Discoveries of Thermal Properties of Polymers using DSC and TGA
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Abstract

The goal of this lab was to analyze the thermal properties of different polymers and see how different mechanisms can alter the phase degradation and phase transition temperatures. TGA was used to analyze the phase degradation temperatures. Temperature, heating rate, moisture absorption, and residue content were all examined to see how the degradation and weight loss would change. DSC was used to analyze the melting (Tm), glass transition (Tg), and crystallization temperatures (Tc). Chemical structure, molecular weight, and block/copolymers were examined to see how they would affect the Tm, Tg, and Tc. In this report samples of different polymers were examined using DSC and TGA, testing and analysis.

Keywords

DSC (Differential Scanning Calorimetry): Differential scanning calorimetry is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature.

TGA (Thermogravimetric Analysis):is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate.

Glass Transition Temperature: is the temperature range where the polymer substrate changes from a rigid glassy material to a soft (not melted) material, and is usually measured in terms of the stiffness, or modulus.

Phase Degradation: Degradation is the process by which a chemical substance is broken down to smaller molecules by biotic means (biodegradability) or abiotic means (hydrolysis, photolysis, or oxidization).

Phase Transition: are the physical processes of transition between a state of a medium, identified by some parameters, and another one, with different values of the parameters.

Introduction

This lab examined the thermal properties of different polymers. By examining how a polymer changes as a response to temperature change different properties can be determined like percent crystallinity (X_C), glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) associated enthalpies, and phase degradation. Polymers are typically semi-crystalline materials, meaning they will have amorphous regions in addition to crystalline regions. Materials with amorphous regions will show a glass transition temperature where the material goes from a hard solid to a soft and rubbery state where the polymer chains are able to slide past each other more easily. Additionally, phase degradation, is important to examine to know when a material degrades. This will be shown at the degradation temperature. Phase degradation/polymer degradation can be caused by increase in temperature, shear action, radiation, moisture, and chemical agents which is useful in simulating real environments. The change in these properties can appear in tensile strength, color, shape, ductility, and more which is critical in understating the performance of the polymer.

A phase transition is the transformation of a thermodynamic system from one phase to another. Phase transition is determined by using a DSC (Differential Scanning Calorimetry). The DSC is a measure of a materials response to heat, specifically a measure of heat capacity as a function of temperature. Samples are heated above their melting temperature and cooled back down to room temperature measuring the change in enthalpy as an indication of a phase transition, be it a Tg, Tc, or Tm. Additionally, the X_c can be found. Thermal phase degradation is when a material degrades due to either chain scission, non-chain scission, random degradation, depolymerization, or side group elimination. Thermal phase degradation is determined by TGA (Thermogravimetric Analysis). This machine measures the change in weight of a polymer as a function of temperature. The gain or loss in weight loss will indicate the degradation of the polymer.

In this report the DSC was used to measure the melting and crystallization temperatures effects of polyethylene, poly (ethylene glycol), poly (vinyl alcohol), and poly(ethylene-b-glycol). The DSC was also used to measure the molecular weight effect and chemical structure effect on glass transition with samples of poly (methyl methacrylate), poly (ethyl methacrylate), poly (butyl methacrylate), and of a regular PET water bottle. The TGA was used to measure the effect of degradation mechanism on poly (vinyl chloride), heat rate effect on polystyrene, moisture absorption on nylon 6 and cellulose, and the residue content of paint.

Experiment and Methods

For DSC testing, a DSC Q 1000 was used. 5 mg of each sample were weighed, placed and sealed in a pan. For each sample precise scanning ramp rates and max temperatures testing parameters were made. For the PE sample the scanning range was 50-150ºC, for PEO 0-100ºC, for PVAOH 150-250ºC, for (PE-b-PEG) 0-150ºC with a scanning rate of 20ºC/minute.

Additionally, the scanning range for PS was 50-150ºC, for PMMA, PEMA and PMBA 0-150ºC, and for EcoVAE 401 -50-50ºC, all with a scanning rate of 20ºC/minute. Lastly, for the PET bottle the scanning rate was set to 20ºC/minute and a scanning range of 30-300ºC. TA Universal Analysis 2000 was used to analyze the DSC graphs.

For the TGA testing a TGA Q 500 was used. Arbitrarily small amounts were placed in the TGA (<5mg) for each material. For the PVC the heating rate was set to 20ºC/minute with a scanning range of 50-600ºC. The PS sample had a scanning range of 50-600ºC and one heating rate of 20ºc/minute, and another scanning rate of 50ºc/minute. Nylon 6 and cellulose had scanning ranges of 50-600ºC and a heating rate of 20ºC/minute. Lastly, the paint sample had a heating rate of 20ºC/minute and a 50-600ºC scanning range. After TGA data was collected TA Universal Analysis 2000 software was used to analyze the results.

Analysis and Results

The phase degradation was analyzed using the TGA. The thermal degradation mechanism was examined using a sample of PVC. The TGA graph can be seen in Figure 1 below.
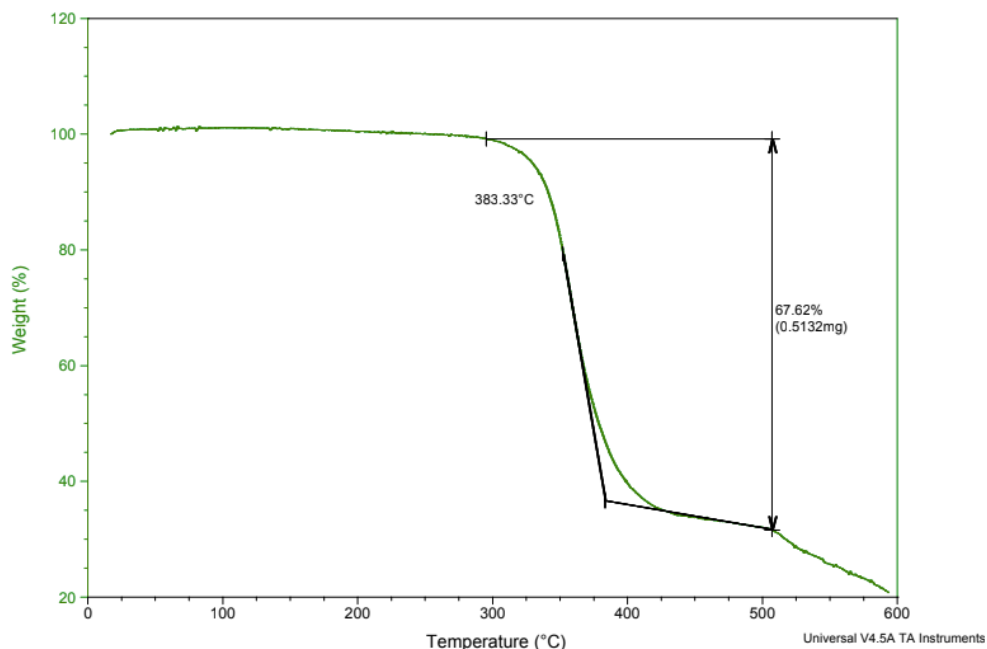

