



Thermal Analysis Investigation of a Poly(Lactic Acid) Biodegradable Plastic

ABSTRACT

With the push in recent years for industry to develop and manufacture products on a more environmentally friendly basis, a variety of new biodegradable polymer systems have been developed to fit that mold. Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester which is produced from lactides and lactic acid monomers that are derived from the fermentation of corn starch and sugar feed stocks. The polymerization of lactic acid into PLA produces a biodegradable thermoplastic polyester that has high mechanical strength, similar to PETE, with good biocompatibility. PLA has most commonly been used in biomedical applications for drug delivery systems as well as sutures and stents, but the number of applications for PLA is constantly growing. Understanding the properties of PLA becomes essential to the future development of new applications. This study will examine a variety of the thermal and mechanical properties of a PLA drinking cup using thermal analysis techniques such as DSC, MDSC[®], Rapid Heat/Cool DSC (RHC) and DMA.

INTRODUCTION

A generic drinking cup made of PLA was used as the sole member of this investigation and was selected simply because of the physical appearance of the cup. The top half of the cup had an optically clear, uniform appearance while the bottom half of the cup had a much more irregular look that gave the appearance of material roughness without any physical texture. It was assumed that the top half of the cup was more amorphous while the bottom half more crystalline. In order to determine the amorphous and crystalline components in the top of the cup versus the bottom of the cup, the investigation started with standard DSC measurements, which is probably the simplest technique. More advanced DSC methods as well as DMA measurements were incorporated into the investigation to refine and verify the results obtained on the PLA cup.

RESULTS & DISCUSSION

A standard DSC heat-cool-heat method was initially run on a sample taken from the top half of the cup, which was assumed to be more amorphous. The data is shown below in Figure 1. The cup sample was heated at 20 deg/min and cooled at a controlled rate of 10 deg/min between 25 and 170°C. All of the DSC and MDSC samples were tested on a Q2000 DSC in TZero Aluminum pans with a nitrogen purge. The first heat, in this instance, shows a small glass transition (T_g) around 58°C with some cold crystallization beginning around 90°C and a melt with a peak temperature of about 148°C. The second heat on this sample after it was cooled at 10 deg/min shows a larger T_g around the same temperature as the first heat, but no evidence of cold crystallization or melting. The results suggest that the top portion of the cup had some amount of amorphous structure, but because the sample undergoes some cold crystallization or crystal perfection immediately before the melt, the amount of crystalline structure in the

sample, as-received, is difficult to determine. Modulated DSC, however, is the perfect tool to investigate the crystalline versus amorphous concentration of a material, as-received, when there is cold crystallization or crystal perfection.

