each of these great long strings of atoms is actually a very large molecule.
- The bonds that hold these atoms together within the molecule or string would be called **intramolecular** bonds (intra means within)
 - intramolecular bonds are so much stronger than any of the other bonds present we often call them **strong intramolecular** bonds
 - **Intramolecular forces** are the forces that hold atoms together within a molecule.(strong)
- **Intermolecular forces** are forces that exist between molecules.(weak)
 - When a polymer is plastically deformed, one of the things that occurs within the microstructure is that molecules slide past one another.
 - There are forces that occur between molecules, so we could call them intermolecular forces (inter means between)
- Plastic deformation occurs largely by the movement of long molecules past one another, overcoming weak forces between molecules as plastic deformation occurs
 - So, as we plastically deform a polymer and the molecules become aligned along the loading axis we get an **increase** in the amount of the load that is supported by primary bonds and less of the load supported by secondary bonds.

❖ The Stress-Strain Behaviour of a Typical Polymer:

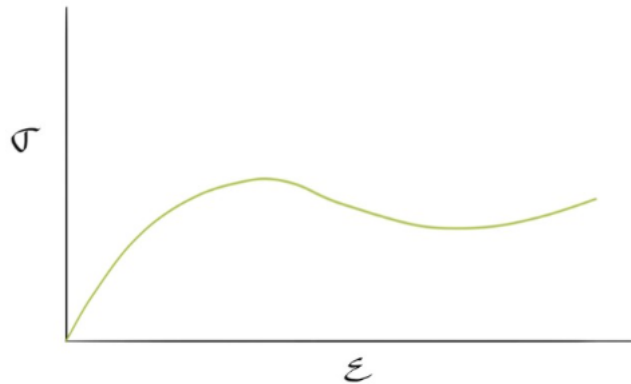


Figure 3. The generalized stress-strain curve for a plastic polymer.

- there is an initial portion of the curve that is approximately linear.
- This region is followed by a curved region and a peak stress.
- After that, the stress decreases, but the unique feature of the polymer curve is that the polymer is somehow able to continue load bearing after the peak
- Recall that metals will always break after the peak, or ultimate tensile strength, because this is where necking occurs and the metal can't strengthen fast enough to overcome the rapidly decreasing cross-sectional area in the neck.
 - This means that some polymers must have a microstructural mechanism that allows them to strengthen in the neck very significantly.
 - Something significant like, say, a change in the proportion of primary bonds to secondary bonds supporting the load.
 - The alignment of polymer molecules with the loading axis in this manner is frequently called **chain orientation**.
- Polymers are sometimes able to continue supporting load well beyond the ultimate tensile strength (onset of necking) as the molecules within a polymer can become elongated and oriented with the loading axis allowing the stronger intramolecular bonds to support the load

❖ DEFINING YIELD STRENGTH AND TENSILE STRENGTH

- Since the polymer continues to support load after necking, we can safely use the peak of the curve itself as an unambiguous point to define the yield strength.
- By convention, the point where the polymer fractures is called the tensile strength.

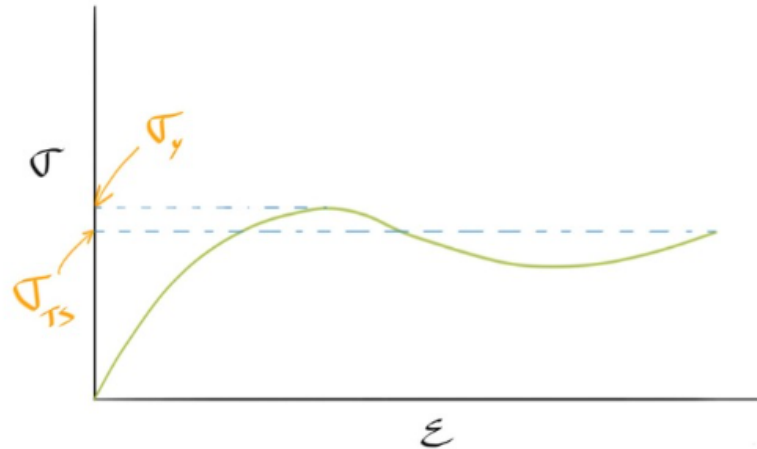


Figure 4. The generalized stress-strain curve for a plastic polymer, showing the yield strength and the tensile strength.

