Title Page

Title (1 pts)

PET Sounds: Plastic Beach Boys

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Two Hypotheses (4 pts)

It is believed that the plastic samples will show a higher percentage of crystallinity after they are annealed rather than before they are annealed. This is due to how annealing works. As the plastic is left to anneal, it is able to cool down much more gradually, and the polymer can form into a more crystalline structure. This increase in the crystalline structure goes in part with the physical properties of the plastic and make a much stronger polymer cast.

It is also believed that the crystallinity peak correlates to the percent crystallinity of the sample. More specifically, it is hypothesized that the lower the crystallinity peak is, the higher the percent crystallinity value is. This can be shown graphically in the thermogram. A lower value on the thermogram indicates that the heat flow of the system is lower, which implies that more of the heat is being taken by the plastic sample in order to breakdown the polymer. Likewise, the more energy a polymer needs to be broken down, the stronger the polymer is.

Abstract (5 pts)

One of the most important advancements made in the modern era of chemistry is the streamlining of polymer chemistry, and more specifically the streamlining of plastics. The streamlining of plastics allowed for the use of multiple different plastics commercially, which ended up being cheaper to produce and use than other materials, such as metal and glass. Another benefit that comes from plastics is the versatility of properties. Different arrangements of the same polymer can allow for drastic alteration of the physical properties that the polymer has. One particular way to go about altering the plastic's properties is through the process of annealing. By melting the plastic and changing the way in which it cools, the plastic becomes much more crystalline and overall stronger. In this lab, the goal is to get an idea of how annealing changes the physical properties of the plastic.

Results (35 pts)

For the main procedure of the experiment, multiple samples of PET must be prepared. There are two different types of PET needed, one from the body of the container supplied, and one from the neck of the container. There is also a third "unknown" sample supplied for the experiment. The masses of the three samples are listed below.

Table 1 – Mass values for each individual sample

Sample Type	Body Sample	Neck Sample	Unknown Sample
Mass (g)	$0.0083 \pm 5\times10^{-5}$	$0.0119 \pm 5\times10^{-5}$	$0.0123 \pm 5\times10^{-5}$

After each of the individual samples are run through the differential scanning calorimeter for three different runs, nine graphs are produced. Figures 1-6 show the graphs of the first and third runs for each of the samples. The graphs also contain key values for thermodynamic qualities of the plastic samples, and values needed to calculate other significant values. The values that can be found by observing the graph are the initial heat flux value (ΔC_p), the glass transition temperature (T_g), the crystallization temperature (T_c), and the melting temperature (T_m). There are also the areas of the two peaks that need to be considered, the area of the crystallization peak (ΔH_c), and the area of the melting peak (ΔH_f).

Table 2 – Values present on the graph of the DSC readings						
Sample Run	ΔC_p (J/g°C)	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_f (J/g)
Body 1	0.348 ± 0.0005	87.09 ± 0.005	135.91 ± 0.005	250.68 ± 0.005	3.2174 ± 5×10^{-5}	29.0308 ± 5×10^{-5}
Body 3	0.122 ± 0.0005	85.52 ± 0.005	149.85 ± 0.005	241.71 ± 0.005	1.7597 ± 5×10^{-5}	29.5723 ± 5×10^{-5}
Neck 1	0.386 ± 0.0005	79.71 ± 0.005	136.34 ± 0.005	244.83 ± 0.005	-18.6734 ± 5×10^{-5}	23.0340 ± 5×10^{-5}
Neck 3	0.133 ± 0.0005	85.93 ± 0.005	150.67 ± 0.005	241.55 ± 0.005	2.0442 ± 5×10^{-5}	33.7237 ± 5×10^{-5}
Unknown 1	0.324 ± 0.0005	73.55 ± 0.005	134.41 ± 0.005	245.03 ± 0.005	-23.3330 ± 5×10^{-5}	27.9136 ± 5×10^{-5}
Unknown 3	0.072 ± 0.0005	72.67 ± 0.005	148.90 ± 0.005	242.07 ± 0.005	0.5807 ± 5×10^{-5}	32.3340 ± 5×10^{-5}

While the values shown through the graph say a lot about the thermodynamic qualities of the samples, there is more that can be calculated to confirm these ideas.

Table 3 – Calculated Values		
Sample Run	C_p (J/g°C) [1 and 2]	Crystallinity (%) [3 and 4]
Body 1	0.337 ± 0.0005	15.50 ± 4×10^{-5}
Body 3	0.111 ± 0.0005	16.70 ± 4×10^{-5}
Neck 1	0.379 ± 0.0005	2.619 ± 4×10^{-5}
Neck 3	0.126 ± 0.0005	19.03 ± 4×10^{-5}
Unknown 1	0.313 ± 0.0005	2.751 ± 4×10^{-5}
Unknown 3	0.061 ± 0.0005	19.07 ± 4×10^{-5}

The text in brackets in the table above correlate to the equations used to calculate the selected values.

