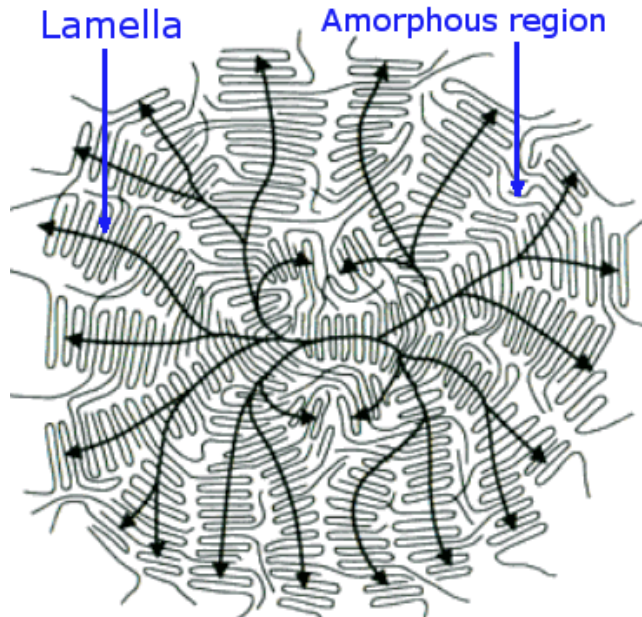


Polymers Lab- Differential Scanning Calorimetry (DSC)

Objectives Evaluate thermal transitions in polyethylene terephthalate (PET) and polypropylene (PP)

Background Polymers are either semicrystalline or totally amorphous. Semicrystalline polymers are composed of tightly packed polymer chains (lamellae) and amorphous regions.

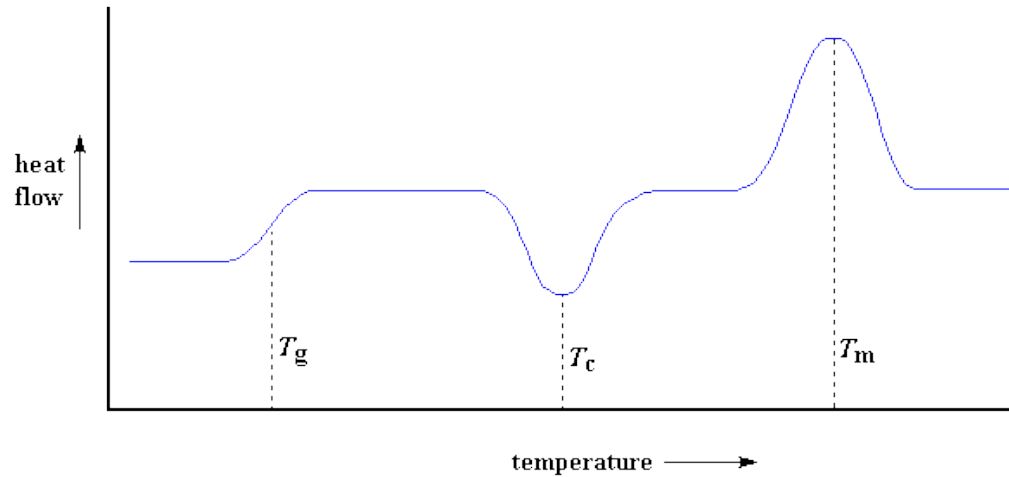


While crystallization is thermodynamically more favorable due to formation of more bonds, a system can cool too quickly and will solidify before crystallization is kinetically possible. This is how amorphous regions form. Common examples of amorphous solids are silica glass and atactic polystyrene. Crystallinity can have a significant impact on the properties of a material. For example, high density polyethylene has a higher degree of crystallinity in comparison to low density polyethylene. This makes it stiffer and more suitable for applications that require higher stiffness (milk jugs) as opposed to applications that warrant more pliable material (single use shopping bags).

Crystalline and amorphous regions have two distinct thermal transitions. Crystalline regions undergo crystalline melting, where the melting temperature (T_m) marks the temperature at which crystalline regions are at equilibrium with the polymer melt. Below this temperature there is a thermodynamic driving force for the polymer to crystallize. Melting is an endothermic process. When polymer crystals melt, the secondary interactions holding crystallites together break. This process requires heat to be absorbed from the environment, and this can be viewed as a peak in a plot of heat flow as a function of temperature. We will discuss this later in the context of DSC data. Amorphous regions undergo what is known as the glass-to-rubber transition (commonly called the glass transition). The glass transition temperature (T_g) is the temperature at which cooperative chain motion is allowed and results in a significant decrease in a material's stiffness. Since the glass transition temperature is heavily dependent on cooling rate and mechanical perturbation, it is a kinetic and not a thermodynamic quantity. This can also be explained by saying that there is no equilibrium between glassy and rubbery states around T_g . While it is not a thermodynamic transition, the glass transition

still causes a significant change in the heat capacity of a material, and this can be viewed as a step function in the plot of heat flow versus temperature.

Below is an example DSC plot during heating.



Initially, the semicrystalline polymer is below T_g and T_m . At T_g , heat capacity increases, so the heat flow per unit temperature increases. At this point, amorphous regions are much more mobile, and are kinetically allowed to crystallize. This is shown as an exothermic peak in the DSC (crystallization is forming of bonds which releases heat into the environment). Upon further heating, the sample melts and heat is absorbed from the environment, which is seen as an endothermic peak in DSC.

- Discussion**
- Describe how DSC works.
 - What processes can be measured in DSC? Compare the difficulty of measuring these different processes using DSC. What are the advantages and disadvantages of DSC in comparison to other techniques which measure the same thing?
 - Why is the data collected from DSC useful?
 - Can DSC be used to analyze molecules, or is it only useful for materials?
- Materials**
- Polyethylene terephthalate (PET), polypropylene (PP)
- Equipment**
- Mettler-Toledo Flash Differential Scanning Calorimeter
- Procedure**
1. Load your sample
 - a. Find the chip labeled PET or PP depending on what material you are testing.
 - b. Write down the chip's ID number.
 - c. Open the lid to reveal the sample holder.
 - d. Remove the sample cover with the magnetic gripping tool.
 - e. Using tweezers, load the sample into the holder so the sample is facing the correct direction (closer to S on the sample cover).

- f. Place the sample cover over the sample and tighten it into place. Then close the lid.
2. Turn on the instrument and STARe software.
3. Go to STARe method window
 - a. Under TA Technique, select Flash DSC
 - b. Select "Dynamic" in the toolbar
 - c. Set the start temperature to 25 °C
 - d. Set the end temperature to 280 °C for PET, 200 °C for PP
 - e. Set the heating rate to the desired rate (vary between 0.5 and 30 K/s)
 - f. Select dynamic again, and mirror your heating ramp with a cooling ramp
 - g. Go to File, Save as, and name your method
4. Go to STARe experiment window
 - a. Under TA Technique, select Flash DSC
 - b. Click the select method button, and choose your method and your chip ID.
 - c. Name your sample.
 - d. In the Module list, select Flash DSC 686
 - e. Press the send experiment button
5. Go to the FSC window and press OK (bottom right corner)
6. Go to STARe evaluation window.
 - a. Open your data
 - b. Go to File, Import/Export, Export Other Formats, and save your data as a text file.
7. Once all of your data is collected, close the software and turn off the instrument.

- References**
1. Young, R. Lowell, P. *Introduction to Polymers Third Edition*. Boca Raton, FL: Taylor & Francis Group.
 2. Differential Scanning Calorimetry. *Polymer Science Learning Center*.
<https://www.pslc.ws/mactest/dsc.htm>