❖ POLYPROPYLENE (PP):

- The recycling code for PP is 5.
- Generally, PP is a little stronger and has a higher elastic modulus than polyethylene.
- This increase in mechanical properties comes from the extra CH₃ (methyl) group on the mer unit

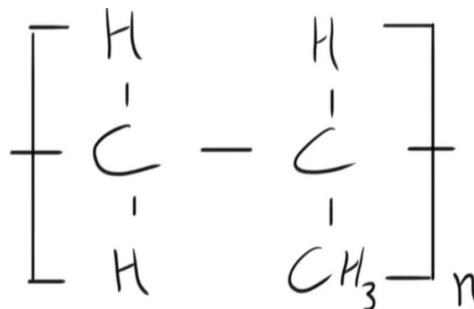
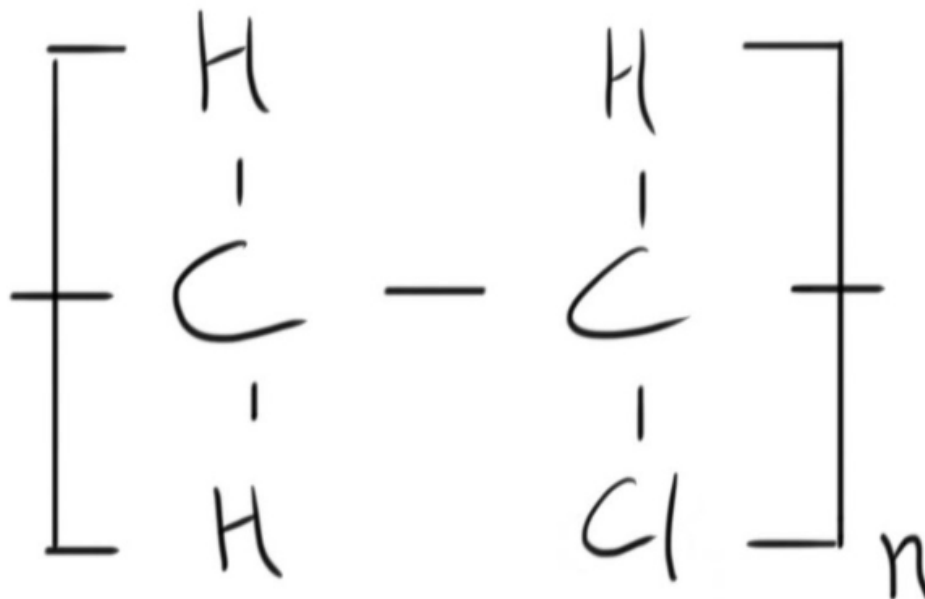


Figure 5. The mer unit for polypropylene. The methyl (CH₃) group makes it slightly harder for chains to slide past one another, increasing the strength.

❖ POLYVINYL CHLORIDE(PVC):

- PVC's name tells us that there must be a chlorine atom in the mer unit.
- The vinyl group is just two carbons bonded with a double bond and one hydrogen missing
- PVC is a very versatile polymer and can have a wide range of properties.
- In its simplest form, it is quite strong, with a relatively high elastic modulus.



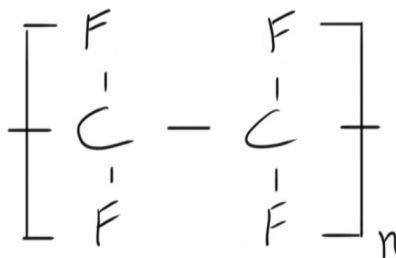
❖ The periodic table and electronegativity:

- As we move across the periodic table from left to right the elements get closer to a very low energy arrangement of their electrons.
- The rightmost column is called the inert gasses and these elements generally don't react with other elements, because they are so stable.
- This trend from left to right causes the elements towards the right to have a stronger attraction to electrons and the elements towards the left to be more likely to get rid of an electron.
- from the top to the bottom of the periodic table the atoms get larger
- Larger atoms mean that the electrons are further from the nucleus and that the nucleus attracts electrons less strongly.
- move from the bottom left to the top right of the periodic table there is an increasing attraction to electrons.
- This trend is captured in the so-called electronegativity.
- Elements with higher electronegativity reside towards the top right of the periodic table.