Figures

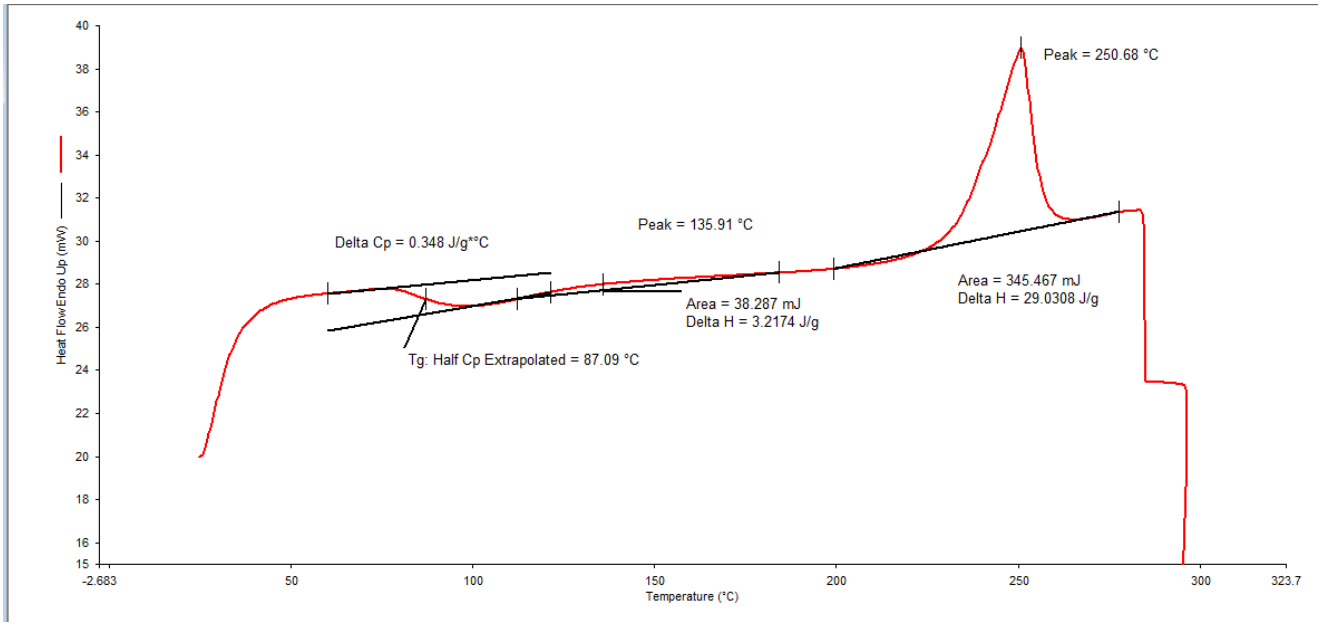


Figure 1 – First run of the piece of plastic from the body of the container. The graph is plotted parametrically, showing the x-axis as temperature, and the y-axis as the heat flow.

