

TA no.81

Thermal analysis of polylactic acid

2007.9

—Crystallinity and heat resistance—

1. Introduction

Recent views on waste disposal and environmental conservation have increased the focus on biodegradable plastic, which can be produced from renewable raw materials and decomposes in the natural environment. Polylactic acid (PLA) is a biodegradable plastic derived from plants that is widely used in packing materials, fibers and medical materials. Crystallinity is an important consideration for the strength, impact resistance, and transparency requirements of these materials and influences biodegradability. Furthermore, lactic acid, the PLA monomer, has asymmetrical carbon atoms and thus has optical isomers. The isomeric ratio and molecular weight of polymers influence crystallinity and heat resistance, so their roles must be considered during the formation process.

In this brief, DSC and TG are used to measure the crystallinity and heat resistance of PLA plastic with different isomeric ratios and molecular weights.

2. Measurement

Four samples were measured. PLA plastic a, b, and c had roughly the same molecular weight but different levo-rotatory(L)/ dextro-rotatory(D) ratios (L ratio: $a < b < c$). Sample c' and sample c had the same L/ D ratio but Sample c' had a lower molecular weight. DSC samples were heated to 200 ° C and then cooled at various rates (quench cooling, 10, 5, 1, 0.5 and 0.1 ° C/ min). No heating or cooling was used for the TG measurements.

The measurements were performed using the DSC6220 Differential Scanning Calorimeter and the TG/DTA6200 Thermo-Gravimetric/Differential Thermal Analyzer. For the DSC measurements,

10mg samples were heated from 20 ° C to 200 ° C at 10 ° C /min. in a nitrogen atmosphere. For the TG measurements, 10-mg samples were heated from room temperature to 400 ° C at rates of 10, 5, 2 and 1 ° C / min. in a nitrogen atmosphere.

3. Results

Figure 1 shows the DSC results when the samples were melted and then cooled at 0.1 ° C / min. Figure 2 shows the DSC results when the samples were quenched rapidly.

As seen in Figure 1, glass transition (Tg) occurred around 60 ° C for all samples. Melting occurred with endothermic peaks at 150 ° C and 170 ° C for Sample b and Sample c/ c', respectively. These results show that the higher the L ratio, the easier it is for crystallization to occur. The crystallinity of Sample was so low that crystallization did not occur, even at a cooling rate of 0.1 ° C/ min. The melting temperature and heat of fusion for Sample c and c' were roughly the same so these results did not show any clear differences in crystallinity due to molecular weight.

While Sample b has a melting peak in Figure 1, there is no melting peak in Figure 2. This result shows the important relationship of the isomeric ratio and the cooling rate during polymer molding manufacturing. Furthermore, while there are no differences between c and c' in Figure 1, there are differences at cold crystallization around 140 ° C and at the melting peak in Figure 2. The size difference of the peaks (heat of crystallization, heat of fusion) indicates that when the L ratio is the same, the sample with the lower molecular weight has higher crystallinity.

