Thermal analysis of Tin, Lead-Tin Alloy and Polyethylene Using DSC and TG-DTA

Eman Mousa Alhajji

North Carolina State University

Department of Materials Science and Engineering

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Jessica Liu

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Abstract

The objectives of the experiment were to determine phase transformations and reaction enthalpies in metals using differential scanning calorimetry (DSC) and to determine phase transformations and thermal degradation behavior in polymers using thermogravimetric /differential thermal analysis (TG-DTA). Two 99.9% tin (Sn) samples and one lead-tin (Pb/Sn) alloy sample composed of 37% lead and 63% tin were tested in PerkinElmer instruments Diamond DSC at a rate of 5, 10 and 20 ºC/min, respectively. One polyethylene terephthalate (PET) sample was examined in SII Nano technology Inc. TG/DTA6200. The melting points were determined to be 232.32 ºC for tin run at 5 ºC/min and 232.53 ºC for tin run at 10 ºC/min, indicating a limited effect of the heating rate on the thermograms. The specific heat of fusion for tin was found to be 59.65 mJ/mg. The melting point of the lead-tin alloy was determined to be 185.40°C. The melting point for PET was determined to be 249°C, and significant degradation and loss of molecular weight started at 350°C. The degradation of PET does not begin until above the melting point, implying that PET is a safe material used in food and drink packing. Good agreements are found between the literature thermal characteristics and the values obtained experimentally, which suggests that DCS and TG/DTA are very accurate in determining thermal characteristics and identifying the melting points for Sn and Sn/Pb alloy.

Introduction

Thermal analysis is a method used in materials science and engineering to characterize the properties of materials as they change with temperature. [1] Thermal analysis is important because it can determine phase transformations, reaction enthalpies and thermal degradation behaviors. [1] A physical change indicates a phase change in metals or a glass transition temperature in polymers. A chemical change indicates the onset of oxidation or degradation of the material. [2,3] There are three main methods commonly used in thermal analysis: differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermal gravimetric analysis (TGA). [1] Differential scanning calorimetry measure the change in heat whereas differential thermal analysis measures the change in temperature and thermogravimetric analysis measures the change in mass, as summarized in Figure 1.