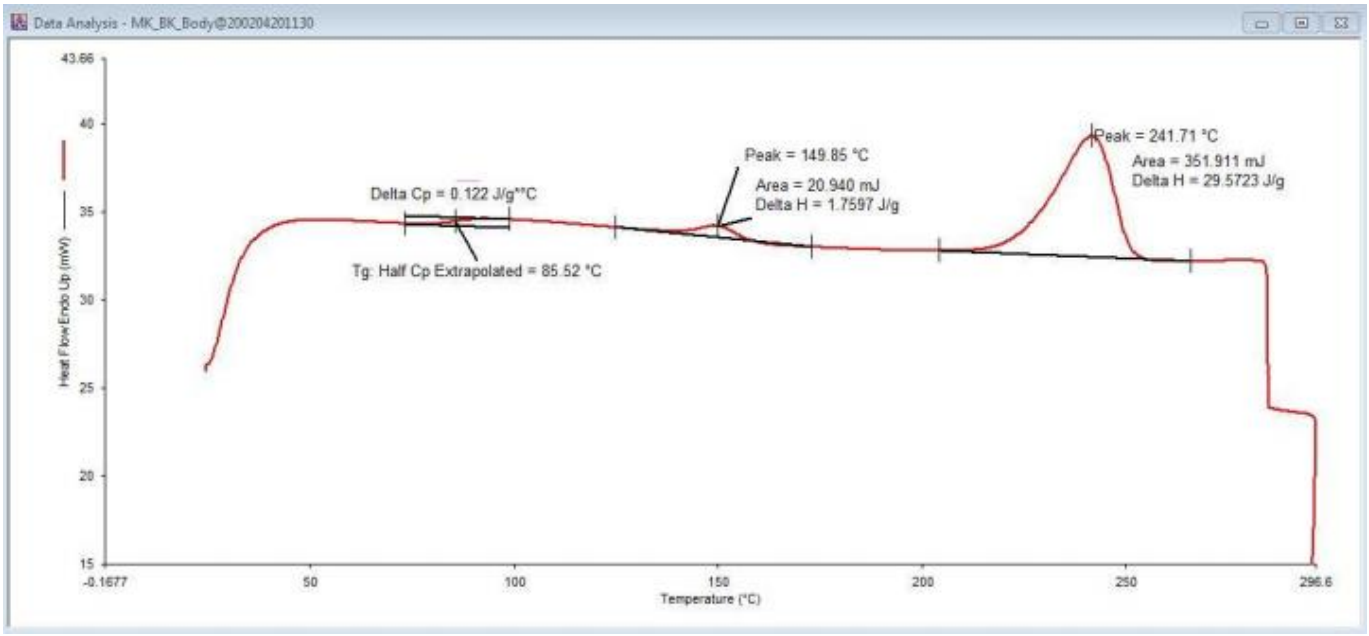


Figure 2 – The third run of the piece of plastic from the body of the container. The graph is plotted parametrically, showing the x-axis as temperature and the y-axis as the heat flow.

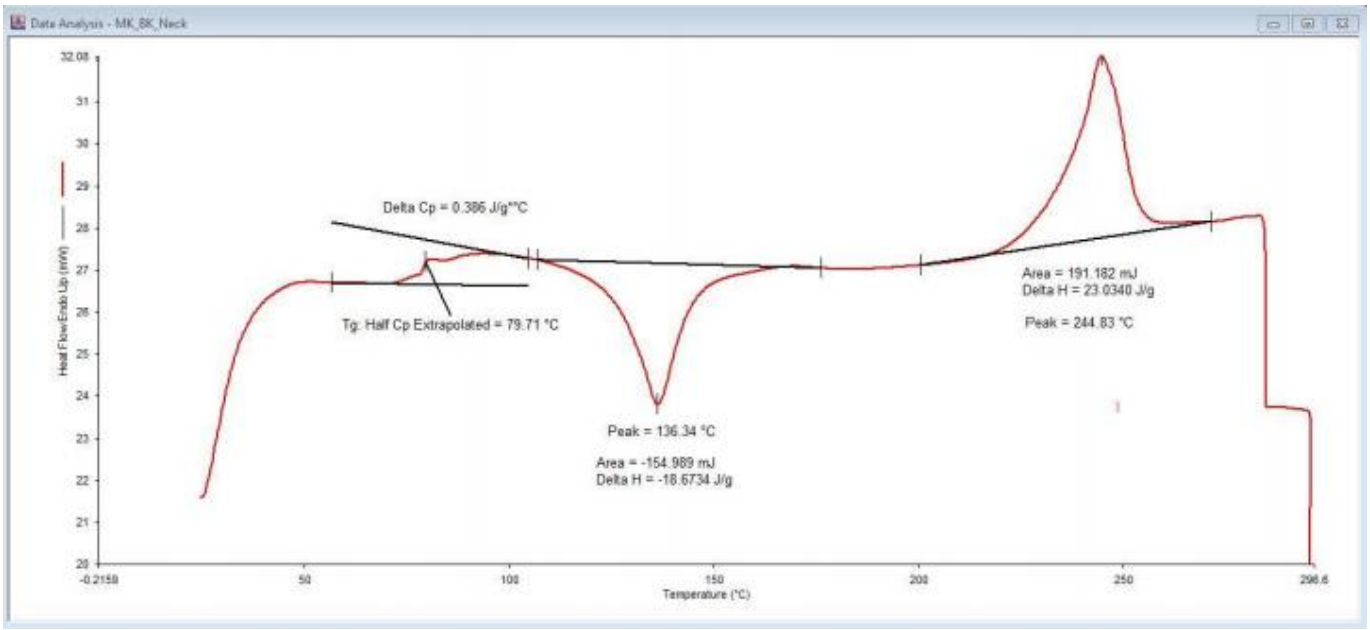


Figure 3 – The first run of the piece of plastic from the neck of the container. The graph is plotted parametrically, showing the x-axis as temperature and the y-axis as the heat flow.