Figure 1. TGA graph of PVC

The weight percent change was 67.62%, which was equivalent to 0.5132 mg for this sample of PVC. It was found that there were two step degradations. The first thermal degradation temperature was show at about 320ºC, and the second degradation temperature was shown at 383.33ºC. According to a study by Evonik, two step degradation is supposed to occur, first at a temperature range between 200-380ºC, and a second degradation at 380-550ºC [1]. This determined that the results of this TGA experiment were comparable to those of theoretical

values. The two-step degradation is due to the breaking of the first C-Cl bond which has a lower activation energy than the C-C bond. The second degradation temperature is the breakdown of the C-C bond, and the rest of the polymer structure. In additional to regular thermal degradation, the rate at which heat was applied was also examined to see if it would affect degradation temperature and weight loss amount.

Degradation was examined by looking at two polystyrene samples that were heated at different rates. One sample of polystyrene, A, was heated at 20ºC/min, the other sample, polystyrene B, was heated at 50ºC/minute. The results of these heating rates can be seen in Figure 2.
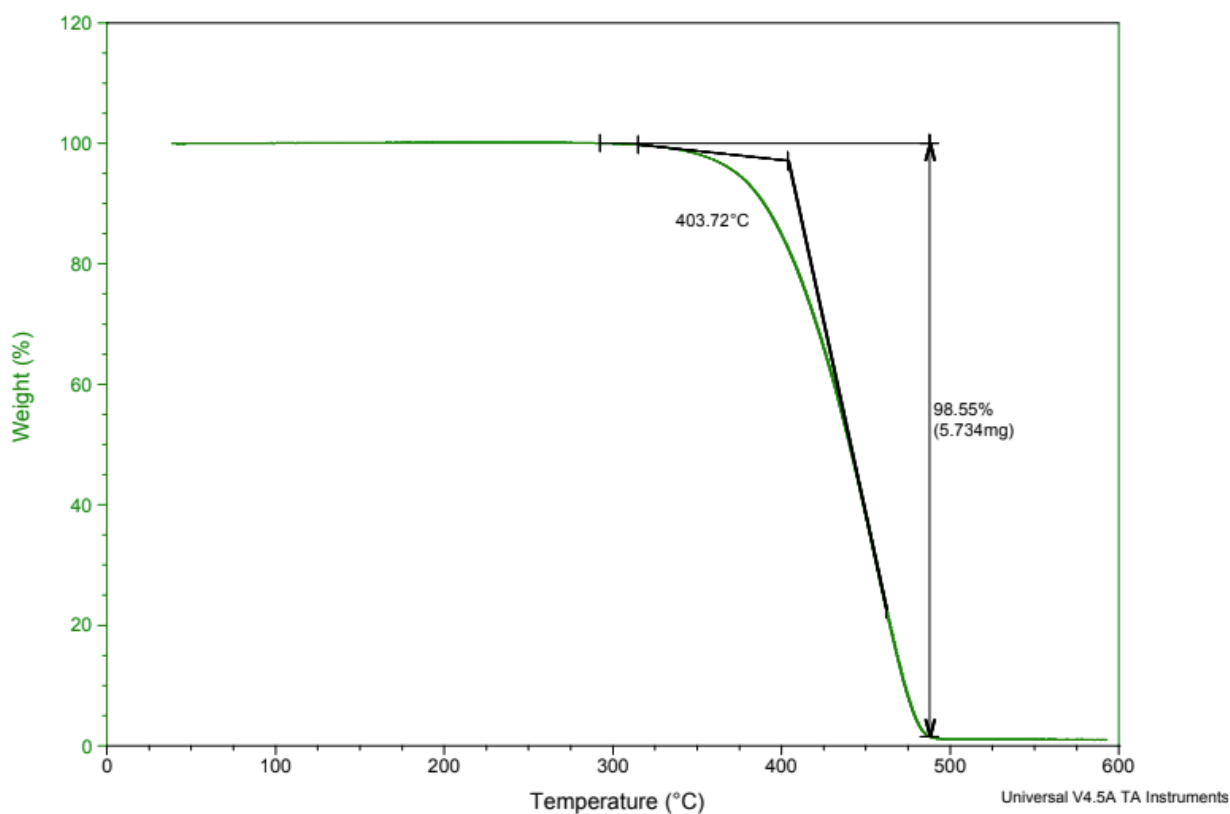
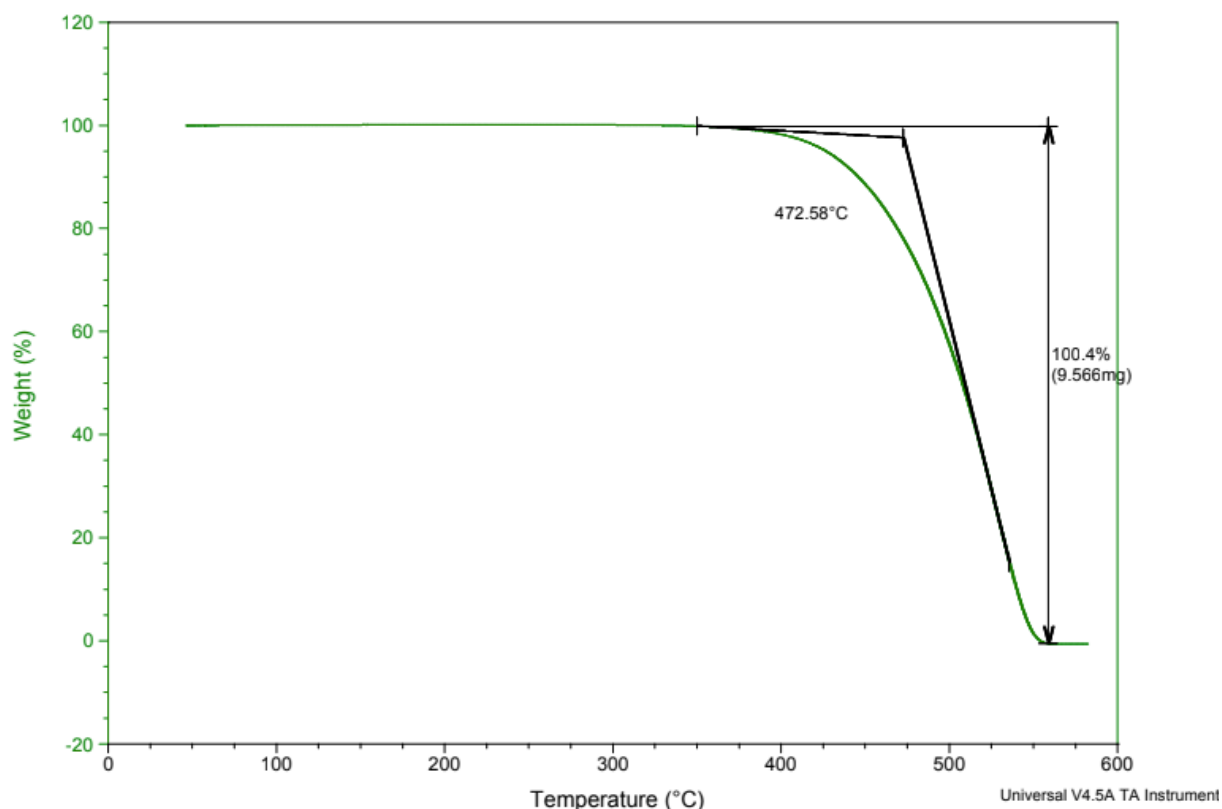Figure 2a. TGA graph of polystyrene sample A heated at 20ºC/minute