- Coming back to PVC now, you'll notice that chlorine (Cl) sits in the second row from the top, just to the left of argon (Ar) and therefore has a high electronegativity.
- When we put a highly electronegative element into a molecule, as we do in PVC, that electronegative element actually pulls on the orbiting electrons and creates a bit of an imbalance across the molecule.
- Because the electron carries a negative charge, this imbalance in the electron cloud can create charged regions of the molecule.
- When a molecule has a negative and positively charged ends, or poles we say that it is a dipole

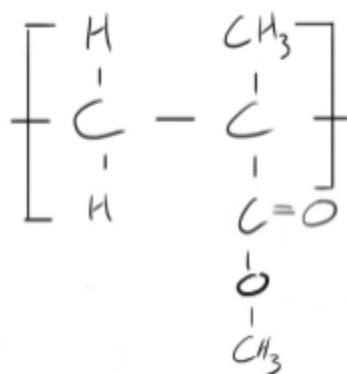
❖ POLYTETRAFLUOROETHYLENE:

- PTFE is used in non-stick surfaces.
- The key to PTFE's success as a nonreactive polymer lies in the large fluorine atoms bonded to each carbon.
- These fluorine atoms are quite large and protect the intramolecular bonds within PTFE from being broken easily.
- Note, that although fluorine is highly electronegative, the PTFE molecule is nonpolar since the fluorine atoms are geometrically symmetrical about the molecule and so the center of positive charge lies at the same point as the center of negative charge.
- Gore-Tex® is a form of PTFE that has been formed into thin films and stretched. The stretching introduces fine holes, or pores, in the film.
- PTFE, is a polymer that repels water (it is hydrophobic) so this means that water tends to form beads on the surface of PTFE.
- This prevents liquid water from passing through the pores in GoreTex®, however, individual molecules of water, as in the vapor phase, can freely diffuse through these pores.
- This is how GoreTex® used in outdoor clothing is able to keep the user dry in the rain while also allowing sweat to evaporate and diffuse out of the clothing.



❖ Polymethylmethacrylate (PMMA):

- The term acrylate tells us that this is an acrylic.
- You may know that some acrylics are used for windows because they can be made beautifully optically transparent.
- The reason that we are able to make PMMA optically transparent is very interesting and starts from the mer unit



- The large side group that is present on each mer unit prevents the molecules from organizing close to one another.
- This ensures the polymer is completely disorganized, or amorphous.
- You see, polymer molecules can become aligned with one another and highly organized, which we call crystalline.
- When a polymer crystallizes, the index of refraction is different from when it is amorphous.
- If the polymer contains parts that are amorphous as well as parts that are crystalline (so-called semicrystalline)
- then light passing through the polymer will not follow a direct path and the polymer will be translucent or opaque.
- So, part of the reason that PMMA is transparent is because the mer unit ensures that it stays 100% transparent.

❖ HOW LONG ARE THESE MOLECULES:

- When polymers are synthesized, it is somewhat difficult to control the length of the molecules
- So, we end up with a few molecules that are really short, a few that are very long and a bunch in between.
- WE ARE LEFT WITH A DISTRIBUTION OF MOLECULAR LENGTHS
- We could use an average.
- Simply sum up all of the molecule lengths and then divide by the total number of molecules.

- The average length of molecules in a polymer are typically described by The average mass of the molecules in the sample

❖ MOLECULAR WEIGHT:

- As we increase molecular weight in a polymer we increase the strength and typically increase the strain to fracture due to the increased entanglement of the long molecules.
- Ultra high molecular weight polyethylene (UHMWPE) is commonly used as a bearing surface in artificial hip replacements because of the high strength and high wear resistance from the extremely long molecules.