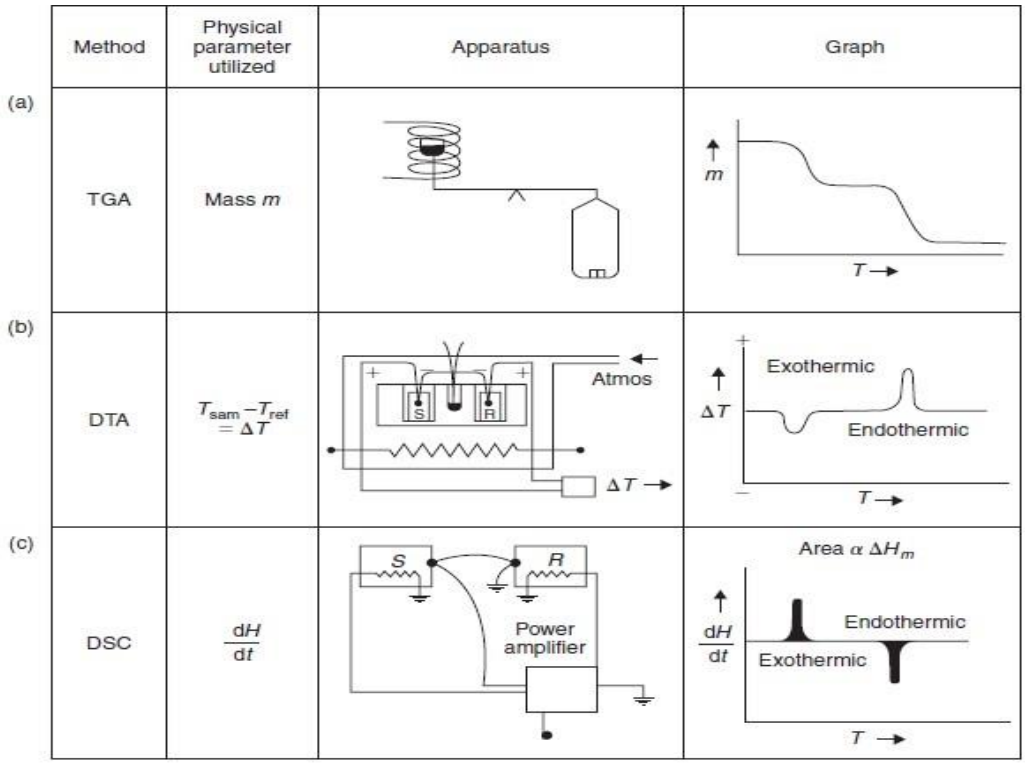

Figure 1. Methods of thermal analysis: (a) Thermogravimetric analysis, (b) differential thermal analysis, and (c) differential scanning calorimetry.[2]

In DSC, the temperatures of the sample and the reference are kept the same by heating them separately. When a change in temperature occurs between the two, the cooler is heated until the difference vanishes. [1,2] The heat flow required to exclude the difference is plotted against the temperature to give the DSC curve. In DSC curve, an endothermic reaction has a positive, upward pointing peak, indicating an increase in the enthalpy of the sample. An endothermic change has a negative, downward pointing peak, indicating an increase in the enthalpy of the reference. [2] The temperature of a phase change in a material can be determined from the DSC curve by drawing a line tangent to the plot before the peak occurs and the line tangent to the peak. The point at which these two lines intersect is the temperature at which the phase change starts.[1] The area of the peak equals the energy per unit mass of the material. Using the peak generated by DSC and the peak from another material with a known specific heat of fusion (ΔH°) that was heated at the same rate as the sample, the specific heat of fusion for the sample can be found as following:

$$\frac{A_s}{A_r} = \frac{\Delta H_s m_s}{\Delta H_r m_r} \tag{1}$$

where A_s is the area of the DSC peak of the sample, A_r is the area of the DSC peak of the reference material, ΔH_s is the specific heat of fusion for the sample, ΔH_r is the specific heat of fusion for the reference material, m_s is the mass of the sample, and m_r is the mass of the reference material.[1]

In DTA, the same source of heat is used to heat the sample and the reference material, and the temperatures are measured separately. The temperature difference between the two is then plotted against the temperature of the heat source as it increases to give a DTA curve. [1,2] The peak on a DTA curve pointing downward indicates an endothermic reaction whereas the peak pointing upward indicating an exothermic reaction. [2]

In TGA, the weight of the sample is continuously measured as temperature increases. [1,2] The same heat source is used to heat the sample and the reference material. The decrease in the mass of the sample indicates oxidation, decomposition or chemisorption. [2]

DTA and TGA curves are usually combined together to give a more comprehensive study of the thermal events occurring in the tested materials. While TG only measures changes caused by mass loss, DTA record changes in material where no change in mass occurs such as melting temperature and glass transition. [2] Figure 2 shows that different sizes and shapes of peaks in a DTA plot correspond to different events occurring in an idealized polymathic material.