Figure 2b. TGA graph of polystyrene sample B heated at 50ºC/minute

It was found the degradation temperature for the polystyrene sample A was lower for the 20ºC/minute heating rate at 403.72ºC, compared to that of polystyrene sample B that a degradation temperature of 472.58ºC with a heating rate of 50ºC/minute. The percent weight loss however was greater in polystyrene B at 100.4 %, compared to polystyrene A that had a weight loss percent of 98.55%. This observation is attributed to kinetics, as an increase on heating rate increases the activation energy and decreases the rate of heat transfer, therefore the polymer breaks down at a higher temperature to make up for the loss of time where heat transfer/degradation could have occurred at lower temperatures [2]. The moisture absorption was also examined using the TGA.

Samples of both nylon 6 and cellulose were examined to the effect of moisture absorption using the TGA. The results of this experiment are shown in Figure 3.
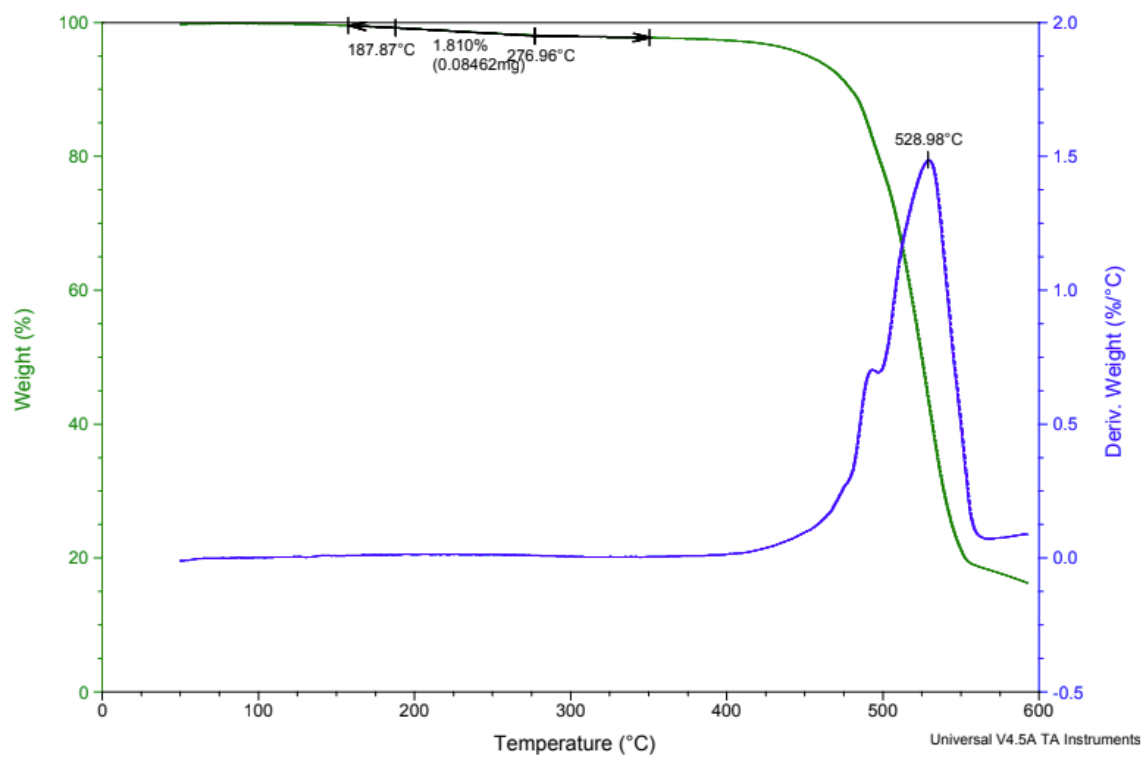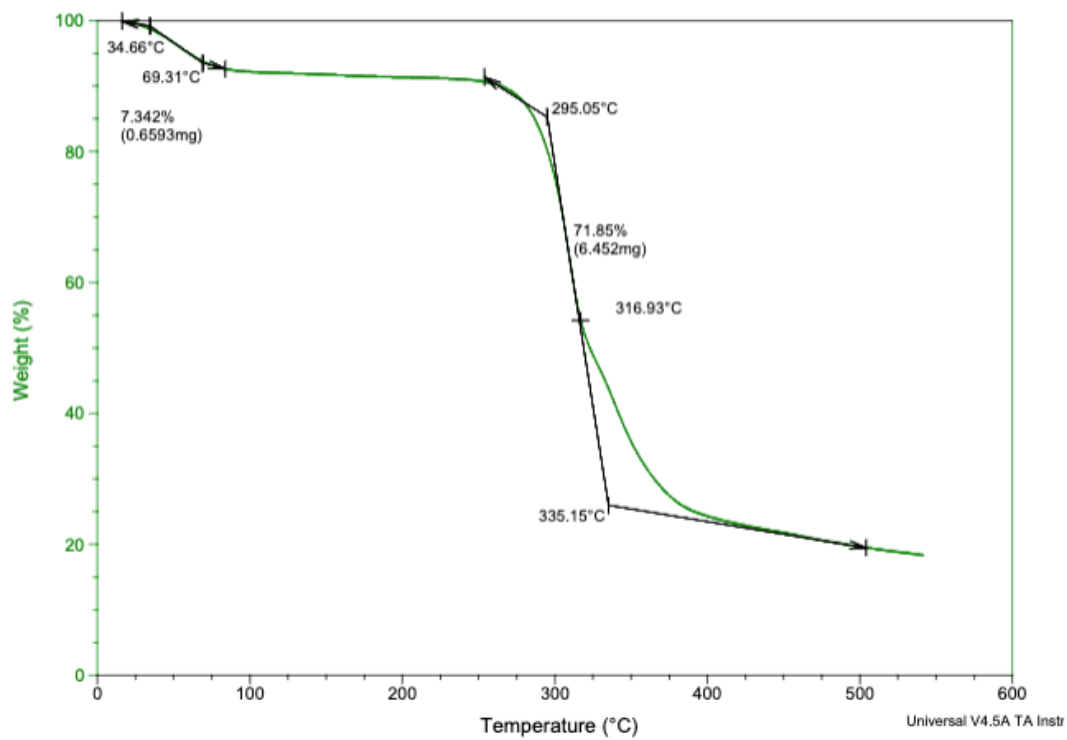
Figure 3a. TGA graph of nylon 6