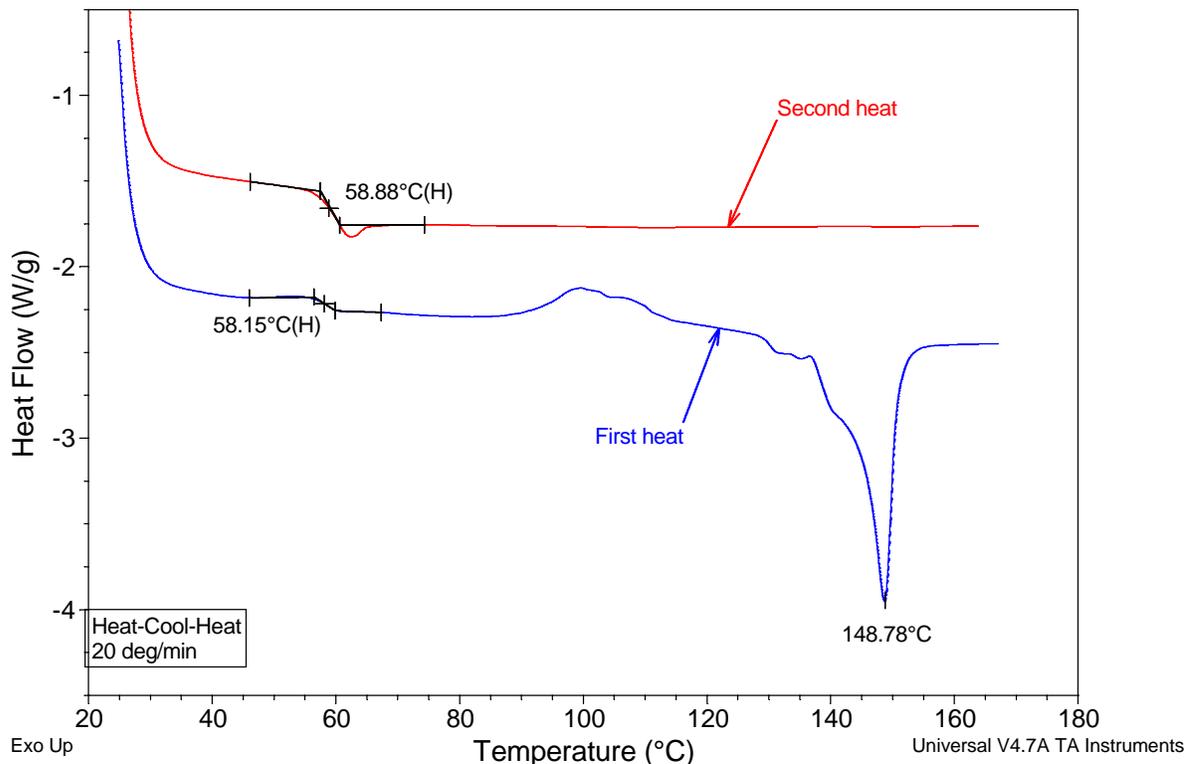


Figure 1: Standard DSC Heat-Cool-Heat experiment of a sample from the top of the PLA cup

Another sample taken from the top half of the PLA cup was loaded into another pan and tested using MDSC. The experimental method was a Heat Only MDSC experiment with 80 second periods and a 3 deg/min heating rate. The sample was again tested between 25 and 170°C. The Modulated results for the top of the cup are shown in Figure 2. The Reversing Heat Flow (Heat Capacity Component) shows a clear Tg around the same 58°C temperature seen in the standard DSC experiment and a majority of the melting endotherm shows up in the Reversing Heat Flow as well. The Non-Reversing Heat Flow (Kinetic Component) shows some Enthalpic Recovery around the same temperature as the Tg followed by the exothermic crystal perfection and a small portion of the melting endotherm. The Reversing and Non-Reversing Heat Flow Curves are integrated using a linear integration line. The limits of integration range from a temperature before the crystal perfection begins through a temperature above the melt peak. In theory, if the absolute total area of Non-Reversing integration is equal to the total area of the Reversing integration, the material, as-received, most likely does not have any crystallinity. In this case, the integrated area of the Reversing Heat Flow is 37 J/g larger than the area in the Non-Reversing Heat Flow, which suggests there exists some concentration of crystallinity that would equate to 37 J/g of energy in the melt in the material as-received.