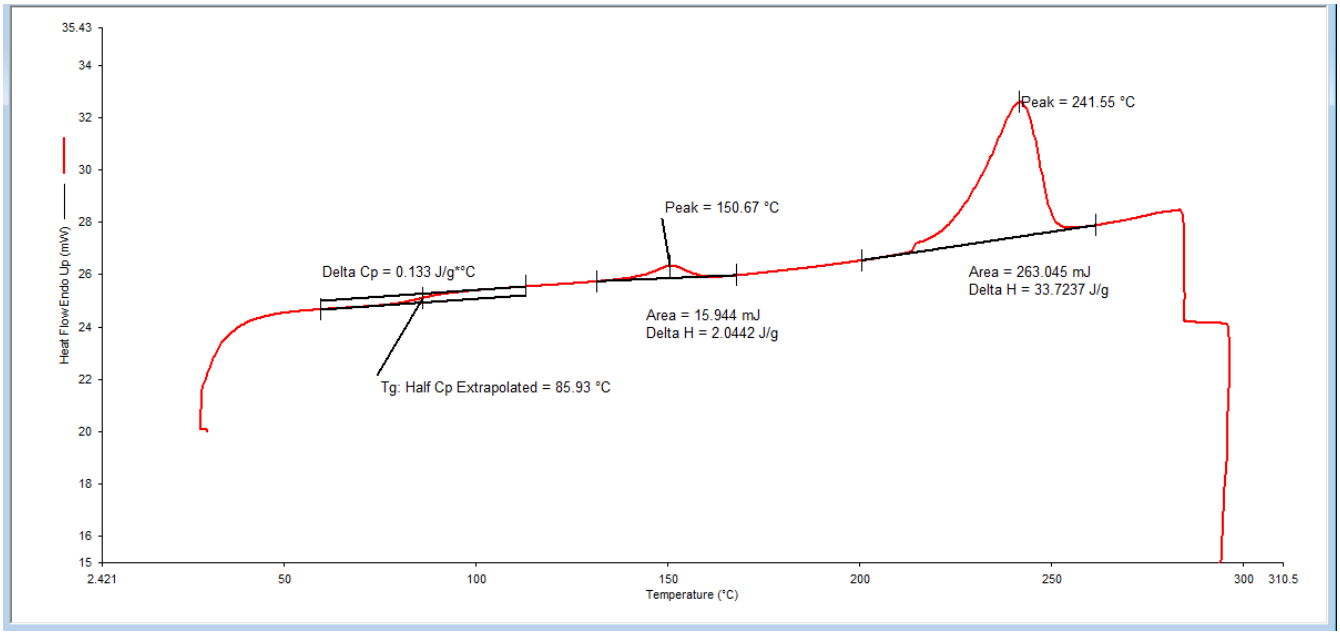


Figure 4 – The third run of the piece of plastic from the neck of the container. The graph is plotted parametrically, showing the x-axis as temperature and the y-axis as the heat flow.

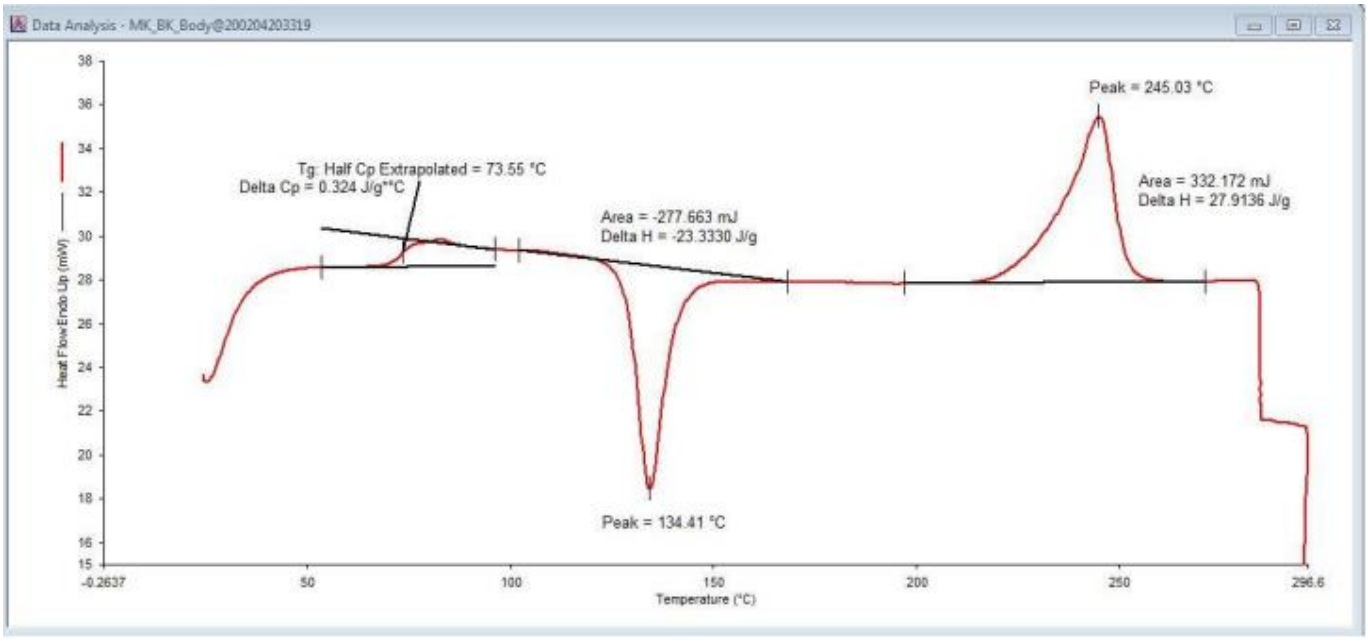


Figure 5 – The first run of unknown plastic. The graph is plotted parametrically, showing the x-axis as temperature and the y-axis as the heat flow.