Figure 3b. TGA graph of cellulose

The nylon 6 sample experienced an overall weight loss percent around 82%, whereas the cellulose experiences a weight loss percent around 80%. Both materials experienced a two-step degradation process where for nylon 6 the first degradation occurred at 188ºC, and for cellulose at 35ºC. At these temperatures both the nylon 6 and cellulose had a weight loss of absorbed water, and then a second degradation which was a degradation of the rest of the polymer. The water loss is due to nylon 6 and cellulose both having water in their reaction, as they both are synthesized through condensation polymerization [3]. The last TGA analysis was for residue content.

To test residue content a sample of paint was analyzed. The TGA graph can be seen in Figure 4 below.
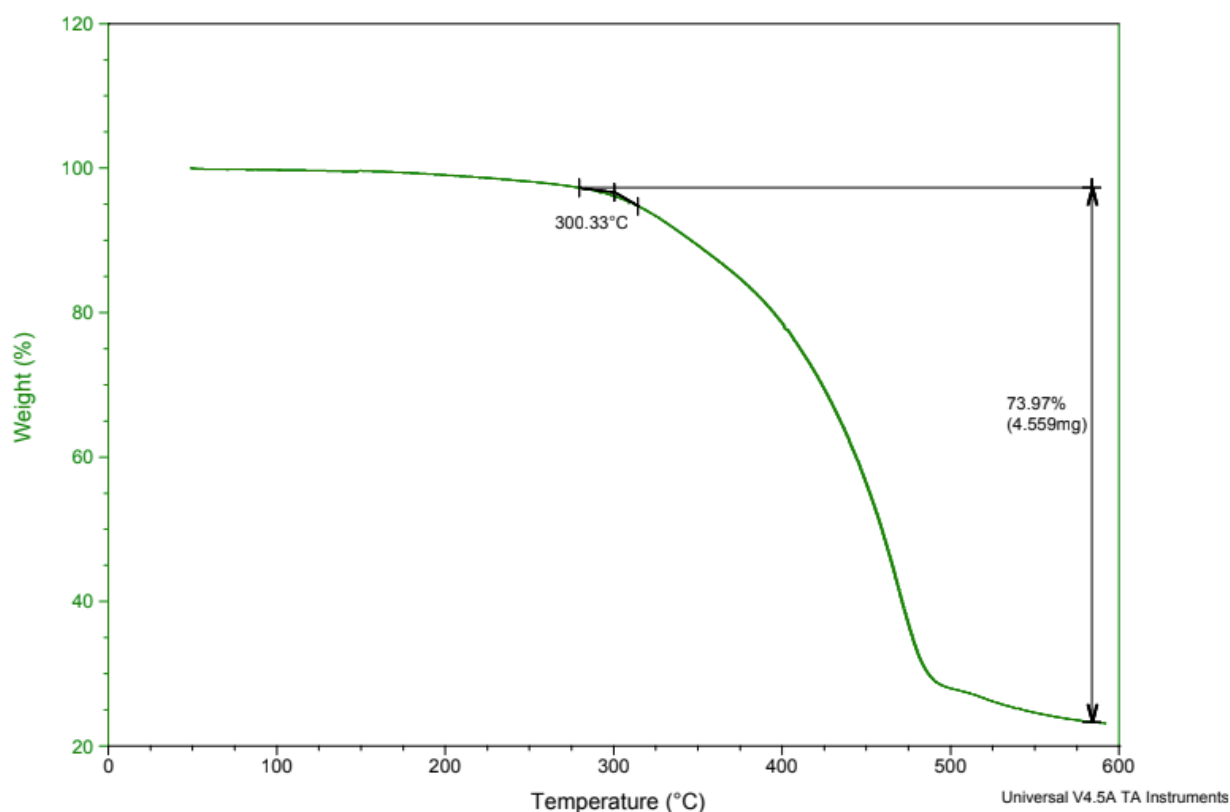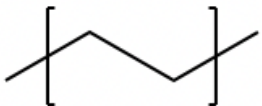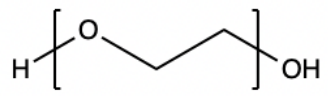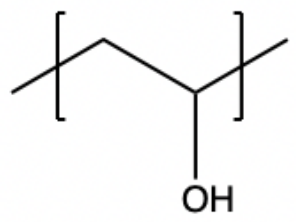

Figure 4. TGA graph of paint

The TGA graph of paint shows a weight loss percent of 73.97%. It's shown that the PVC value was at about 25% which indicated that the rest of the material present consisted only of pigment and additives. During the heating process some volatile compounds evaporated in addition to hydrogen and carbon content.