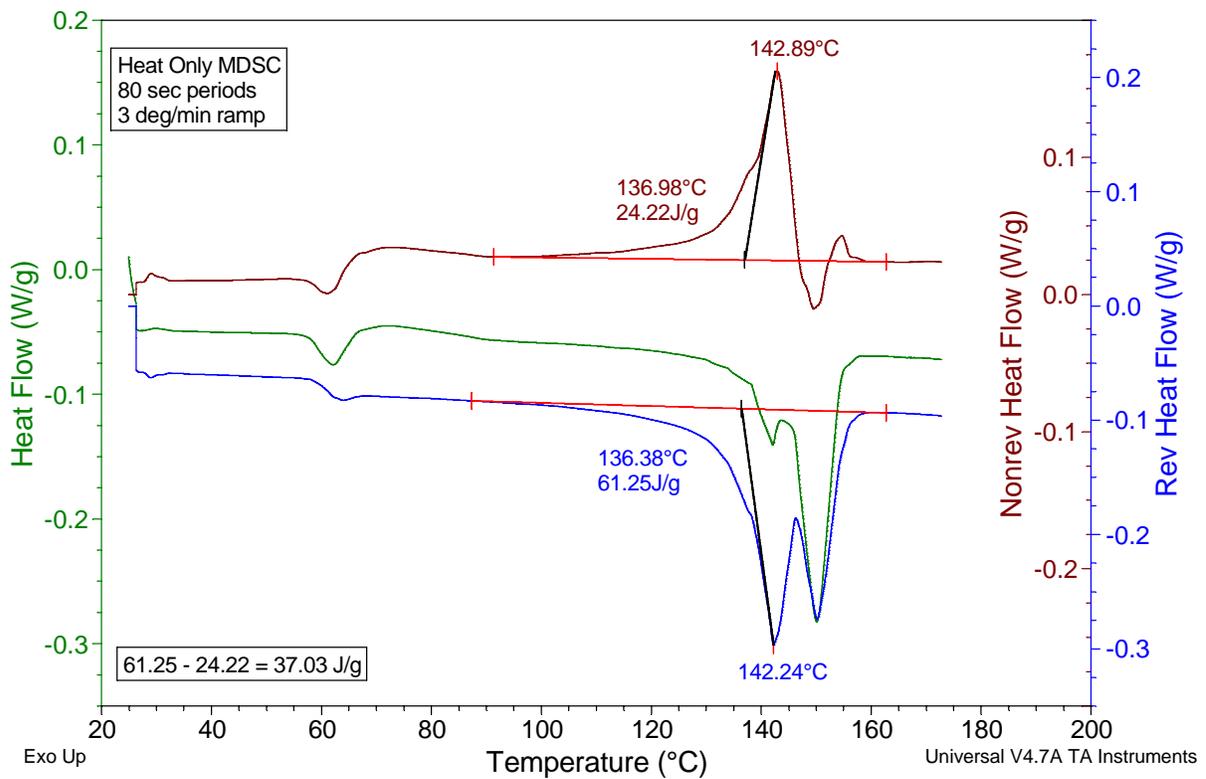


Figure 2: MDSC results on a sample taken from the top of the PLA cup

A sample taken from the bottom of the PLA cup was tested using the same Modulated conditions as the sample from the top of the cup. The results are shown in Figure 3. While there are some similarities between the MDSC results of samples taken from the top and the bottom of the cup, there is one major difference that directly points to a major difference in material structure. The Tg is approximately at the same temperature as before and there is still some enthalpic recovery, crystal perfection and melting that show up in both the Non-Reversing and Reversing Heat Flows out beyond 120°C. The major difference seen in the bottom of the cup is a large cold crystallization peak that begins around 80°C. This peak suggests that some of the amorphous structure in the material is ordering and converting to a more structured, crystalline structure which was an event that did not show up in the sample from the top of the cup. The other interesting characteristic determined from the MDSC results is the fact that the area of the Non-Reversing Heat Flow, including the cold crystallization, and the Reversing Heat Flow are nearly the same value. This result suggests that the sample did not have any crystallinity to begin with and all of the crystalline material that melted was formed during the cold crystallization, which is counter to the initial assumption based off of the optical appearance that the sample was more crystalline.

