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Thermal characterization of Polylactic Acid by Thermal Analysis

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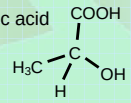
Introduction

Biodegradable plastic has gained attention in recent years due to concerns about waste disposal and environmental conservation. Polylactic acid (PLA) is a biodegradable plastic derived from plants and continues to be widely used in packing, fibers and medical materials. Crystallinity is an important consideration for the strength, impact resistance, and transparency requirements of these products and also influences biodegradability. Furthermore, lactic acid, the PLA monomer, has asymmetrical carbon and thus optical isomers. The isomer ratio and molecular weight of polymers influence crystallinity and heat resistance, so they are factors in the molding process.

In this paper, the crystallinity and heat resistance of polylactic acid are evaluated using DSC and TG. Three samples had roughly the same molecular weight but different optical isomer L-form/D-form ratios and two samples had the same L-form/D-form ratio but different molecular weights.

Experiment

L-lactic acid 

Sample 1:
- Polylactic acid ; **a**, **b**, **c** and **c'**
- L-form ratio ; **a** < **b** < **c** = **c'**
- Molecular weight ; **a** = **b** = **c** > **c'**

Instrument :
DSC6220 and TG/DTA6200
(SII NanoTechnology Inc.)

Measurement Condition :

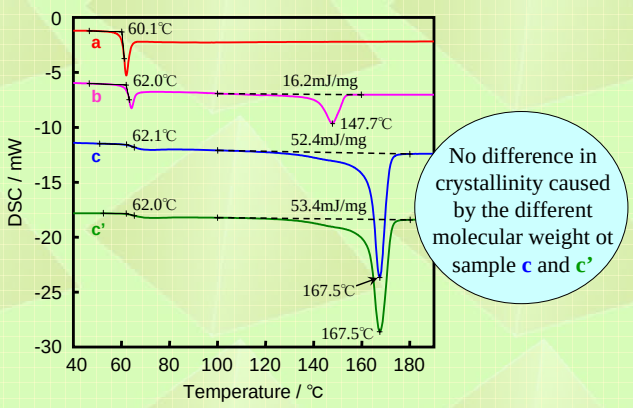
DSC measurements

Samples were heated to 200℃ and then cooled at various rates (quench, 10, 5, 1, 0.5 and 0.1℃/min). The samples were then heated from 20℃ to 200℃ at 10℃/min in N_2 atmosphere.

TG measurements

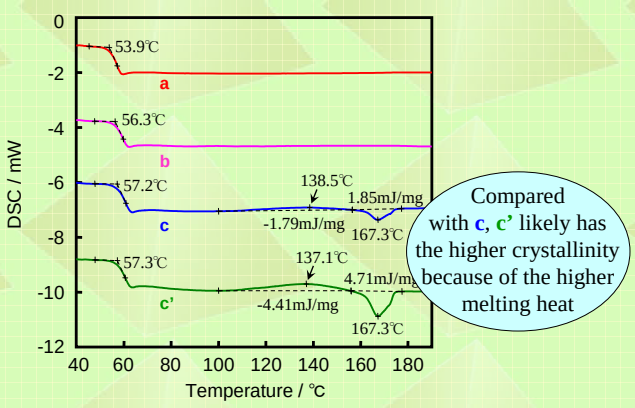
Samples were prepared without any thermal treatments, but simply heated from room temperature to 400℃ at rates of 10, 5, 2 or 1℃/ min.

DSC measurements after thermal treatment



DSC curves after 0.1℃/min cooling

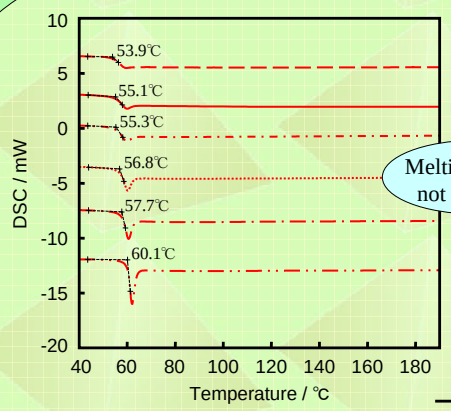
No difference in crystallinity caused by the different molecular weight ot sample **c** and **c'**