The DSC was used to measure phase transformations of different polymer samples. The effect of chemical structure of polymers was examined using the DSC. Samples of PE, PEO, and PVAOH were examine, their results can be seen in Table I.

Table I: Effects of Chemical Structure on Tm and Tc on using DSC

Polymers	Chemical Structure	Tm (C)	Tc (C)
PE		110.61	88.14
PEO		60.27 C	40.64
PVAOH		183.91 C	171.16 C

It was observed that PVAOH had the highest Tm and Tc, followed by PE and PEO. This trend can be attributed to their chemical structure. It is important to understand the Tm equation to understand why the chemical structure would affect the Tm and Tc so greatly [Eqn. 1]

$$Tm = \Delta H / \Delta S$$

Eqn. 1: Melting Temperature Equation

The structures of polymers affect the overall melting temperatures greatly. PVAOH has a high melting temperature due to the side hydroxyl group on the main chain, and the strong, long back bone of further increase the melting temperature thus lowering the amount of entropy thereby increasing the Tm. The stiff chain of PE makes it have a higher Tm in addition to its high

packing ability causing it also to have low entropy thus a higher Tm. PEO has a lower Tm due to its stereochemistry lowering the packing ability, thus increasing the amount of entropy, and therefore reducing the melting temperature [4]. It was also observed that the Tc is lower than the Tm. This is a result of recrystallization not requiring macroscopic diffusion unlike the melting temperature that requires additional energy to break down the material to its viscous state [5]. This lab examined also the effect melting and crystillization on block copolymer. A DSC graph of block co polymer PE-b-PEG is shown in Figure 5 below.
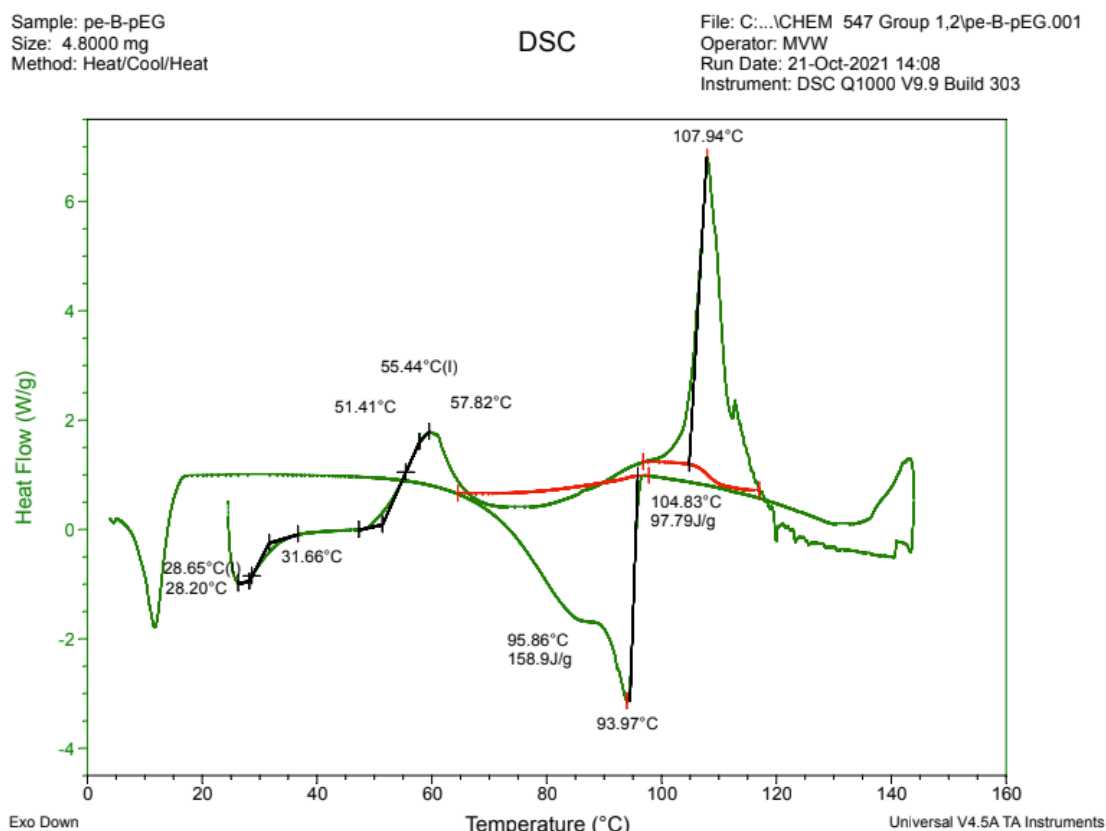

Figure 5. DSC graph of PE-b-PEG

The block polymer shows multiple phase transition points. These multiple phase transition points are due to the multiple melting temperatures and multiple crystallization temperatures are due to the multiple components of the block polymer. The crystallization temperature for the PEG was 28.65ºC, and its melting temperature was 57.82ºC. The values agreed with literature values where the PEG crystallization temperature was 54-66ºC and had a crystallization temperature between 1-60ºC [7]. For The melting temperature for PE was 107.94ºC, and the recrystallization temperature was 93.97ºC. Additionally, this value agreed with the theoretical values where melting temperature for PE is around 105-115ºC, and recrystallization temperature is around 90-110ºC [8]. In addition to seeing the chemical and block structure effects on melting and crystallization temperature, observing the effects of molecular weight on glass transition was also of importance.

The effect of molecular weight on the glass transition temperature was examined by using different samples of polystyrene. The results of this experiment can be seen in Table II.