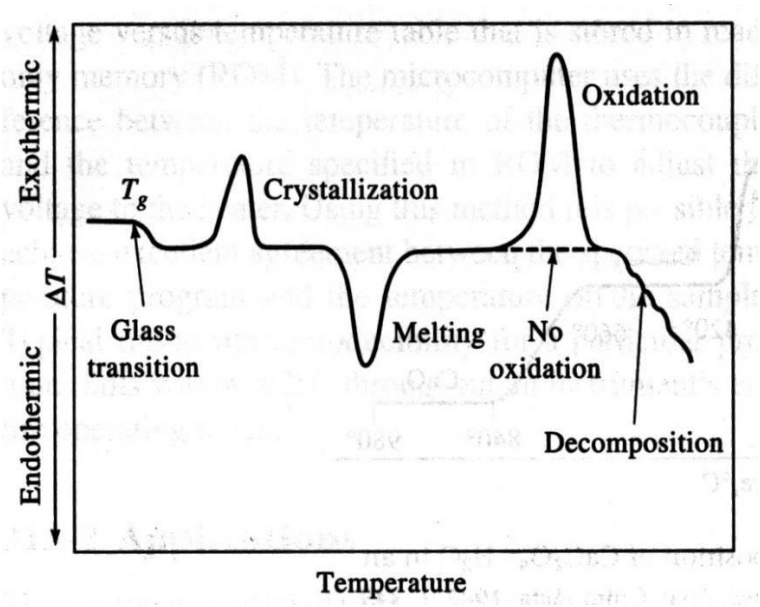

Figure 2. DTA curve of an idealized polymer.[2]

The objectives of the experiment were to determine phase transformations and reaction enthalpies in metals using DSC and to determine phase transformations and thermal degradation behavior in polymers using TG-DTA. Two 99.9% tin (Sn) samples and one lead-tin (Pb/Sn) alloy sample composed of 37% lead and 63% tin were tested in PerkinElmer instruments Diamond DSC at a rate of 5, 10 and 20 ºC/min, respectively. One polyethylene terephthalate (PET) sample was examined in SII Nano technology Inc. TG/DTA6200.

Experimental procedure

The instruments used for the thermal analysis of metals and polymers were PerkinElmer instruments Diamond DSC and SII Nano technology Inc. TG/DTA6200. The metallic materials being examined were 99.9% tin (Sn) and lead-tin (Pb/Sn) alloy composed of 37% lead and 63% tin. The polymeric material being examined was polyethylene terephthalate (PET) obtained from a plastic water bottle. The experiment was performed at a pressure of 1 atm. All samples and DSC pans were handled with tweezers in order to minimize any transformation of oils or dust to the samples. [1]

The first part of this experiment was to preform thermal analysis of two Sn samples and one Pb/Sn alloy sample using Differential Scanning Calorimetry (DSC). Each sample was prepared as following. First, the weight of the sample was measured to be about 10 mg and was recorded to the nearest 0.1 mg. Then, the sample was placed in an empty aluminum DSC pan. A caution was taken when the sample was handled. An aluminum cover disk was placed over the DSC sample pan. The DSC sample pan was sealed using the Perkin-Elmer pan crimper. Then, the sample was inserted into the appropriate heating chamber contained within the DSC. An empty pan was obtained to serve as the reference pan and was inserted into the appropriate heating chamber contained within the DSC. The following parameters were entered into the software. During all of the three DSC runs, purge gas of N_2 was flowing at approximately 20 mL/min. All of the three samples were held initially at 150.00 ºC for four minutes and tested with heat ranging from 150.00 ºC to 300.00C. The first run was performed at 5.00 ºC/min for the Sn sample measured to be 10.6 mg. The second run was performed at 10.00 ºC/min for the Sn sample weighted 10.2 mg. The third run was performed at 20.00 ºC/min for the Pb/Sn of 10.6 gm. An indium (99.999%, 4.7 mg) heating curve was provided in the course locker. This curve was used as the reference

spectrum in the enthalpy calculation. The sample was initially held at 100.00 ºC for four minutes and then increased to 200.00 ºC at 5.00 ºC/min with N_2 flowing at about 100 mL/min.

The second part of the experiment was to conduct thermal analysis of polymers using Thermogravimetry and Differential Thermal Analysis (TG/DTA). The PET sample was weighted and recorded to be 10.8 mg. The sample was placed in an empty aluminum TG/DTA pan and then onto the sample pan holder inside the TG/DTA equipment. An empty pan was obtained and placed onto the reference pan holder. The sample was heated from 25.00 ºC to 500.00 ºC at 20 ºC /min.