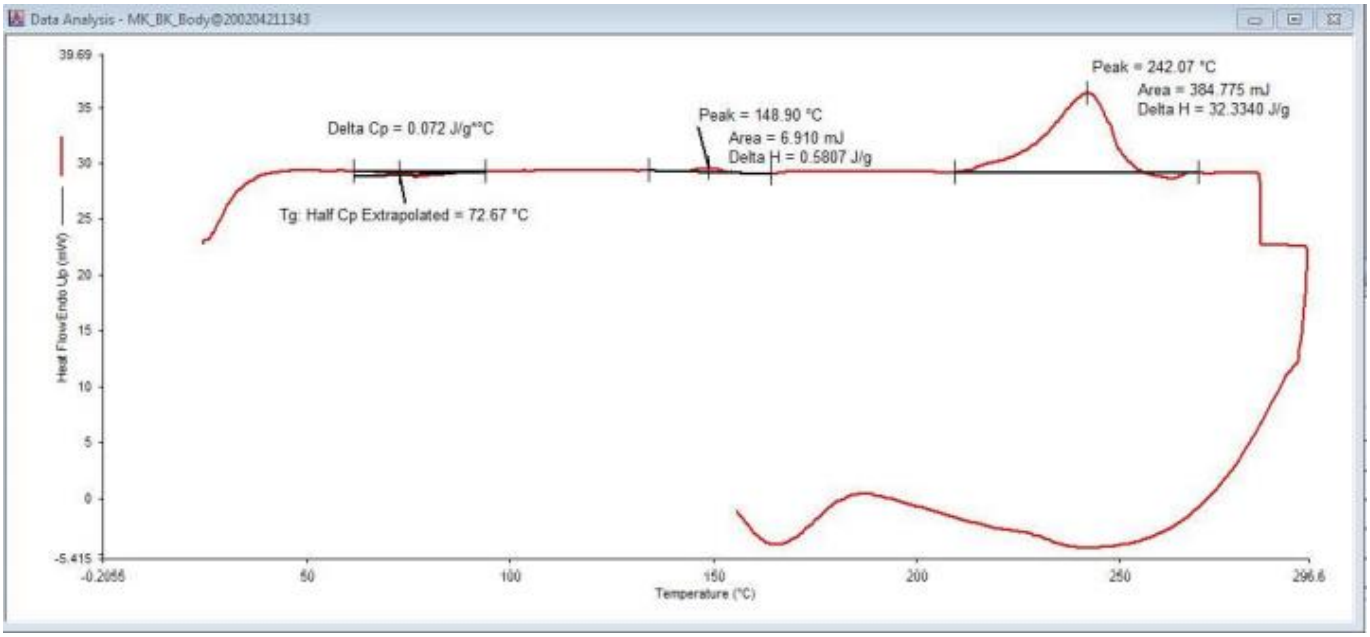


Figure 6 – The third run of unknown plastic. The graph is plotted parametrically, showing the x-axis as temperature and the y-axis as the heat flow.

Sample Calculations (15 pts)

1. $C_p = \Delta C_p - (C_s \cdot m)$

$$C_{p_{B3}} = 0.122\ \frac{\text{J}}{\text{g}\cdot\text{°C}} - \left(0.900\ \frac{\text{J}}{\text{g}\cdot\text{°C}} \cdot 0.0083\ \text{g}\right) = 0.115\ \frac{\text{J}}{\text{g}\cdot\text{°C}}$$

2. $$\delta C_p = \sqrt{\delta\Delta C_p{}^2 + \left((C_s \cdot m)\sqrt{\left(\frac{\delta C_s}{C_s}\right)^2 + \left(\frac{\delta m}{m}\right)^2}\right)^2}$$

$$\delta C_{p_{B1}} = \sqrt{0.0005\ \frac{\text{J}}{\text{g}\cdot\text{°C}}{}^2 + \left(\left(0.900\ \frac{\text{J}}{\text{g}\cdot\text{°C}} \cdot 0.0119\ \text{g}\right)\sqrt{\left(\frac{0\ \frac{\text{J}}{\text{g}\cdot\text{°C}}}{0.900\ \frac{\text{J}}{\text{g}\cdot\text{°C}}}\right)^2 + \left(\frac{0.00005\ \text{g}}{0.0119\ \text{g}}\right)^2}\right)^2}$$

$$= 5 \cdot 10^{-4}\ \frac{\text{J}}{\text{g}\cdot\text{°C}}$$

3. $\%_{crys} = \frac{\Delta H_f - |\Delta H_c|}{\Delta H_{100\%}} \cdot 100\%$

$$\%_{crys_{B3}} = \frac{29.5723\ {}^{\text{J}}/_{\text{g}} - \left|1.7597\ {}^{\text{J}}/_{\text{g}}\right|}{166.5\ {}^{\text{J}}/_{\text{g}}} \cdot 100\% = 16.70\%$$