Table II: Different MW Polystyrene and according Tg's

MW	Tg (C)
PS MW 3	75.88
PS MW 50	77.71
PS MW 125	97.18
PS MW 280	104.44

Table II shows that an increase in the molecular weight of polystyrene increases the Tg of the polymer. Equation 2 demonstrates the relationship between the molecular weight of a polymer and its Tg. As the molecular weight increase it will reduce the K constant thus reducing the amount of change that can be made on the Tg.

$$T_g = T_g^\infty - \frac{K}{M_n}$$

Eqn. 2: Glass Transition Temperature Equation

This relationship can be shown in Figure 6.
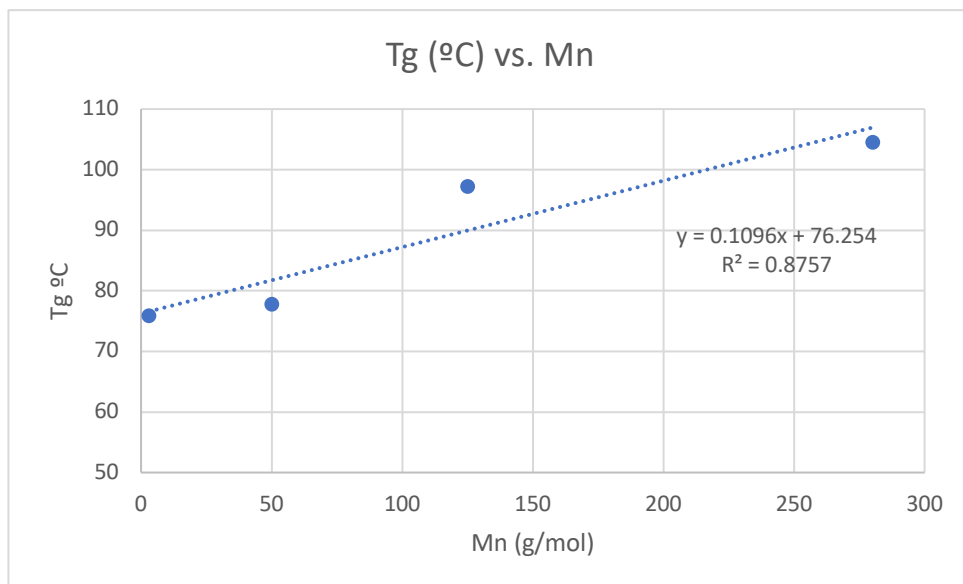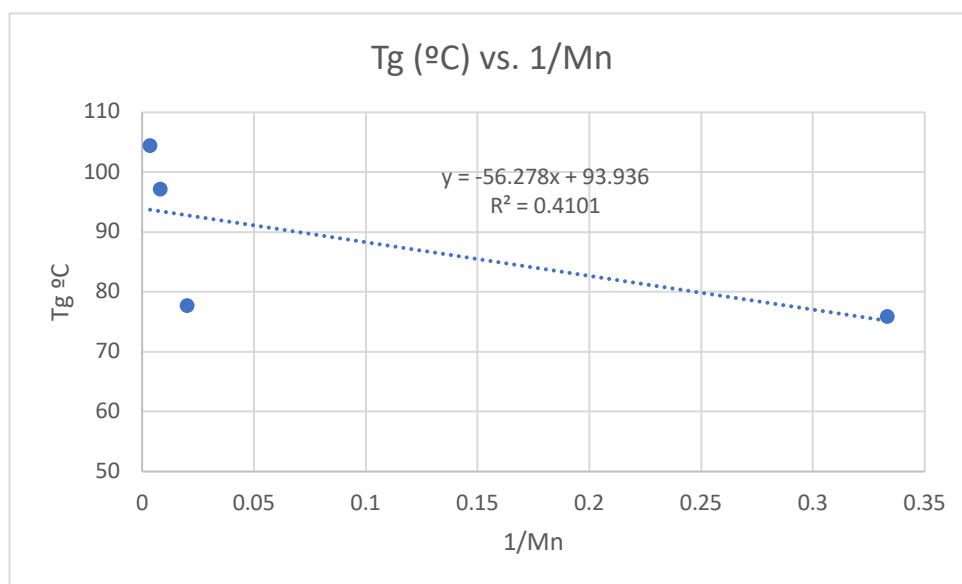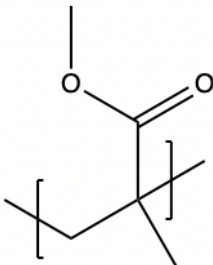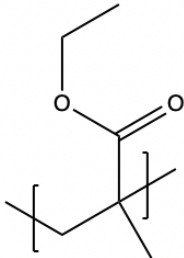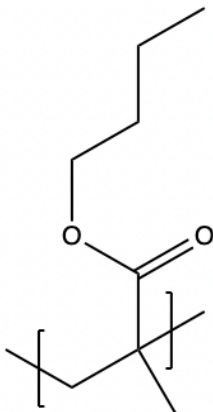

Figure 6a. Tg ºC vs. Mn

Figure 6b. Tg vs. 1/Mn

The large disparity in R^2 values determines that the Tg vs. Mn graph is more reliable than that of the Tg vs. 1/Mn graph. Reason being that the Tg vs. Mn graph more appropriately fits the molecular weights.

In addition to the molecular weight effect, the chemical structure effect on Tg was also examined. The results are shown in Table III.

Table III: Effects of chemical structure on Tg using DSC

Polymers	Chemical Structure	Tg
PMMA		104.24
PEMA		69.71
PBMA		34.71

The glass transition is affected by stiff chains, polar functional groups, bulk side groups, and increase in molecular weight. The reduction in glass transition temperature is due to the alkane group attached to the single bonded oxygen. PMMA only has a methyl group attached that's why it has the highest Tg, followed by PEMA that has the second highest Tg due to its ethyl

group, followed last by PBMA that has a butane group. The larger the alkane group or alkyl side chain that is attached the less the Tg will be.