❖ HOW DO THESE MOLECULES STACK UP:

- We already know that polymer molecules, although often linear, are not straight.
- But that doesn't mean that they are always totally disordered.
- We also saw that some order can develop when a polymer is plastically deformed, so-called chain orientation.
- Well, there are other ways that polymers can order themselves and in some cases they can do it on their own, without any external loading.
- The molecules in a simple polymer like polyethylene will often fold back and forth on themselves, forming a so-called semi-crystalline polymer.



- Now, since the molecules are so long a polymer will never be able to crystallize 100%, which is why you see the amorphous tie molecules
- high density polyethylene (HDPE) has a higher percentage crystallinity than low density polyethylene (LDPE).
- Since the crystalline regions are held together more strongly by secondary bonds than the amorphous regions, these regions are stronger and, in fact, increasing the crystallinity of a polymer is another way to increase its strength.
- It will also typically increase the resistance to chemical dissolution and allow the polymer to be used at a higher temperature.



Figure 18. A cartoon sketch of LDPE and HDPE showing the increased and longer branches in LDPE, preventing extensive crystallization.

❖ **CHANGING THE INTRAMOLECULAR BONDS:**

- All Hydrogen needs is a somewhat electronegative element and hydrogen gets positive.
- Hydrogen is so special in this ability to create a strong dipole that we have named a special type of intermolecular bond after it: the Hydrogen Bond.
- The hydrogen bond may occur when hydrogen is bonded in a molecule to oxygen (O), nitrogen (N), or fluorine (F). Kevlar®, for example, contains a hydrogen bonded to nitrogen and this allows strong Hydrogen bonding between molecules, contributing to a very strong polymer.

❖ **CROSS-LINKING OF POLYMERS:**

- Cross-linking can also be used to increase the strength of polymers.
- Cross-linking involves strong bonds(**intramolecular** bonds(covalent))
- Example: Vulcanizing rubber
 - When the latex is harvested from latex trees it is a creamy white somewhat viscous liquid.
 - Once left to dry out the latex becomes a solid, but is not very strong and has a relatively low elastic modulus.
 - To make this a much more useful material sulfur compounds are added and the latex is heated.
 - In the process the sulfur compounds create new strong, primary, bonds between the original molecules.
 - This limits their ability to move past one another, thereby increasing the strength
 - These cross-links also ensure that the molecules are pulled back to their original positions after a load is applied and released

- Important in elastomers
- Too much cross-linking causes the polymer to become hard and brittle
- Example: polyethylene
 - used in some pressurized water distribution systems is cross-linked to ensure that it can withstand the pressure in the system
 - also withstand the higher temperatures of hot water in residential water systems.

❖ IMPORTANT FACTS:

- increasing chain length increases the strength of a polymer
- High molecular weight=high yield strength
- HDPE mostly contains linear polymer chains
- Van Der Waal forces are INTERmolecular(weak)

❖ TEMP CHANGES:

- Polymers are sensitive to temperature changes
 - Much of the behavior of polymers is due to the weak, intermolecular, bonds.
 - These bonds, or interactions, can be disrupted much more easily by the thermal energy, even when the temperature is relatively low: close to room temperature.
-
- In a metal or a ceramic, most of the properties are determined by the nature of the strong, primary, bonds holding them together
 - and these bonds have bond energies significantly higher than the thermal energy close to room temperature.