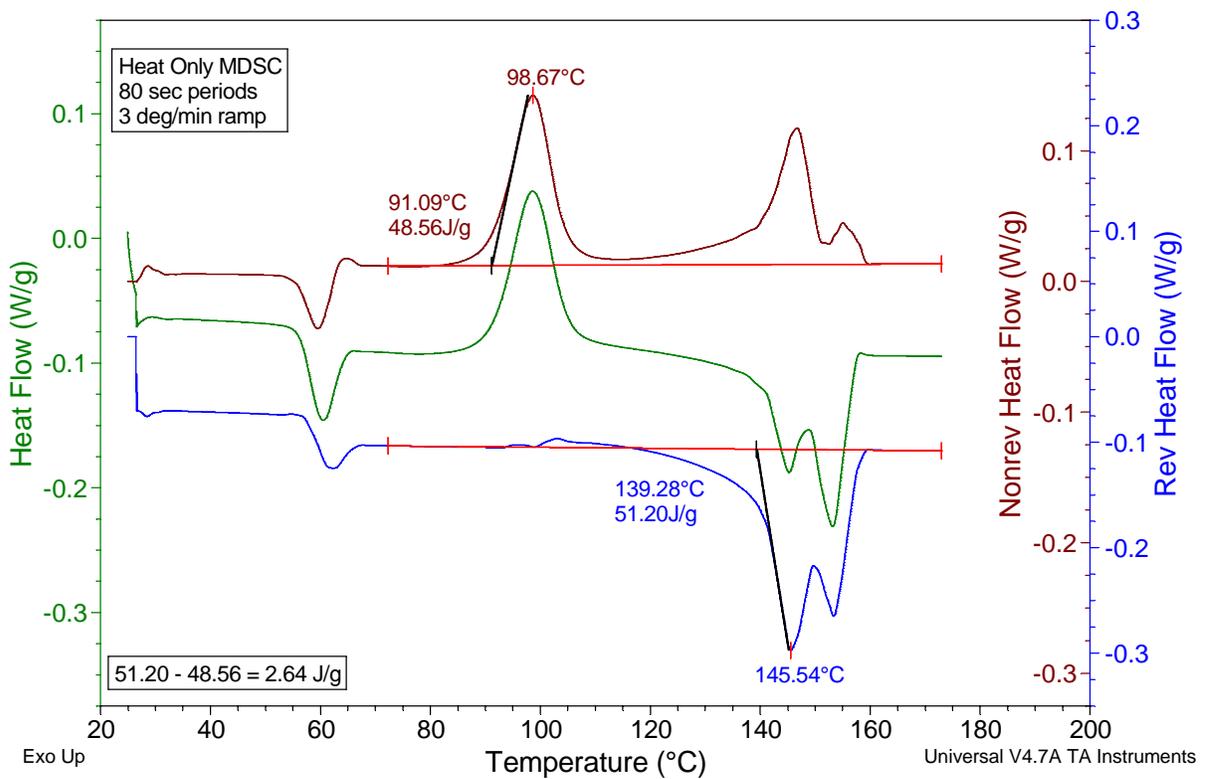


Figure 3: MDSC results on a sample taken from the bottom of the PLA cup

In order to verify that all of the crystallinity was formed during the heating ramp and was not in the sample initially, a Rapid Heat-Cool DSC (RHC) experiment was used to heat the sample at 1000 deg/min in an attempt to suppress the cold crystallization. For the RHC experiment, a Beta RHC DSC was used and approximately 0.3mg of sample was tested in aluminum pans custom designed for the RHC. The test temperature range was widened to -150°C on the low end and 225°C on the high end in order to accommodate the higher heating rate of 1000 deg/min. The Heat Flow results for the RHC experiment are shown in Figure 4 and show only a T_g around 76°C and nothing else. The shift up in temperature of the T_g in this case is simply a result of the increased heating rate when compared to MDSC and DSC, which both have heating rates over an order of magnitude slower. There is no evidence of cold crystallization upon heating and the fact that there is no evidence of melting suggests that there is no crystalline material in the sample to melt. For comparison purposes, the same sample taken from the bottom of the cup was allowed to crystallize by slowing heating the material to a temperature around 125°C and then tested again in the RHC at 1000 deg/min. The results for the material that was allowed to crystallize, shown in Figure 5, prove that a sample with crystalline material that melts will show that melting endotherm even if heated at 1000 deg/min with very little shift in the onset of melting. If the sample initially had any crystalline structure, the melt should have shown up in the first RHC experiment.