Image J version 1.50i image processing software was used to calculate the area under the peak on the DSC curves and the melting temperatures. [1]

Results and Discussion

On the basis of data that was obtained from differential scanning calorimetry, DSC curves of the heat flow as a function of temperature for the tin and lead-tin alloy samples were generated and then used to determine the melting temperatures of tin. The melting temperatures were determined at the intersection of the tangent lines drawn from the straight part of the curve and the peak.

Figure 3 shows the DSC curves for In and Sn at 5 ºC/min. the melting. The melting temperature for the Sn sample that was run at 5 ºC/min was determined to be 232.32 ºC. The specific heat of fusion for tin can be calculated using Equation 1. In order to solve for ΔH^s , the area under the peak of indium and tin curves, the mass of tin and indium and the specific heat of fusion for indium were required to be known. The area under the indium curve was found to be 702 pixels whereas the area under the tin curve was determined to be 3320 pixels using the Image J image processing software. The specific heat of fusion for indium was given to 28.45 mJ/mg.

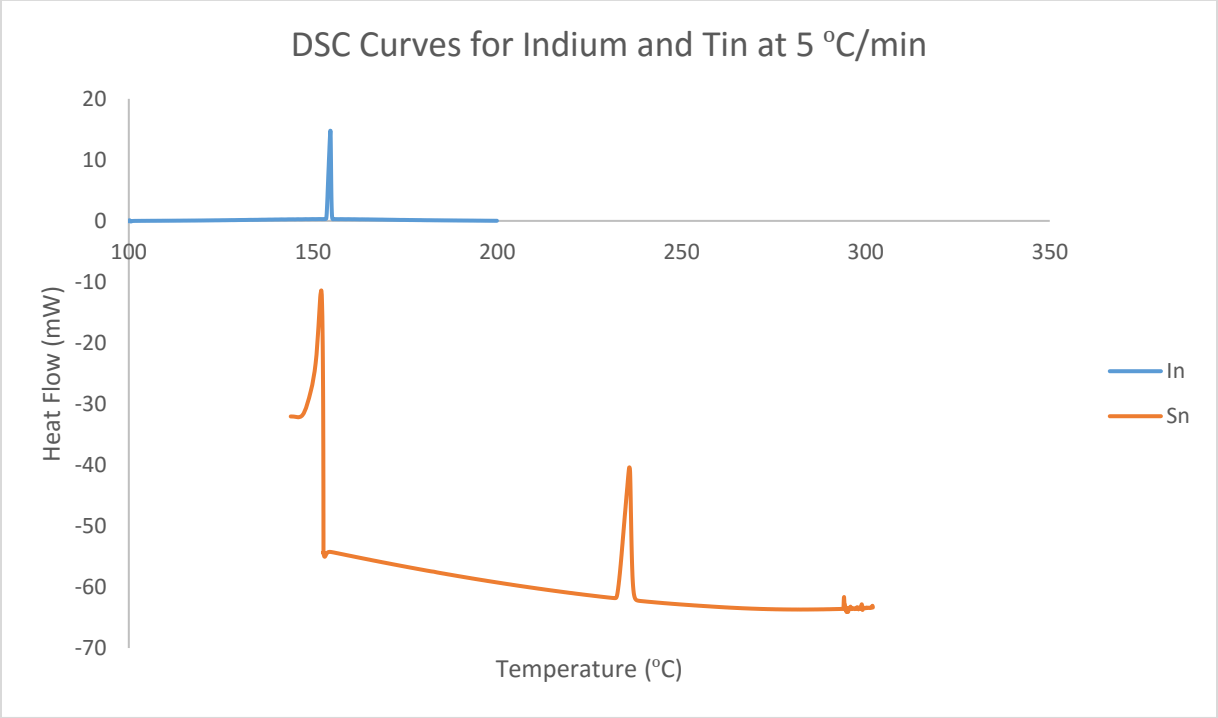

Figure 3. DSC curves of the heat flow versus temperature for Indium and Tin at 5 ºC/min.