- the stress-strain behavior for a typical plastic polymer in different temperatures

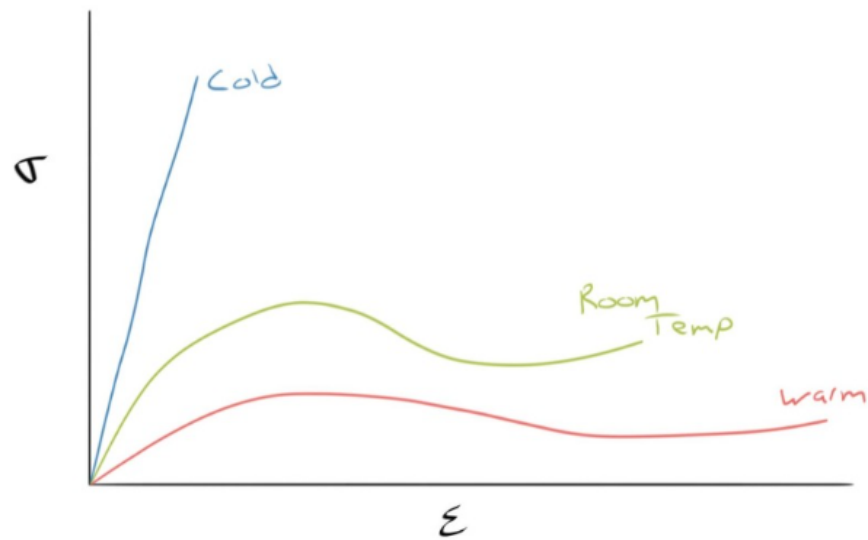


Figure 19. A stress-strain curve for a hypothetical plastic polymer at three temperatures. It is not uncommon for polymers to experience significant changes in mechanical properties with relatively small changes in temperature.

★ INCREASING HEAT ON POLYMERS:

- Polymers are viscoelastic
- PVC can be used at a higher service temperature.
- There are at least two important temperatures that you should be aware of when it comes to heating a polymer up:
 - glass transition temperature
 - and the melting temperature
 - Above the melting temperature the polymer will flow like a thick liquid because there is enough thermal energy to disrupt the weak intermolecular bonds and allow the molecules to flow freely past one another.
 - Upon heating, you may be able to imagine that the thermal energy will start to beat the intermolecular bond energy in the amorphous regions first, where the molecules are further apart. (glass transition temp)
 - With continued heating the thermal energy will eventually be enough to disrupt the intermolecular bonds in the crystalline regions and all of the molecules will be free to flow past one

another and the polymer will begin to flow like a thick liquid: melting.

- Therefore, the lower temperature, when the amorphous regions were disrupted is known as the glass transition temperature.

→ GLASS TRANSITION TEMPERATURE:

- ◆ The temperature upon heating, when molecules possess enough thermal energy to overcome the secondary, intermolecular interactions within the amorphous regions of the polymer

❖ TIME:

- polymers can have very different mechanical properties depending on how quickly we apply a load.
- polymers tend to behave in a more brittle fashion when loaded really quickly.
- When loaded quickly there is not enough time for them to move and instead the polymer fractures.
- However, Over the long time period, the molecules will slowly move past one another leading to a slow, but permanent, deformation process.
 - Example: A heavy desk is placed on a carpeted floor. If the desk is removed immediately there is only a small amount of deformation in the carpet and this deformation typically disappears within a matter of seconds or minutes. However, if the desk is left for several months, the deformation is significant and it will take a very long time, with a lot of vacuuming to reverse the load, for the deformation to disappear, if it ever does completely.

❖ Optical transparency of Plexiglas®:

- polymer being completely amorphous
- Photons of visible light interact with the electrons within a polymer, rather than by moving molecules relative to one another
- Crystalline and amorphous region have different index of refraction
- There will be scattering events which results in the semi-crystalline polymer to appear translucent
- HOW DO WE MAKE IT TRANSPARENT:
- Polymers are never 100% crystalline
 - 100% Amorphous (Plexiglas)

- This ensured that there were no boundaries between crystalline regions and amorphous regions that would scatter the light.
- Large side group prevents crystallization
 - Example: Sapphire(Al_2O_3)
 - Window glass-amorphous-clear
- When light passes through without scattering the polymer is transparent
- glassy metals that are fully amorphous but opaque.
- Even a single crystal metal, such as a silicon semiconductor, or a nickel-based single crystal jet turbine blade are both opaque, so neither being fully amorphous, nor fully crystalline ensures optical transparency.
- it all has to do with how the material absorbs light energy

❖ LOOK AT CHAPTER 9