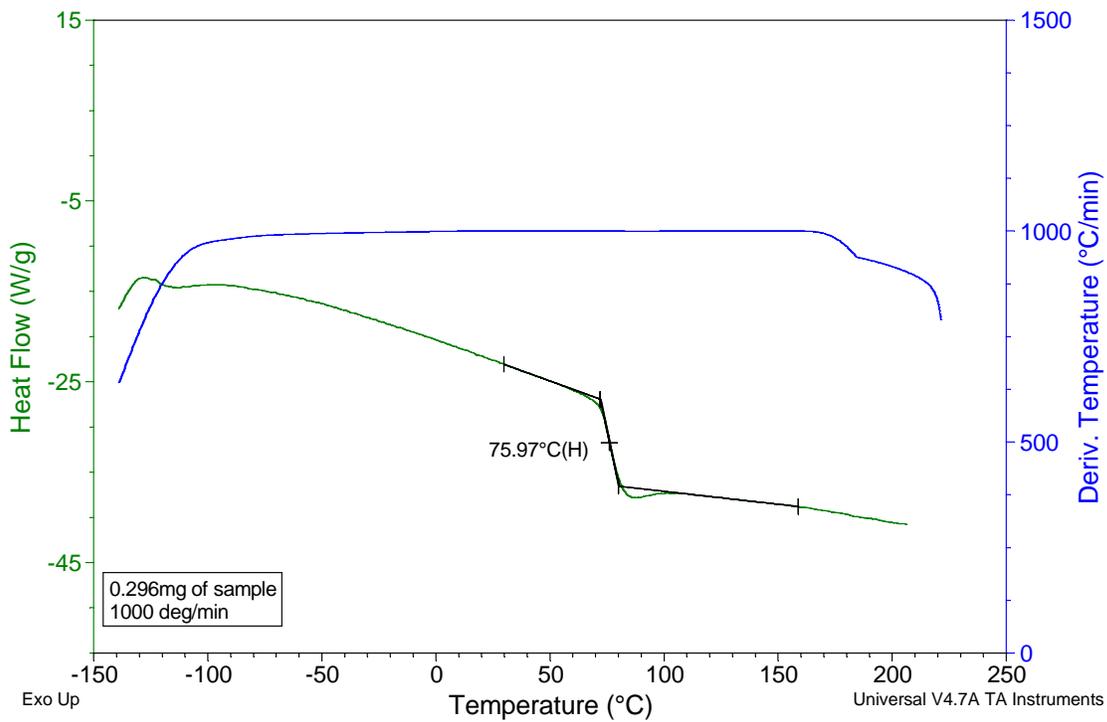


Figure 4: The bottom of the cup, as-received, tested in the RHC at 1000 deg/min

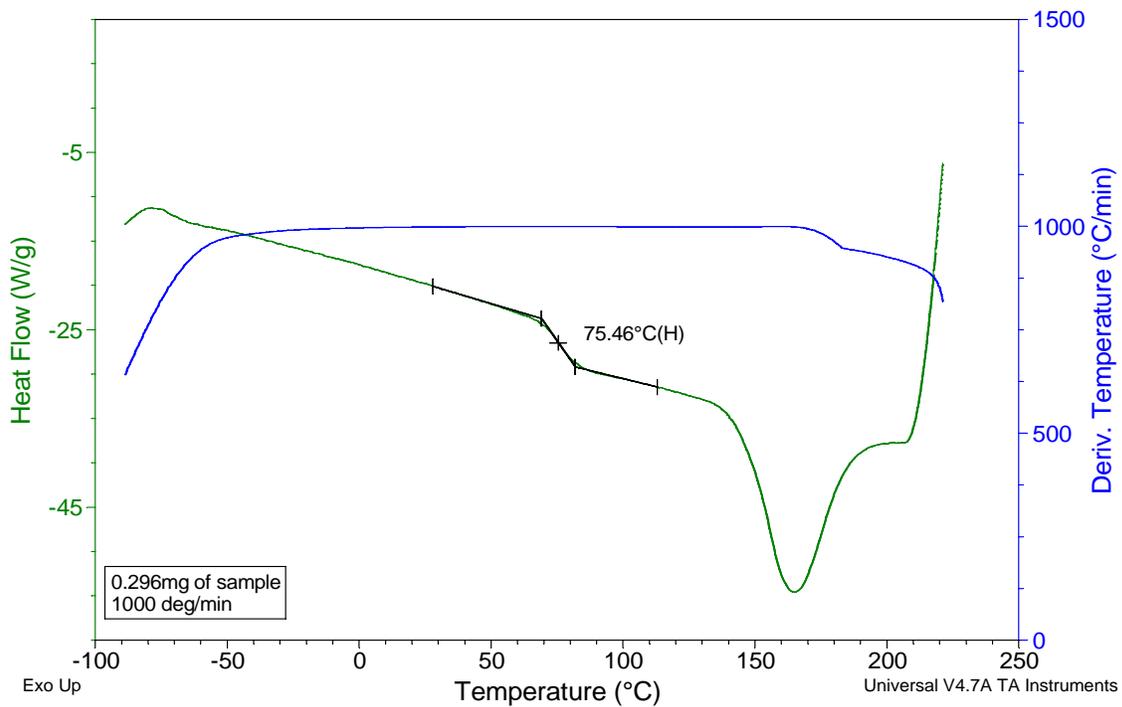


Figure 5: The bottom of the cup tested in the RHC at 1000 deg/min after it was allowed to crystallize

To verify the conclusions made about the top of the PLA cup that there was indeed some crystalline structure in the material initially, the same RHC experiment was run on a

sample taken from the top of the cup. The results shown in Figure 6 actually show two endothermic peaks around 75 and 125°C. Based on some of the previous experiments, however, the first endotherm around 75°C is most likely the result of some enthalpic recovery that overshadows the T_g since the other RHC experiments at 1000 deg/min show the T_g right around 75°C as well. The second endotherm is associated with initial crystallinity that melts around 125°C which compares well with the MDSC experiments of the same material that begins to melt around 120°C minus the crystal perfection.