4. $$\delta\%_{crys} = \sqrt{\left(\frac{\sqrt{\delta\Delta H_f{}^2 + \delta\Delta H_c{}^2}}{\Delta H_f - |\Delta H_c|}\right)^2 + \left(\frac{\delta\Delta H_{100\%}}{\Delta H_{100\%}}\right)^2} \cdot \%_{crys}$$

$$\delta\%_{crys_{B1}} = \sqrt{\left(\frac{\sqrt{0.00005\ {}^{J}/_{g}{}^{2} + 0.00005\ {}^{J}/_{g}{}^{2}}}{29.0308\ {}^{J}/_{g} - \left|3.2174\ {}^{J}/_{g}\right|}\right)^{2} + \left(\frac{0}{166.5}\right)^{2}} \cdot 15.50\% = 4 \cdot 10^{-5}\ \%$$

Discussion, 1 (min) – 2 (max) pages, single spaced (35 pts)

The hypotheses that were thought up before the lab procedure was performed. The first hypothesis believes that the percent crystallinity of a sample relates to the physical properties of the sample and would show that annealing the sample would result in an increase to the percent crystallinity. The data received from the calculation for percent crystallinity reflects this hypothesis, as for all three runs, the samples had a greater percent crystallinity after they were annealed rather than before, even the sample that was previously annealed. The proof of this hypothesis clearly shows the physical advantages that can come from annealing a polymer, particularly PET.

The second hypothesis states that the crystallinity peak found on the thermogram samples correlates to the percent crystallinity of the sample. By looking at the thermograms and the calculated percent crystallinities of the sample, a clear correlation is found. Particularly, this tends to be the heat flux value of the crystallinity peak. The higher the percent crystallinity is of the sample, the great the heat flux at the crystallinity peak is. This makes sense, as a higher heat flux indicates an endothermic process, and a lower heat flux indicates an exothermic process.

By simply looking at the data of the samples, the identity of the unknown sample can be found. The clearest proof of this is found in the data for the percent crystallinity (Table 3). The readings for both the initial run and the annealed run for the neck sample and the unknown sample share near identical values to each other. These readings contrast with the percent crystallinity readings of the body sample, which did not contain values precise to the other two samples. Therefore, because of this data, it is safe to believe that the unknown sample comes from the neck of the sample container.

Other forms of data can also prove this identification, such as the thermogram readings (Figures 1-6). Figures 1, 3, and 5 are the readings of the initial samples, and figures 2, 4, and 6 are the readings of the samples after they have been annealed. The fact that figures 2, 4, and 6 all have the same general shape implies that the shape of the thermogram of the initial sample that has been previously annealed should have a shape similar to the annealed shape. Looking at Figure 1, this is found to be true, as the shape of the thermograms for figure 1 and 2 share the same similar shape, with two positive endothermic peaks for the crystallization and temperatures. This comparison shows that the sample of the body has been previously annealed. Likewise, the shapes of figures 3 and 5 and figures 4 and 6 share the same general shapes, with the crystallization peaks changing from negative to positive after the samples have been annealed. This confirms that both the neck sample and the unknown sample are not annealed initially.

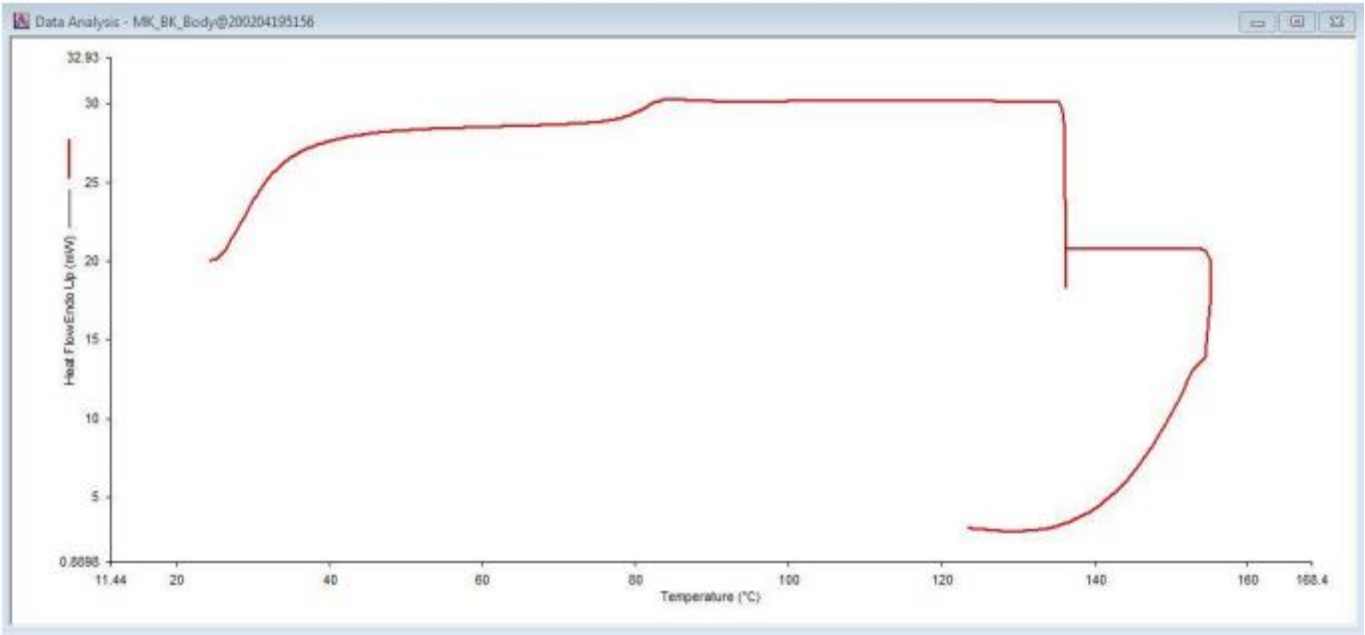
The shapes of the thermograms are significant for showing the flow of energy in the system between the sample and the medium it is in. One major point lies in the crystallization peak of the sample. As stated previously, as a sample goes from unannealed to annealed, the direction of the graph changes sign. Not only that, but the overall area of the graph is greatly reduced. This change in area is because of all the extra energy that is contained in the amorphous polymer sample due to the molecular interference exhibited between individual polymer chains. Because of this extra energy, more heat is needed to reach the crystallization temperature, and rearrange the polymers. With the annealed sample, there is less energy in the system, which causes the lower crystallization peak. The peaks also change shape because of the flow of energy. The unannealed sample has a negative peak, which correlates to an exothermic reaction, because of all the energy from the amorphous sample being released. The positive peak that the annealed sample shows is energy flowing into the polymer to break the crystalline formation. The comparison between the two crystallization peaks also show that there is more energy in the amorphous sample than the energy required to weaken the crystalline structure.