As a result, the specific heat of fusion for tin was determined to be 59.65 mJ/mg, calculated as following:

$$\Delta H_s = \frac{A_s \Delta H_r m_r}{A_r \Delta H_s m_s} = \frac{3320\ pixels\ (\frac{28.45 mJ}{mg})(4.7 mg)}{702\ pixels\ (10.6\ mg)} = 59.65 \frac{mJ}{mg}.$$

The melting temperature for the Sn sample run at 10 ºC/min was determined to be 232.53 ºC using the intersection method on the DSC curve shown in Figure 4. No significant change in the melting temperature was found between the Sn sample run at 5 ºC/min and the Sn sample run at 10 ºC/min.

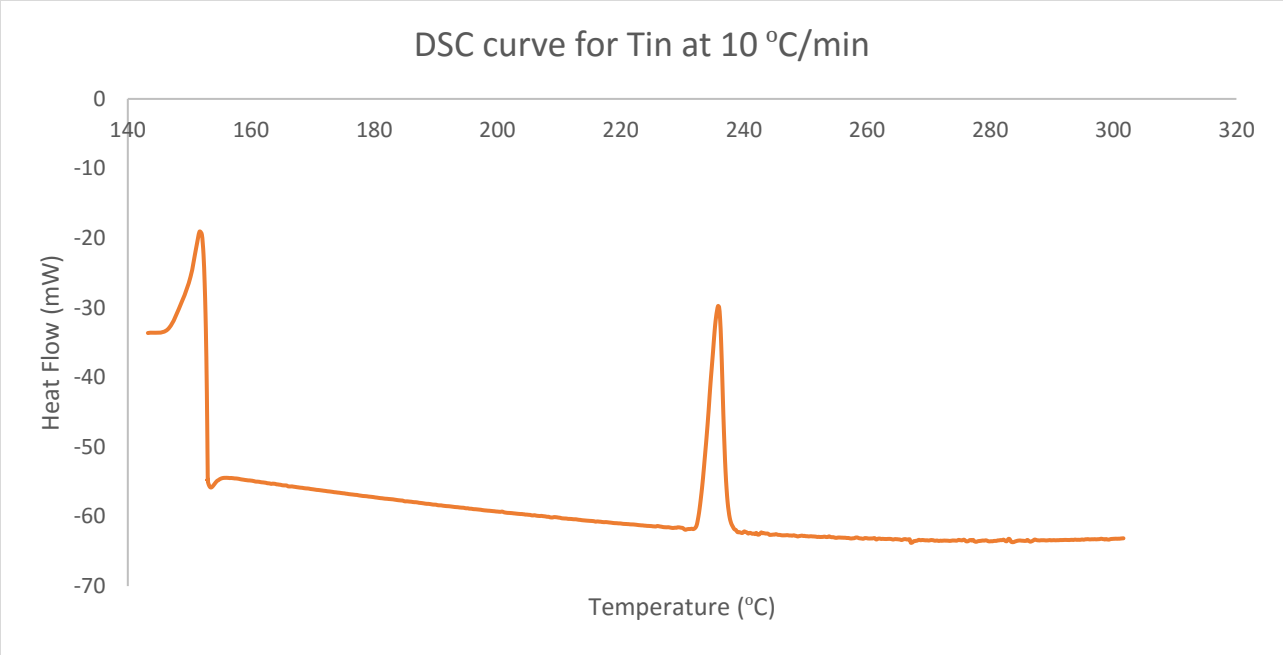

Figure 4. DSC curve of the heat flow versus temperature for Tin at 10 ºC/min.

Figure 5 shows DSC curve of the heat flow versus temperature for Pb/Sn Alloy at 20 ºC/min. The melting temperature of the Pb/Sn Alloy was estimated to be 185.40 ºC.