A random copolymer of EcoVAE 401 was also examined to see its effect on the glass transition temperature. The DSC graph produced is shown below (Figure 7).
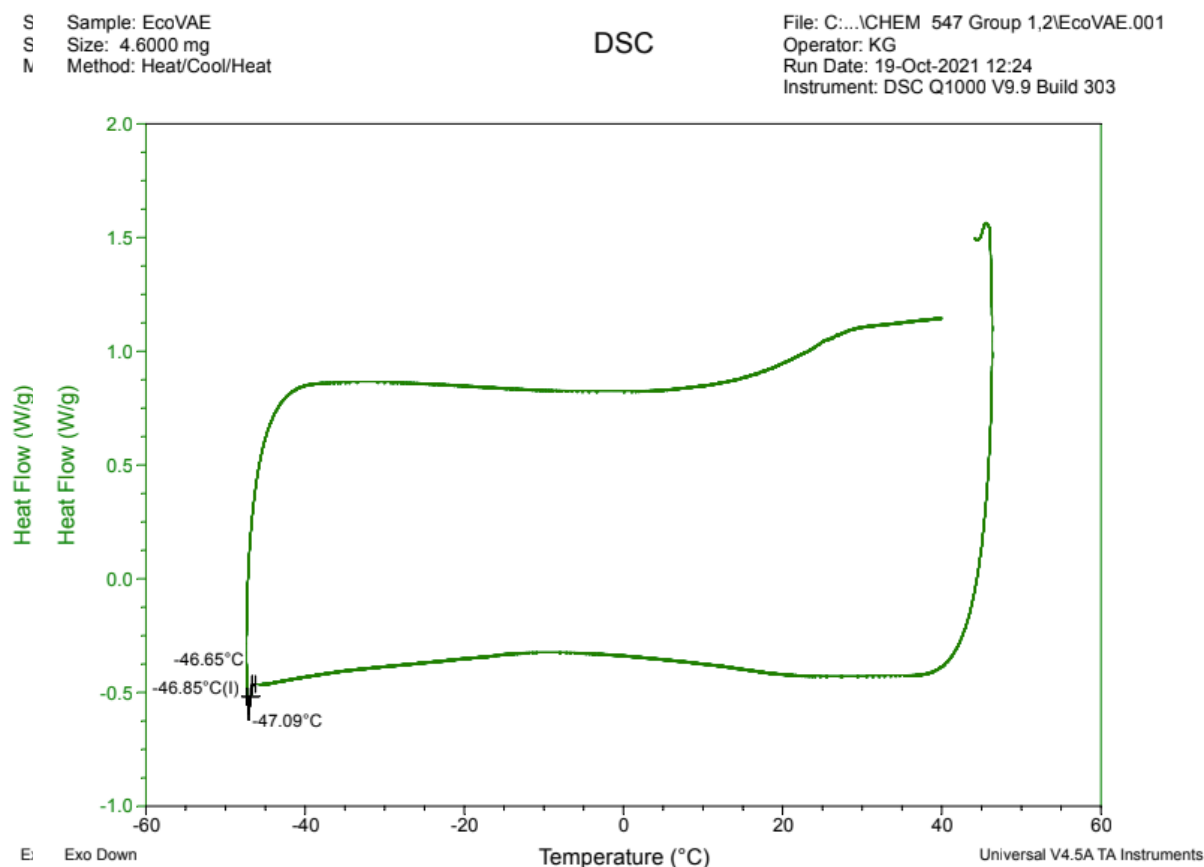
DSC

-46.65°C
-46.85°C(I)
-47.09°C

Heat Flow (W/g)

Temperature (°C)

Exo Down

Universal V4.5A TA Instruments

Figure 7: DSC graph of copolymer EcoVAE 401

EcoVAE 401 is copolymer consisting of PE and PVA. It experiences a Tg at -47ºC. This glass transition temperature is determined by the copolymer properties. The Fox Equation is used to explain this phenomenon as the Tg is a mixture of both the PE Tg of -80ºC, and the PVA Tg of 30ºC.

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

Eqn. 3: Fox Equation

Lastly, a real use application was examined. DSC tests of the neck and body of a standard PET water bottle was examined. Figure 8 depicts these results.
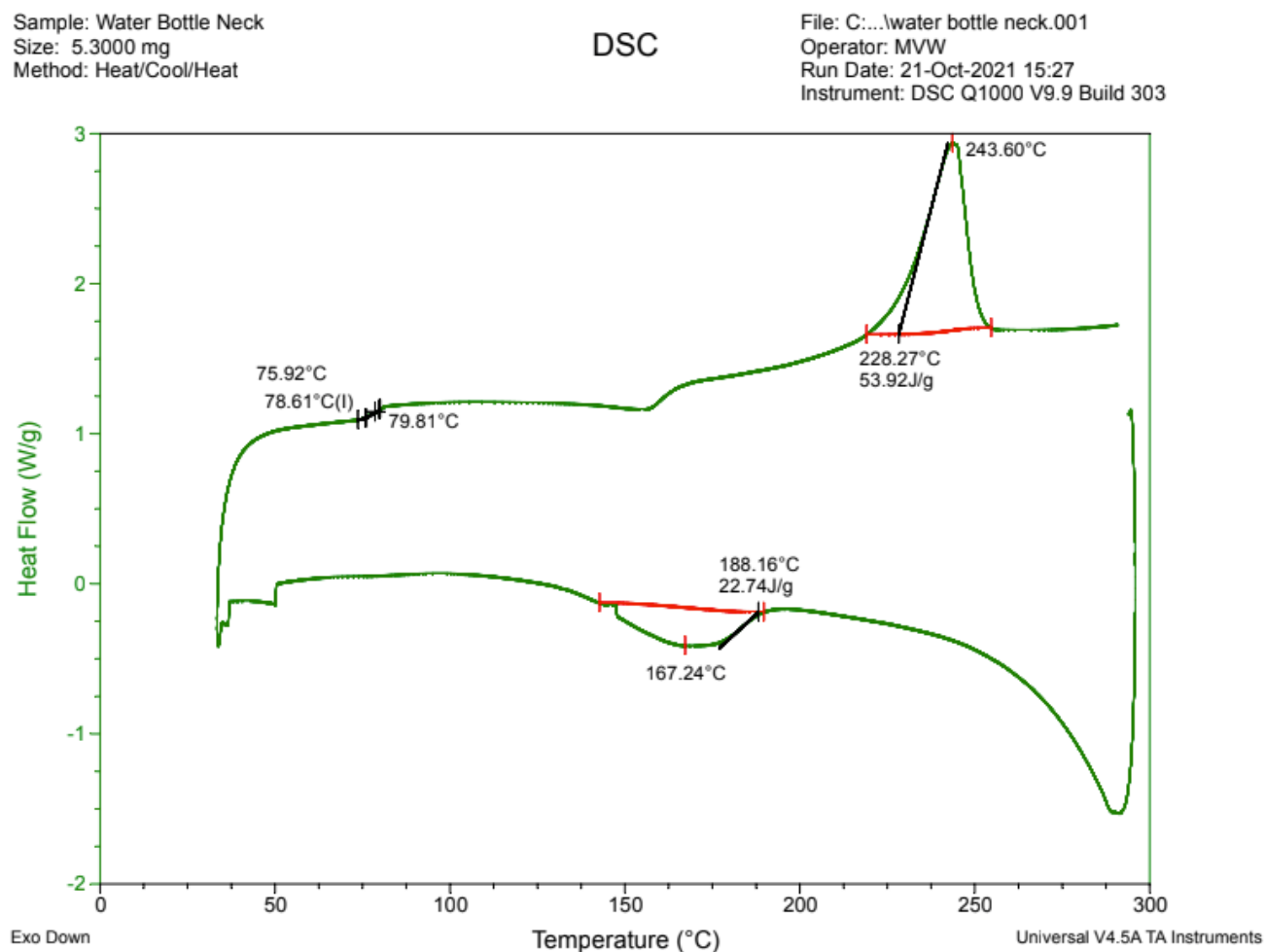