The glass transition marks a point in the heating process where the individual polymer strands of PET are rearranged from a disordered amorphous form into an organized crystalline form. The energy that is inserted into the system allows for the polymers to be more easily rearranged. As mentioned earlier, the more crystalline the polymer is, the more energy is needed to reach these significant points, which results in an increase of temperature. This implies that the glass transition of a more crystalline sample will be higher than that of a less crystalline sample.

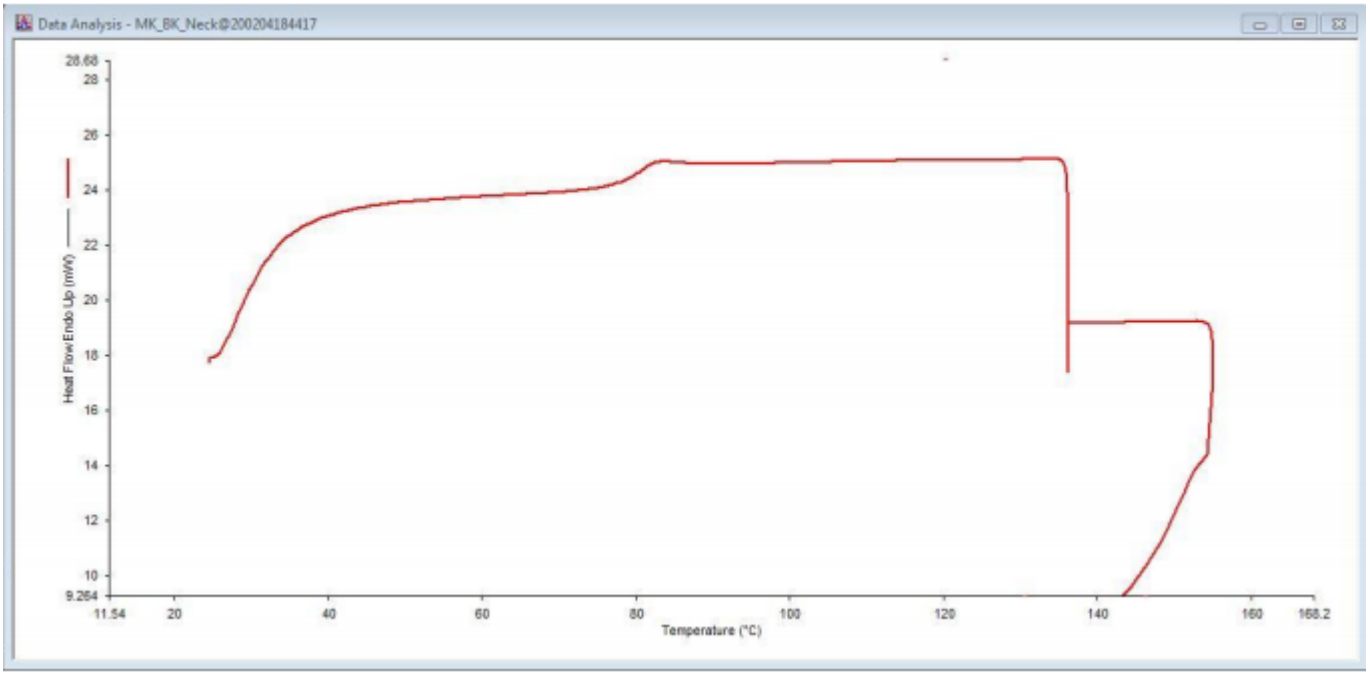
As with the glass temperature, the annealing process causes the physical structure of the polymer to become more crystalline. With the slower cooling time that comes with annealing, the individual strands of polymers have a much easier time forming a more stable structure. In contrast to the glass transition temperature, the molten polymer has a much easier time forming into different shapes and arrangements, and therefore can create a much more stable crystalline structure. This crystalline structure has a lower energy conformation, and therefore the polymer will tend towards this crystalline shape once it gets enough energy.