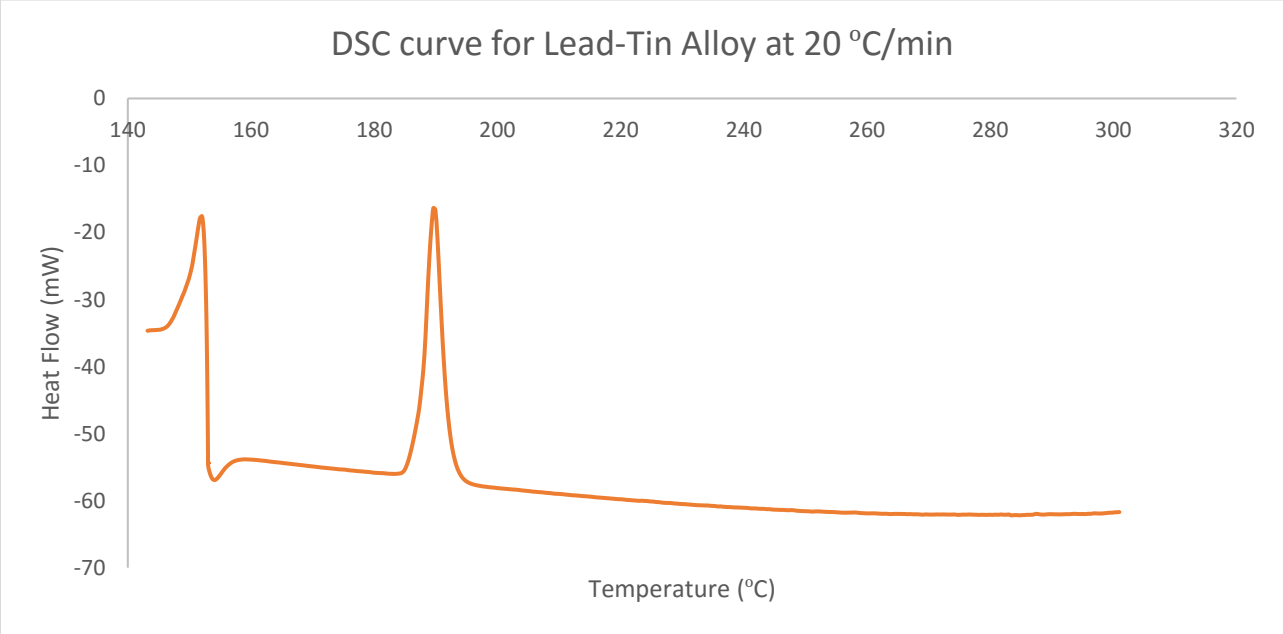

Figure 5. DSC curve of the heat flow versus temperature for Lead-Tin Alloy at 20 ºC/min.

The two Sn samples had very similar melting temperature even though one was run at a rate twice as fast as the other one. An increase in the heat rate caused an insignificant increase in the melting temperature. This indicates that the heating rate does not have a considerable influence on the on-set melting temperatures and the thermograms obtained. [4] More specifically, the heating rate has a limited effect on small masses because they have larger surface area exposed. [4]

Since the heating rate has a limited influence on the phase transition temperatures, the melting temperatures for the Sn and Pb/Sn alloy samples measured experimentally can be compared with equilibrium phase diagram of lead-tin alloy shown in Figure 6. The equilibrium phase diagrams are assumed to have a heating/cooling rate of 0 ºC/min. [1] A good agreement was found between the experimental results of the Sn melting temperatures of about 323.40 ºC and the literature value of the Sn melting temperature of 232.01 ºC. [3]

Moreover, the specific heat of fusion for Sn in the experiment was determined to be 59.65 mJ/mg, which was found to be very close to the literature value of 59.50 mJ/mg. [3] Some potential errors could be caused by the estimation of the areas under the peak.