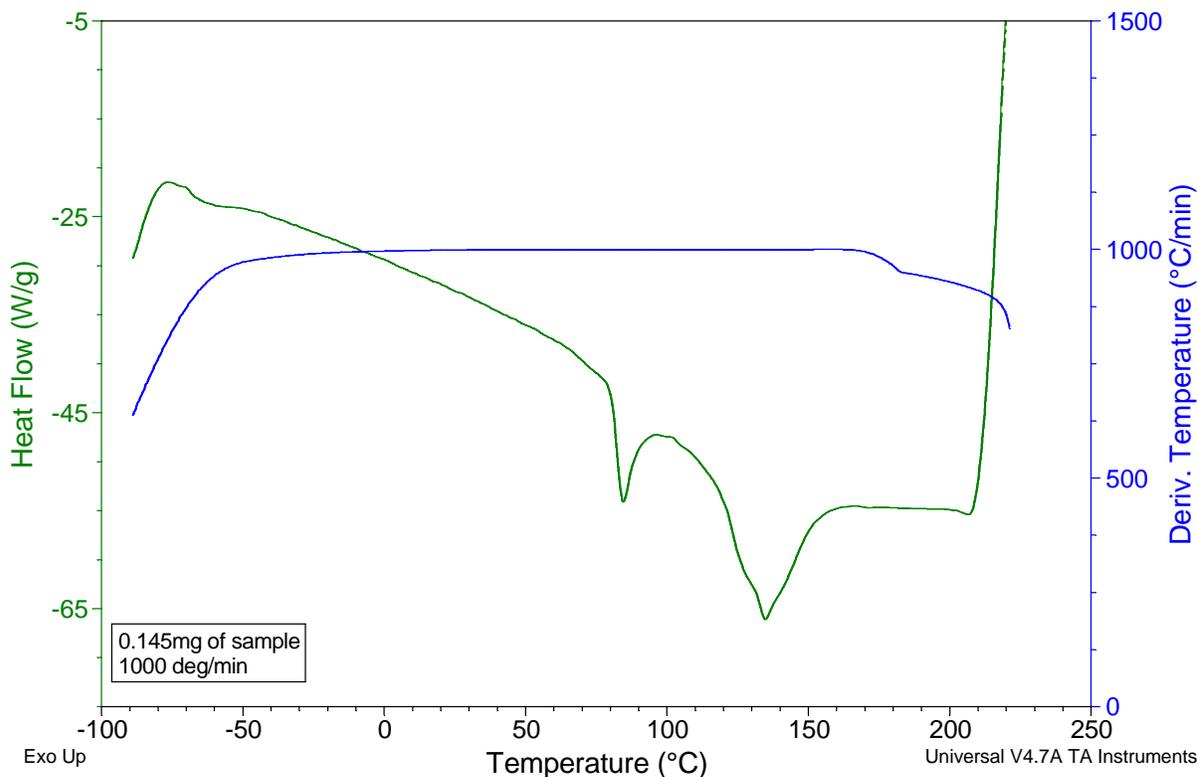


Figure 6: The top of the cup, as-received, tested in the RHC at 1000 deg/min

Another technique available to examine the crystallinity or the change in crystallinity as a function of temperature is the DMA. Figures 7 and 8 are experiments run on the same PLA cup samples using the RSA DMA. The results collected on a sample from the top of the cup in Figure 7 show that the Storage Modulus of the sample drops around 60°C where the material goes through the T_g and then plateaus before dropping again around 130°C where the material melts. Both of these events correlate quite well with the results collected by DSC. Figure 8, which are the results collected from a sample from the bottom half of the cup show a drop in Storage Modulus around 60°C for the T_g and then a significant increase in Modulus around 100°C, which is usually indicative of an increase in stiffness/mobility and correlates very well with the cold crystallization shown in the MDSC results around the same temperature. Figure 9 shows an overlay comparison of the Storage Modulus between the two samples.

