Polymer Experiment 2: Differential Scanning Calorimetry of Poly(Ethylene Terephthalate)

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ABSTRACT

Using a differential scanning calorimetry, a multitude of things can be calculated concerning the structure and purity of poly(ethylene terephthalate). During the course of the experiment, the following values were determined. The entropy of fusion for PET was found to be -0.08 J/g*K; the glass temperature was found to be 75.73 °C; the weight percent of DEG in the PET was found to be 7.1%; the percent of crystalline in PET was found to be 21.86%; the percent of crystalline in quenched PET was found to be 4.21%. The importance of this is that the structure of PET changes when heated and rapidly cooled. The rapidly cooled PET forms much less crystals than the original, produced PET, which goes through a much slower cooling process in production.

INTRODUCTION

The objective of this experiment was to determine the temperature of fusion, the crystalline fraction, the weight percent of DEG, and the glass transition temperature of a poly(ethylene terephthalate), also known as PET. These values can be calculated from data obtained from a differential scanning calorimetry (DSC) instrument. By testing a sample of PET in a DSC machine, the enthalpy of fusion can lead to calculating these unknowns.

The value of the temperature of fusion is given by the DSC graphical printout, listed as the onset temperature. Using this temperature, the weight percent of DEG can be calculated using equation 1.1.

$$T_{fus}(℃) = 271 - 5.5(\text{wt\% DEG})$$

Equation 1.1

The glass transition is given by the DSC graphical printout, shown by a sharp decline prior to the endothermic change. When the polymer, after being heated, is rapidly cooled, crystallization occurs, as can be illustrated through the increased crystalline percent between the original and quenched sample. The difference in the state of matter with the increased crystals present causes a quick change in temperature and the dip causing the glass transition.

The percent of crystalline in the PET sample can be calculated in the following manner, according to equation 1.2.

$$\%\text{Crystalline} = \frac{\Delta H_{fus,exp}}{\Delta H_{fus,cry}}$$

Equation 1.2

The final value of interest, the entropy of fusion, is calculated through equation 1.3.

$$\Delta S = \frac{\Delta H_{fus}}{T}$$

Equation 1.3

EXPERIMENTAL

During the course of this experiment, three scans were conducted using a DSC machine (the basic diagram is shown in Figure 1).

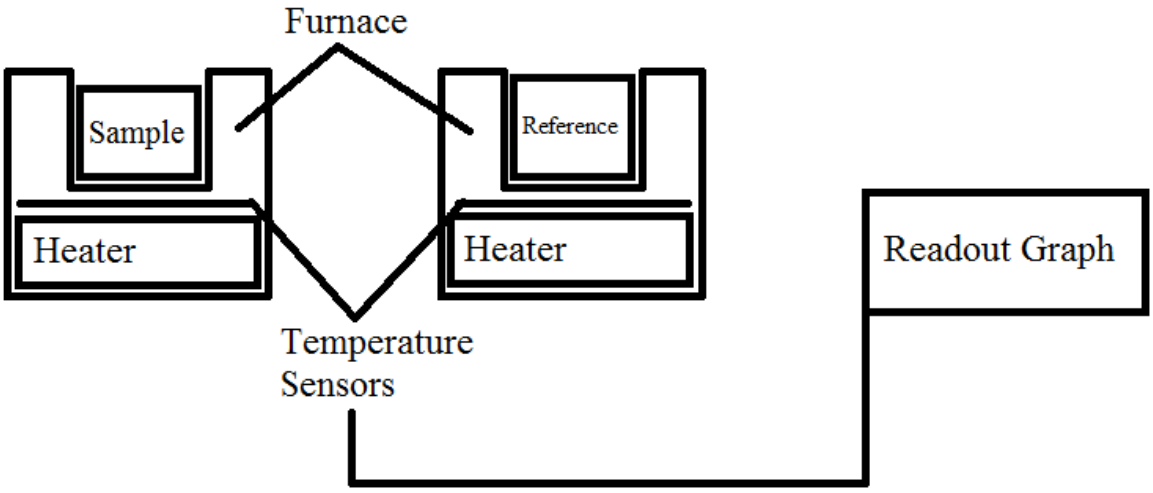

Figure 1: Basic Diagram of DSC Instrument

The purpose of the first scan was to determine the calibration needed when calculating the enthalpy from the graphical printouts. By testing indium, which is a well known substance, the error present in the machine can be easily accounted for.