For the Pb/Sn alloy, it can be obtained from the phase diagram that the melting temperature of Sn at 63 % Sn is 185.10 ºC. The experimental result of 185.40 ºC agrees with the theoretical value. [3] These agreements demonstrate that DCS is precise in determining the melting temperatures at which phase changes occur. [1,2]

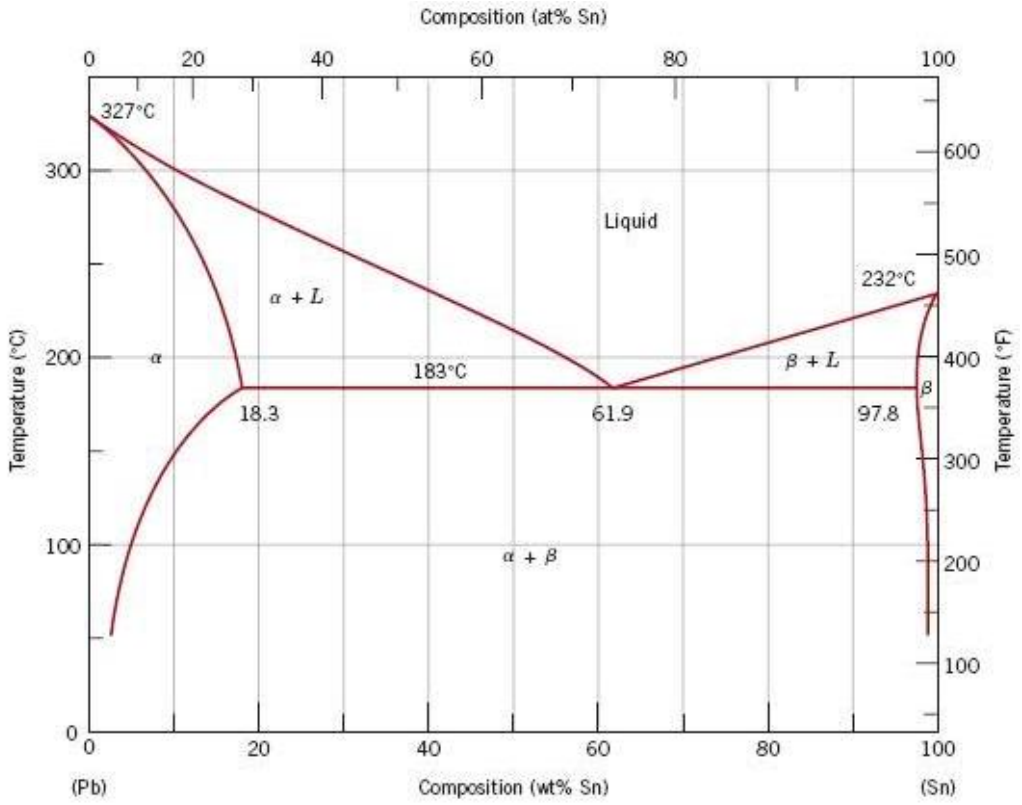

Figure 6. Pb/Sn phase diagram. [3]

For PET, the thermogravimetric analysis and differential thermal analysis results were plotted as shown in Figure 7. TGA curve, in blue, shows a steady horizontal line then a rapid decrease in the mass of the sample starting at approximately 350°C. DTA curve, in green, shows peaks at 249°C, 375° C and 425°C. Since no mass change was observed near the peak at 249°C and the peak was downward indicating endothermic process, the melting point was determined to occur at this temperature. [1,2] With changes in mass, oxidation was determined by the upward point peak around 375°C and decomposition by the downward pointing peak at approximately 425°C. [1]