The readings from the experiment clearly show how the annealing process can greatly alter the physical properties of polymers, as well as how the thermodynamic qualities change in relation to these physical properties. The wide range of physical and thermodynamic properties that can be altered through the process of heating and cooling just goes to show the versatility that polymers display, and how useful polymers can be in the fields of material science and physical chemistry.

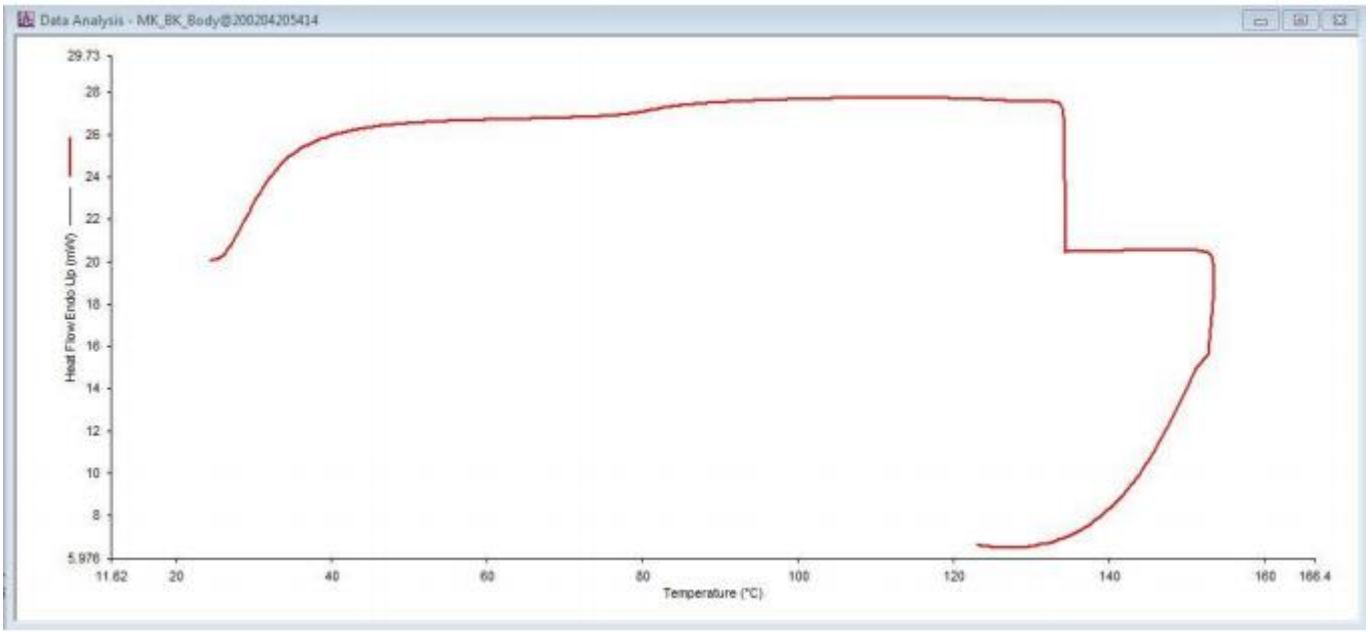
Supporting Figures



S.F. 1 – Run 2 of the body sample of PET. This thermogram details the annealing process of the sample.



S.F. 2 – Run 2 of the neck sample of PET. This thermogram details the annealing process of the sample.



S.F. 3 – Run 2 of the unknown sample of PET. This thermogram details the annealing process of the sample.

Lab Notebook

	mass (g)	Tg ©	dT	ΔCp (J/gC)	Cp (J/gC)	ΔHc	ΔHf	T crys	T melt	% crys	
Body 1	0.0119	87.09	255	0.348	0.337	3.2174	29.0308	135.91	250.68	15.50	4.25E-05
Body 2	0.0119										
Body 3	0.0119	85.52	-255	0.122	0.111	1.7597	29.5723	149.85	241.71	16.70	4.25E-05
Neck 1	0.0083	79.71	255	0.386	0.379	-18.6734	23.0340	136.34	244.83	2.619	4.25E-05
Neck 2	0.0083										
Neck 3	0.0083	85.93	-255	0.133	0.126	2.0442	33.7237	150.67	241.55	19.03	4.25E-05
Unkn 1	0.0123	73.55	255	0.324	0.313	-23.333	27.9136	134.41	245.03	2.751	4.25E-05
Unkn 2	0.0123										
Unkn 3	0.0123	72.67	-255	0.072	0.061	0.5807	32.334	148.90	242.07	19.07	4.25E-05
	ΔH100%	Cs Al (J/gC)									
	166.5	0.900									