However, before any tests can be conducted, a few initial checks of the instrument must first be made. The nitrogen cylinder must be open, with its flow meters reading around 30 and 120. The liquid nitrogen cylinder's valve must be opened. The software must be booted up, and the machine needs a few minutes to warm up.

The pre-made indium sample must be placed in the first position (according to the software, it is position 101). Set the software to heat the sample from 100°C to 180°C at a rate of 10°C/min. Enter the name of the sample, the mass, and position into the software and start the experiment.

While running, prepare the PET sample by cutting a fragment that will fit inside the aluminum crucible. Obtain the mass, and seal the crucible with a press. Load the sample into

the second position, and save the indium data. Set the instrument to heat the sample from 40°C to 290°C at a rate of 10°C/min, enter the mass of the PET, the position, and start the experiment. While this experiment is running, the indium sample data should be analyzed.

Once the PET sample is finished running, remove it from the instrument, and sit the container on a plate to cool for 10 minutes. At that point, put the sample back in the instrument and run it again, this time naming it the quenched sample. Analyze the original sample while the quenched is running, then analyze the quenched once it's finished.

DATA AND RESULTS

For the indium scan, the data obtained and calculated are reported in Table 1. Since the DSC machine was malfunctioning at the time of the experiment, there is no attached graph obtained from the instrument. Instead, the "measured" data was obtained from previously gained information, as reported in the laboratory.

Table 1: Indium		
	Value	**Units**
Sample Mass	6.21	mg
Peak Temperature	169.41	C
Theoretical MP Temperature	156.6	C
Onset Temperature	156.302	C
Integral	156.492	mJ
Enthalpy	25.2	J/g
Lit Enthalpy	28.45	J/g
Calibration	1.13	unitless

The data obtained for the original PET sample, as shown in the attached graph, has been calculated and is displayed in Table 2.

Table 2: Original PET		
	Value	**Units**
Sample Mass	12.8	mg
Peak Temperature	245.07	C

Onset Temperature	231.95	C
Integral	-464.57	mJ
Enthalpy	-36.29	J/g
Calibration	-40.98	J/g
Lit Enthalpy (crystalline)	166	J/g
Entropy	-0.08	J/g*K

The data obtained for the quenched PET sample, as shown in the attached graph, has been calculated and is displayed in Table 3.

Table 3: Quenched PET			
Transition		**Value**	**Units**
	Sample Mass	12.80	mg
Glass	Onset Temperature	75.73	C
	Midpoint Temperature	78.20	C
Exotherm	Peak Temperature	138.53	C
	Onset Temperature	131.70	C
	Integral	346.63	mJ
	Enthalpy	27.08	J/g
	Calibration	30.57	J/g
Endotherm	Peak Temperature	245.09	C
	Onset Temperature	229.21	C
	Integral	-436.15	mJ
	Enthalpy	-34.07	J/g
	Calibration	-38.47	J/g
	Lit Enthalpy		J/g

The remaining few calculated values to be obtained are presented in Table 4.

Table 4: Calculated Values		
Unknowns	**Value**	**Units**
Percent DEG Present	7.1	%
Percent Crystalline	21.86	%
Percent Crystalline (Quenched)	4.21	%

CALCULATIONS/EQUATIONS

This experiment implemented the following six equations. The first used was the determination of the enthalpy of fusion from the integral of the DSC printout.

$$\Delta H_{fus} = \frac{\text{Integral}}{\text{mass}}$$

Where ΔH_{fus} is the enthalpy of fusion of the material [J/g]; Integral is the integral of the peak on the DSC graph [mJ]; and mass is the sample mass used in the experiment [mg].

$$\Delta H_{fus} = \frac{156.492\ \cancel{\text{mJ}}}{6.21\ \cancel{\text{mg}}}$$

$$\boxed{\Delta H_{fus} = 25.2\frac{\text{J}}{\text{g}}}$$

The second equation used in this experiment was employed to determine the calibration factor needed when calculating enthalpies using the DSC.