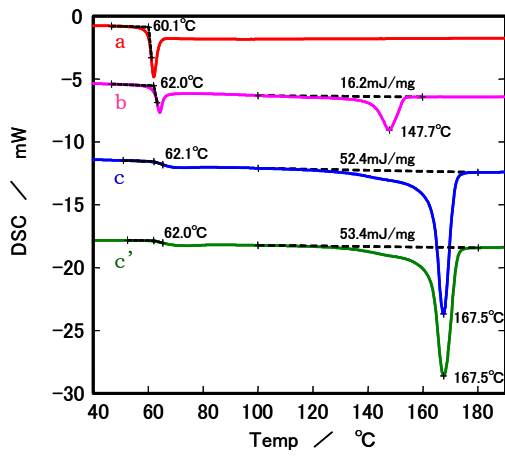


Figure 1. DSC results after cooling at 0.1 °C/ min

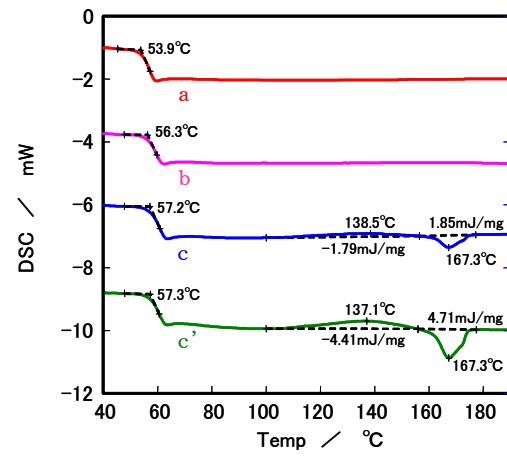


Figure 2. DSC results after quench cooling

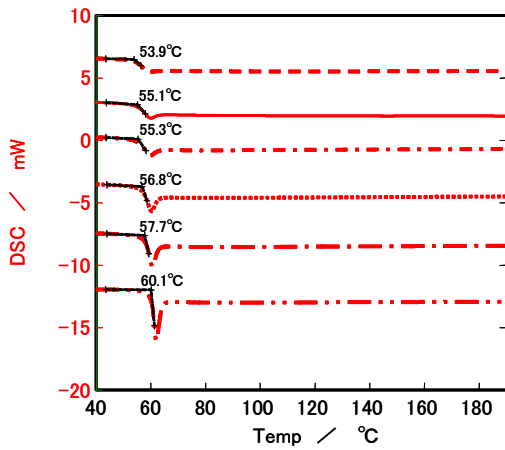


Figure 3. DSC results for Sample a

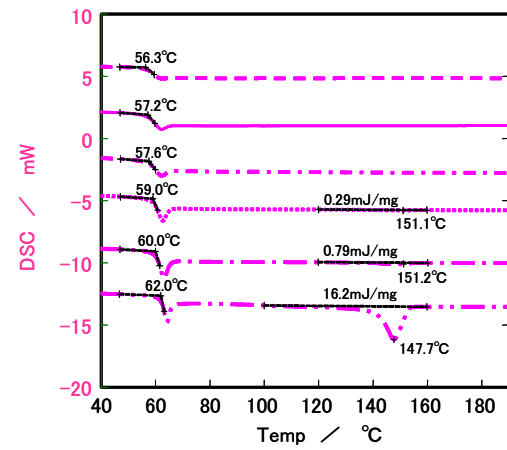


Figure 4. DSC results for Sample b

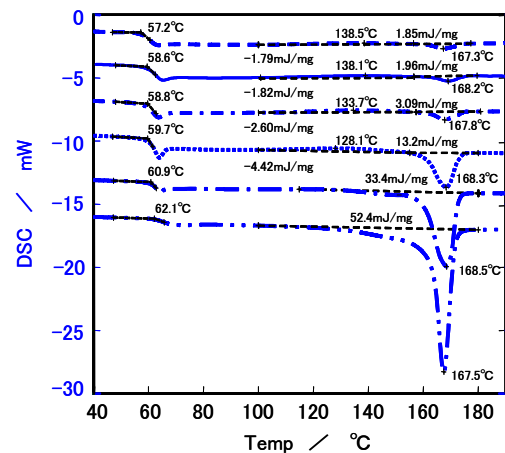


Figure 5. DSC results for Sample c

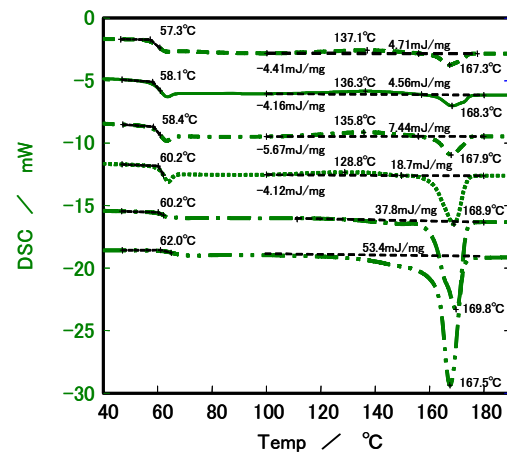


Figure 6. DSC results for Sample c'

- After quench cooling
- After cooling at 10 °C/ min
- - - After cooling at 5 °C/ min
- After cooling at 1 °C/ min
- · — After cooling at 0.5 °C/ min
- · - · - After cooling at 0.1 °C/ min

Figures 3 to 6 show the DSC results for Sample a, b, c and c' at different cooling rates. Sample a did not show a melting peak under any cooling condition and was considered nearly amorphous, regardless of the cooling rate. Sample b showed a melting peak when the cooling rate was 1 °C / min or less. This result shows that to increase the crystallinity, the cooling rate must be at this rate or slower. For Sample c and c', there was no difference in crystallinity at a cooling rate of 0.1 °C / min. However, when the cooling rate was 0.5 °C / min or greater, Sample c' had a large heat of fusion. This shows that the crystallinity of Sample c' is higher.