Figure 8a: DSC graph of PET bottle neck

Sample: Water Bottle Body
Size: 5.0000 mg
Method: Heat/Cool/Heat

DSC

File: C:...\water bottle body.001
Operator: MVW
Run Date: 21-Oct-2021 16:15
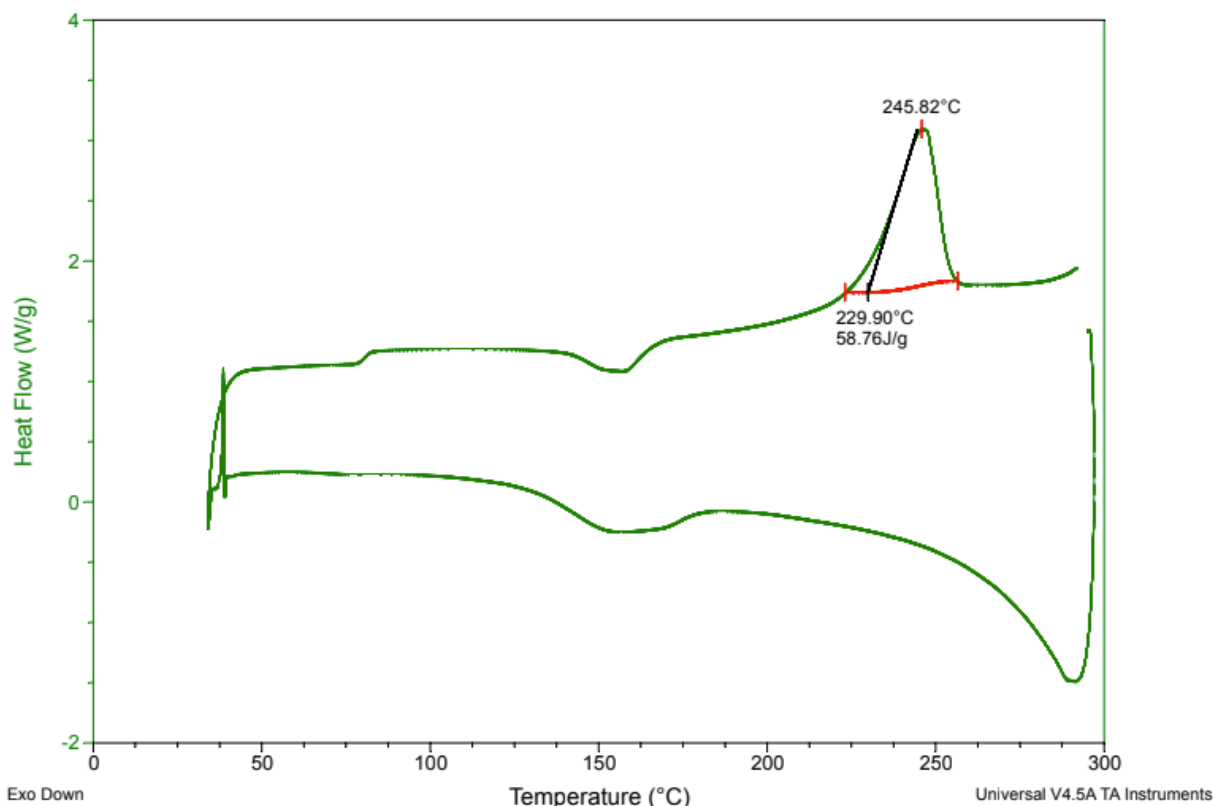Instrument: DSC Q1000 V9.9 Build 303

Figure 8b. DSC graph of PET bottle body

The PET bottle is more ordered at the neck and has a higher crystallization due to the manufacturing process as it is blow molded. At that point there is greater orientation and it is why more crystallization structure is produced [10]. The Tg temperatures for both graphs were around 167ºC. This temperature represents when a polymer goes from a glass/rigid state to a soft rubbery state. The crystallization temperatures were around 79ºC. This temperature signifies when the polymer returns from a rubbery state back into a hard, glass like state. Typically, in the DSC analysis a lower glass transition temperature should be shown in the body of the bottle due to its amorphous regions. The graphs made in the DSC testing for both the body of the bottle and the neck of the bottle had many shared characteristics which should not be the case, therefore the is part of the experiment should be redone to gather more accurate results.

Conclusion

In this lab the thermal properties of different polymers were examined. The goal of the lab was to see how different parameters affect the glass transition, melting temperature, crystallization temperature, and degradation temperatures. It was found that the degradation temperature

was affected by temperature, heat rate, moisture absorption, and residue content. It was found that an increase in heating rate increased the thermal degradation temperature due to the increase in activation energy and the diminishing of the rate of heat transfer. It was also seen that materials like nylon 6 and cellulose lose a considerable amount of water weight when heated due to their synthesis through condensation polymerization. It was also found that after heating of paint, the residue content contains the pigment and the additives. In terms of phase transformation, it was found that the chemical structure of a material specially a polymer packing ability, polar groups, and stiff back chain increase the melting temperatures. It was also found that crystallization temperature lower than the melting temperature as the polymer upon crystallization does not have to diffuse in the same manner as when it melts so it can crystallize at a lower temperature. Lastly, it was found that an increase in molecular weight, and less amount of alkyl groups on the end of a polymer increase the Tg of a polymer.

I learned how to appropriately use a DSC and a TGA. I learned how they both differ and that the TGA offers complementary data to the DSC as in the degradation temperature. Additionally, I learned that the degradation is significantly higher than the melting temperature, and it is the point when a material fully breaks down its chemical structure. Future improvements can be made to this lab by having standard parts of a PET bottle that are cut at the right location. The PET bottle DSC results for the neck and bottle were too similar which should not have been the case.

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