$$\text{Calibration Factor} = \frac{\Delta H_{fus,lit}}{\Delta H_{fus}}$$

Where Calibration Factor is the needed value to correct calculated enthalpies of fusion [unitless]; $\Delta H_{fus,lit}$ is the literature value for the enthalpy of fusion of the material [J/g]; and ΔH_{fus} is the enthalpy of fusion calculated directly from the DSC printout [J/g].

$$\text{Calibration Factor} = \frac{28.45\frac{\cancel{\text{J}}}{\cancel{\text{g}}}}{25.2\frac{\cancel{\text{J}}}{\cancel{\text{g}}}}$$

$$\boxed{\text{Calibration Factor} = 1.13}$$

The third equation used during this experiment was to calculate the weight percent of DEG present in the original polymer.

$$T_{fus}(℃) = 271 - 5.5(\text{wt\% DEG})$$

$$\text{wt\% DEG} = \frac{T_{fus}(℃) - 271}{-5.5℃}$$

Where $T_{fus}(℃)$ is the temperature of fusion for the polymer (or the onset temperature of the DSC graph) [°C]; and wt% DEG is the weight percent of DEG present in the polymer [unitless].

$$\text{wt\% DEG} = \frac{231.95\cancel{℃} - 271}{-5.5\cancel{℃}}$$

$$\boxed{\text{wt\% DEG} = 7.1}$$

The fourth equation used during this experiment was to calculate the percent of crystalline polymer present in the original sample.

$$\%\text{Crys} = \frac{\Delta H_{fus,exp}}{\Delta H_{fus,lit}} * 100$$

Where %Crys is the percent of crystalline polymer [unitless]; $\Delta H_{fus,exp}$ is the experimental value obtained for the enthalpy of fusion [J/g]; and $\Delta H_{fus,lit}$ is the literature value if the entire polymer had been crystalline [J/g].

$$\%\text{Crys} = \frac{36.29 \frac{J}{g}}{166 \frac{J}{g}} * 100$$

$$\boxed{\%\text{Crys} = 21.86\%}$$

The fifth equation used during the course of this experiment was the calculation for the percent crystalline present in the quenched sample.

$$\%\text{Crys}_{qu} = \frac{\frac{\text{Integral}_{fus} - \text{Integral}_{cry}}{1000 mg}}{\frac{\Delta H_{fus,cry}}{\text{mass}}} * 100$$

Where $\%\text{Crys}_{qu}$ is the percent of crystalline polymer in the quenched sample [unitless]; Integral_{fus} is the integral value for the melting crystalline polymer [mJ]; Integral_{cry} is the integral value for the formation of crystalline polymer [mJ]; $\Delta H_{fus,cry}$ is the enthalpy of fusion if the entire sample had been crystalline [J/g]; and mass is the mass of the sample used in the experiment [g].

$$\%\text{Crys}_{qu} = \frac{\frac{(436.15 \cancel{mJ} - 346.63 \cancel{mJ})}{1000 \cancel{mg}}}{\frac{166 \frac{J}{g}}{0.01128 \cancel{g}}} * 100$$

$$\boxed{\%\text{Crys}_{qu} = 4.21\%}$$

The sixth and last calculation used in this experiment was the determination of the original polymer's entropy.

$$\Delta S = \frac{\Delta H_{fus}}{T}$$

Where ΔS is the entropy of the system [J/g*K]; ΔH_{fus} is the enthalpy of fusion of the system [J/g]; and T is the temperature of the system [K].

$$\Delta S = \frac{40.98\,\frac{J}{g}}{(231.95 + 273K)}$$

$$\boxed{\Delta S = 0.0811\,\frac{J}{g * K}}$$

DISCUSSION/CONCLUSION

This is where the explanation of data and results occurs. This should summarize what was accomplished by doing the experiment. Be sure to include a thorough error analysis (both qualitative and quantitative when appropriate). Be sure to compare results with expected values such as theoretical or literature values when possible (you may need to locate these values – they will not always be given to you), and discuss any discrepancies not accounted for by experimental uncertainty.