DSC curves after quench

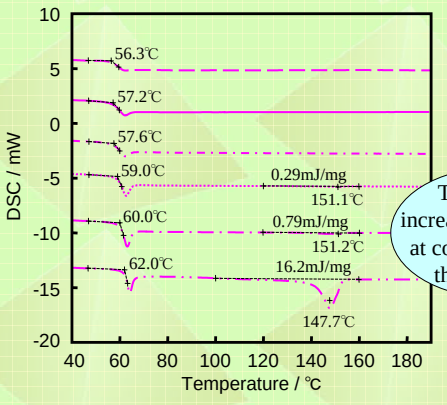
Compared with **c**, **c'** likely has the higher crystallinity because of the higher melting heat

Cooling rate dependent



DSC curves for sample **a**

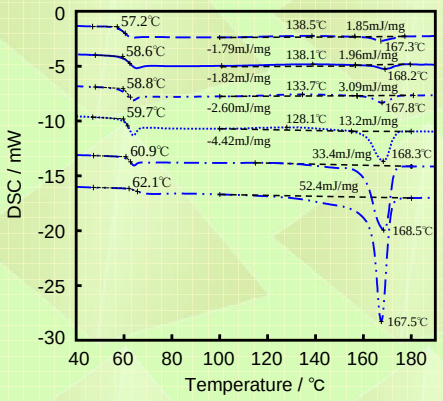
Melting peak is not observed



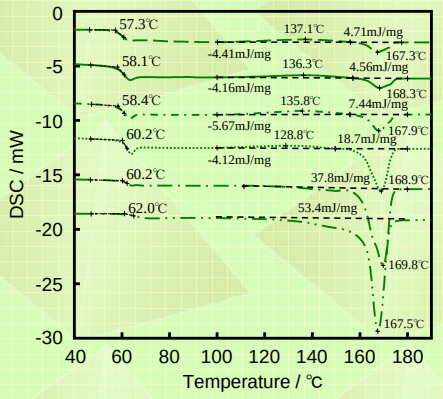
DSC curves for sample **b**

Tendency to increase crystallinity at cooling rate less than 1℃/min

- After quench
- After 10℃/min cooling
- After 5℃/min cooling
- After 1℃/min cooling
- After 0.5℃/min cooling
- After 0.1℃/min cooling



DSC curves for sample **c**



DSC curves for sample **c'**

Comparison of the relative crystallinity*

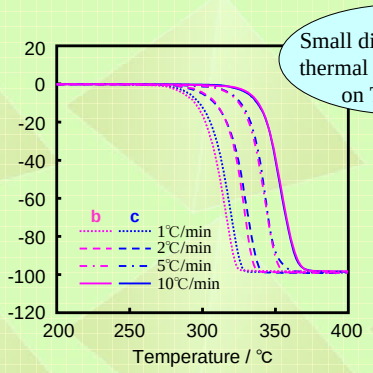
Sample \ cooling rate [℃/min]	0.1	0.5	1	5	10	quench
a	—	—	—	—	—	—
b	0.303	0.015	0.005	0	0	0
c	0.981	0.625	0.164	0.009	0.003	0.001
c'	1	0.708	0.273	0.033	0.007	0.006

The higher the L-form ratio is, so is the crystallinity.

Smaller molecular weight **c'** has the higher crystallinity

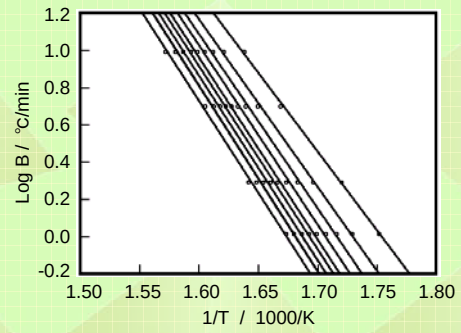
* : Sample **c'** melting heat (after 0.1℃/min cooling) is set as 1.

TG measurements



TG curves for sample **b** and **c**

Small difference in the thermal decomposition on TG curves



Arrhenius plot for sample **c**

Calculation results of Activation Energy

Sample	ΔE[kJ/mol]	Lifetime*[hr]
b	144	15.4
c	155	21.6
c'	136	10.9

*:230℃, Reaction fraction 10%

Smaller L-form ratio **b** reacts quickly

Smaller molecular weight **c'** reacts quickly

Conclusion

Crystallinity and heat resistance are important factors in PLA plastic molding. This study shows that DSC can be used to learn about crystallinity and the validity of crystallization conditions. Furthermore, thermal decomposition measurements TGA were able to evaluate heat resistance at molding temperatures.