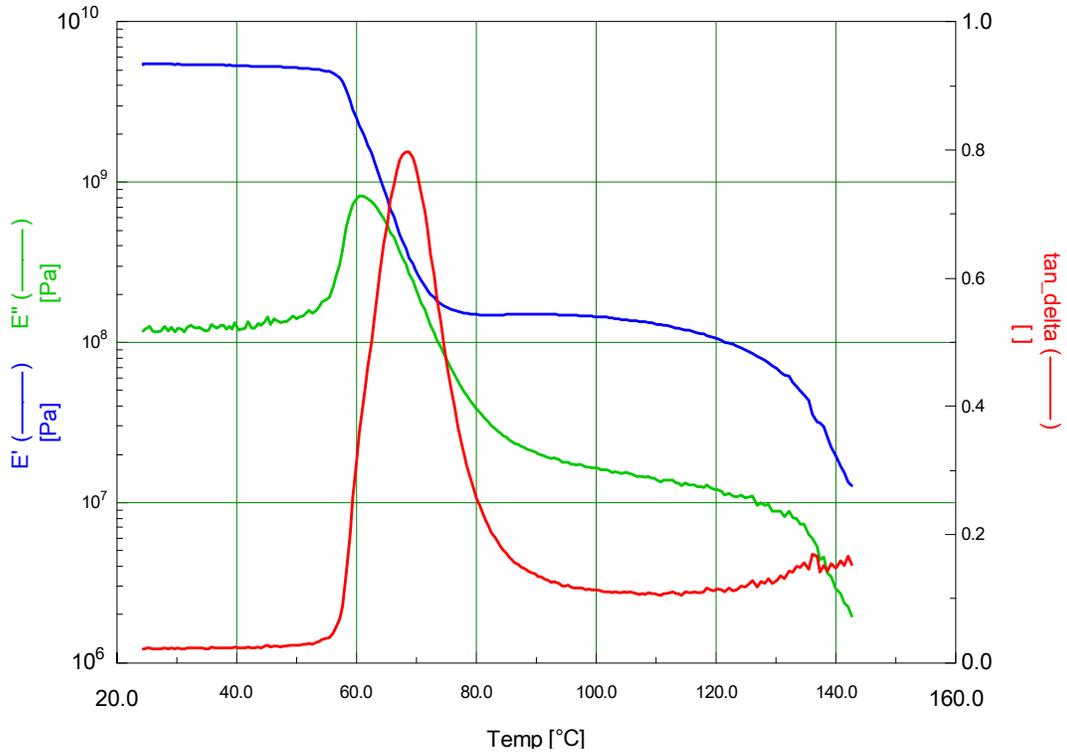


Figure 7: DMA data from the top portion of the cup

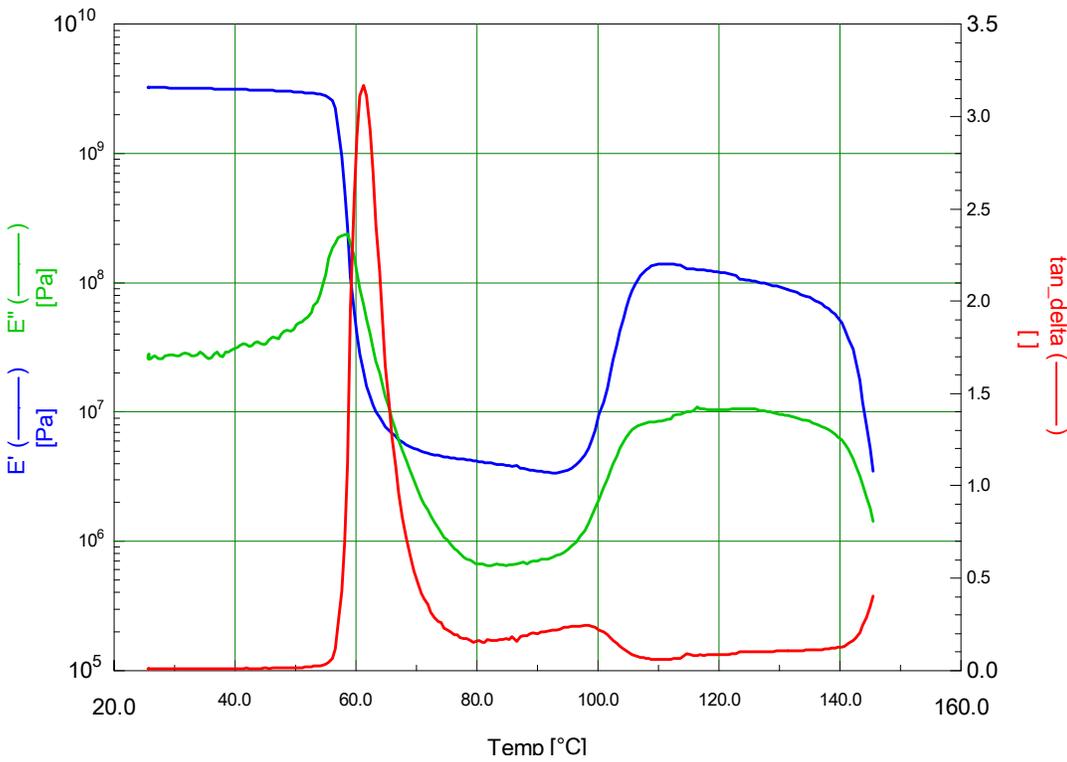


Figure 8: DMA data from the bottom portion of the cup

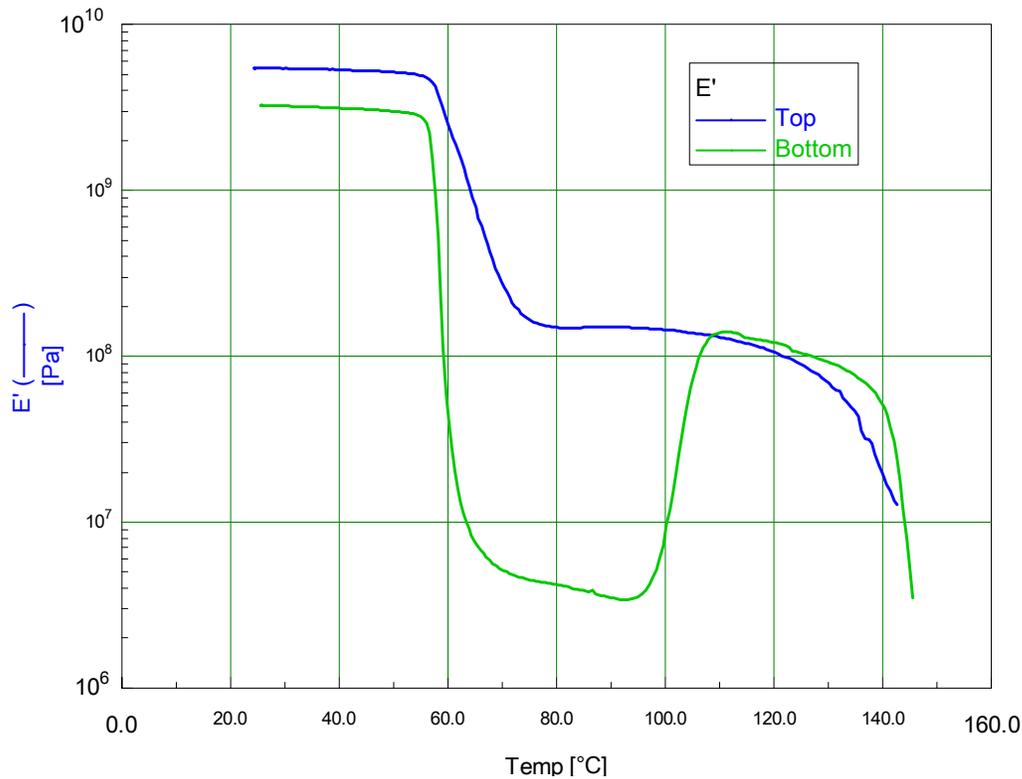


Figure 9: Overlay of the E' DMA data from both the top and bottom sections of the cup

CONCLUSIONS

A plastic drinking cup made from the biodegradable plastic, poly(lactic acid) was examined using DSC, MDSC, Rapid Heat/Cool DSC and DMA. The aim of the investigation was to compare two areas that appeared optically and structurally different, with the supposition that a difference in crystallinity may be responsible. Results were consistent across techniques showing a difference initial crystallinity between the two sections.

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