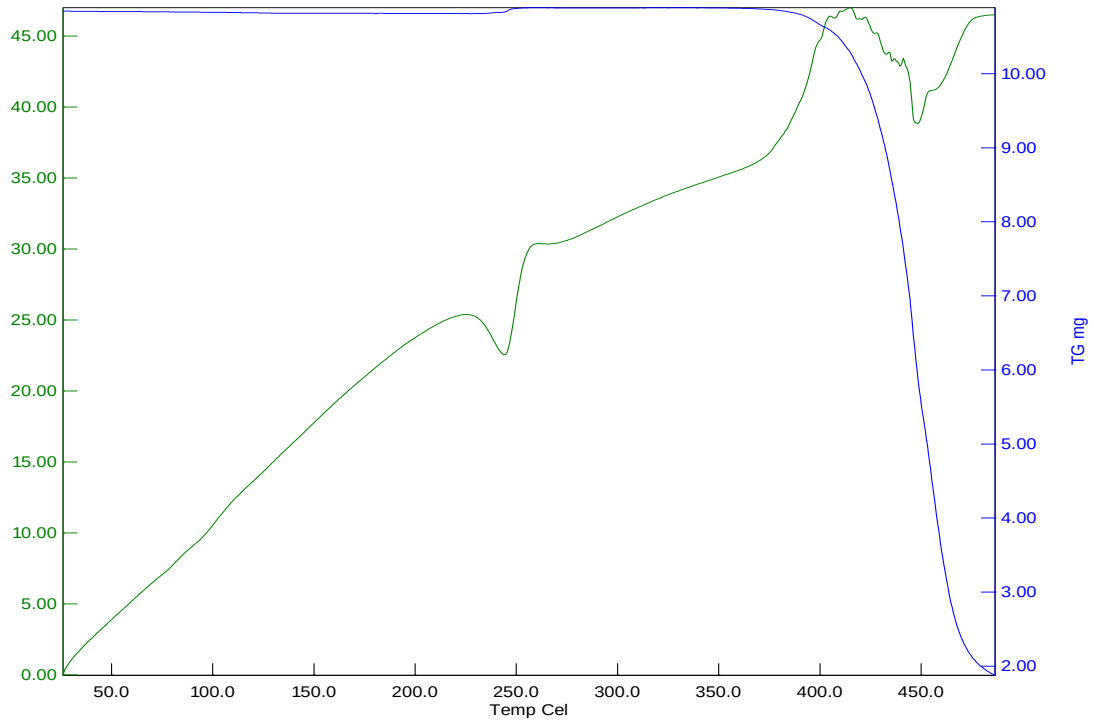

Figure 7. TG (blue)-DTA (green) curves of temperature change and change in mass as a function of temperature for PET.

The DTA curve for PET shows similar events happening in the DTA curve for ideal polymers shown in Figure 2. The melting temperature of PET was determined to be 249°C, which agreed with the literature value of 248°C.[5] PET degrades significantly above a temperature of 350°C as it rapidly loses mass. [2] These results agree with the literature findings. The degradation of PET does not begin until above the melting point, implying that PET is a safe material used in food and drink packing. [1,5]

Conclusion

The objectives of the experiment were to determine phase transformations and reaction enthalpies in metals using differential scanning calorimetry (DSC) and to determine phase transformations and thermal degradation behavior in polymers using thermogravimetric

/differential thermal analysis (TG-DTA). Two 99.9% tin (Sn) samples and one lead-tin (Pb/Sn) alloy sample composed of 37% lead and 63% tin were tested in PerkinElmer instruments Diamond DSC at a rate of 5, 10 and 20 ºC/min, respectively. One polyethylene terephthalate (PET) sample was examined in SII Nano technology Inc. TG/DTA6200.

Overall, the experiment was successful. It accurately identified the melting points and the specific heat of fusion and degradation behavior. The melting points were determined to be 232.32 ºC for tin run at 5 ºC/min and 232.53 ºC for tin run at 10 ºC/min, indicating a limited effect of the heating rate on the thermograms. The specific heat of fusion for tin was determined to be 59.65 mJ/mg. The melting point of the lead-tin alloy was determined to be 185.40°C. The melting point for PET was determined to be 249°C, and significant degradation and loss of molecular weight started at 350°C. Good agreements are found between the literature thermal characteristics and the values obtained experimentally.

The experiment suggests that DCS and TG/DTA are very accurate in determining thermal characteristics and identifying the melting points for Sn and Sn/Pb alloy. The experiment can be further improved by using fine-grained powder to achieve greater contact area and better equilibrium. [1] In addition, lower heating rate would permit completeness of reactions and better estimation of the phase transition temperatures. [1]

References

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