By setting the heat of fusion of Sample c' after cooling at 0.1 °C / min to one, the relative crystallinity was calculated from heat of fusion. The results in Table 1 show that the higher the L ratio, the higher the crystallinity. The results for Sample c and c' show the influence of molecular weight. While there was little difference in the crystallinity after cooling at 0.1 °C / min, these results confirm that molecular weight has an influence on crystallinity that is dependant on the cooling rate.

Figure 7 shows the TG/DTA results for Sample b and c at different heating rates. The TG results show little difference in thermal decomposition so there were no clear differences in heat resistance. Next, kinetics analysis was performed using the Ozawa method with the TG results for Sample b, c and c' at different heating rates. Figure 8 shows the results of the kinetics analysis for Sample c. Table 2 shows the activation energy results. These results show that Sample c', which has a low molecular weight, reacts quickly. When the molecular weight is the same, samples with a lower L ratio have a faster reaction. These results confirm that heat resistance differs by molecular weight and L ratio.

Table 1. Comparison of relative crystallinity* by cooling rate (°C / min)

Rate	0.1	0.5	1	5	10	Quench cooling
Sample a	-	-	-	-	-	-
b	0.303	0.015	0.005	0	0	0
c	0.981	0.625	0.164	0.009	0.003	0.001
c'	1	0.708	0.273	0.033	0.007	0.006

* The heat of fusion of Sample c' after cooling at 0.1 °C / min was set as 1.

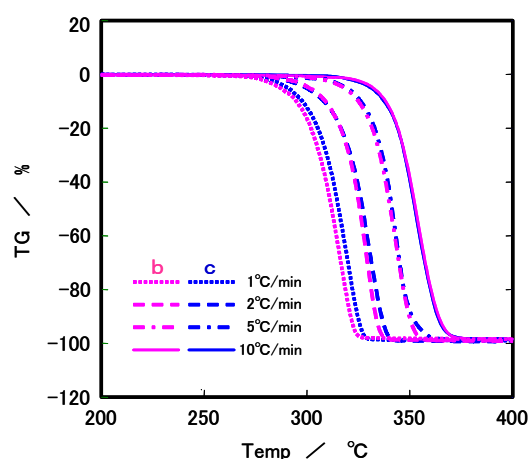


Figure 7. TG results for Sample b and c

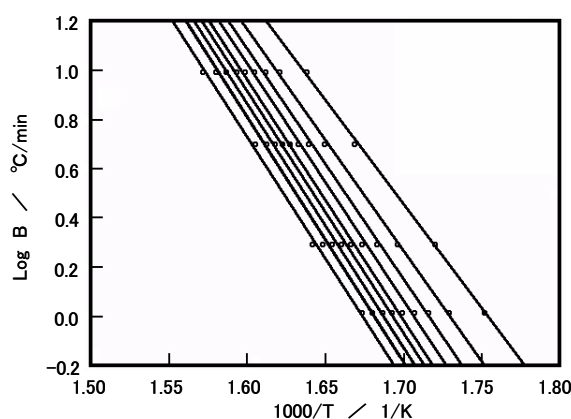


Figure 8. Arrhenius plot results for Sample c

Table 2. Calculation results for activation energy

Sample	ΔE [kJ/mol]	Constant Temperature Degradation Time (Life Time) (hr.)
b	144	15.4
c	155	21.6
c'	136	10.9

* 230 ° C, 10% reaction

4. Summary

In this brief, DSC and TG/DTA were used to measure PLA, a biodegradable plastic. Two important factors during the polymer molding manufacturing of PLA plastic are crystallinity and heat resistance. The DSC results showed the relation between the cooling rate during polymer molding manufacturing and the crystallization rate, which revealed the relevance of crystallinity and crystallization conditions. The TG/DTA measurements made it possible to evaluate the heat resistance at the formation temperature.