APPLICATION NOTE

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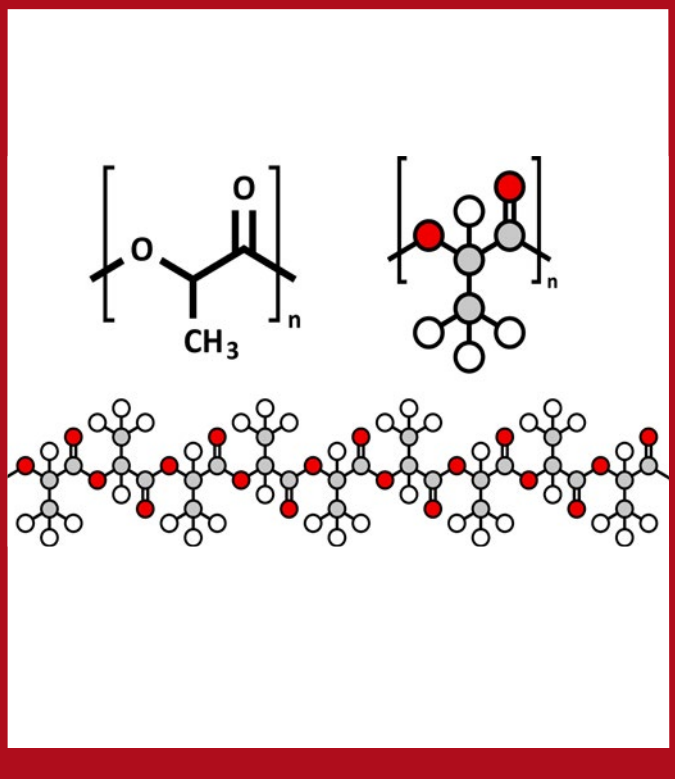
NEXTA DSC & NEXTA STA



Thermal analysis of biodegradable plastic - polylactic acid (PLA)

INTRODUCTION

Polylactic acid (PLA) is a biodegradable plastic that is derived from plants, such as sugar cane. Its properties are similar to polypropylene and polyethylene, yet it can biodegrade in as little as six months. In addition to helping to solve current issues with plastic pollution in our oceans, PLA is used for new medical applications where its ability to harmlessly dissolve in the body makes it useful for internal plates and screws.

Despite its ability to decompose in a relatively short space of time, PLA is able to withstand normal applications where petrochemical-derived plastics are commonly used. This, and the fact that PLA can be manufactured using the same equipment as polypropylene and polyethylene, means that this relatively new plastic is the second most common bioplastic in use today. Applications are diverse and focus heavily on the single use plastic industry, such as plastic films, bottles and food containers.

The chemistry of PLA is not quite straightforward in that the PLA monomer, lactic acid, has asymmetrical carbon atoms that behave as optical isomers, D and L. The ratio of D isomers to L isomers affects the degree of crystallinity of the material, which in turn impacts the strength, impact resistance and transparency of the finished product. Plus, the isomeric ratio and molecular weight of PLA also affects its heat resistance, which means that these properties must be closely monitored during the manufacturing process.

Thermal analysis plays a large part in measuring the crystallinity and heat resistance of PLA plastic during manufacturing. Two techniques are employed, differential scanning calorimetry (DSC) that shows the relation between cooling rate during manufacturing and crystallinity, and simultaneous thermogravimetric analysis (STA) that evaluates the heat resistance at the formation temperature. Hitachi instruments NEXTA DSC200 and NEXTA STA200, with their high sensitivity and excellent baseline performance, are ideal for PLA characterization measurements during manufacture.

Hitachi High-Tech Analytical Science's family of thermal analyzers have been employed in the field for more than 45 years, delivering world-class performance for precise materials characterization measurements, such as PLA analysis.

HITACHI INSTRUMENTS FOR THERMAL ANALYSIS OF PLA

NEXTA DSC

The NEXTA DSC200 is a high-performance DSC instrument, designed to be easy to use and ideal for the characterization of the crystallinity of PLAs. High sensitivity and world-class baseline performance give you precise control over the cooling rates. The NEXTA DSC200 is also an extremely versatile instrument, with options for automated operation, and can be expanded post-installation for new applications.

NEXTA STA200

Hitachi's NEXTA STA200 makes it easy to ensure that raw materials meet specification through finely tuned thermal analysis. With an unsurpassed level of baseline stability, world-class sensitivity, and advanced TGA and DSC capability, the NEXTA STA slots easily into polymer quality control and research and development programs.

For heat resistance and crystallinity determination of PLAs, these two instruments work perfectly together to deliver precise and accurate results. Ultra-high levels of sensitivity with an unsurpassed level of baseline stability ensures reliable and repeatable results are achieved every time. And features like the 50-sample auto-sampler, help to speed up analysis time to ensure production targets are met with no loss of quality.

ALL-INCLUSIVE SOFTWARE WITH CAPACITY FOR NEW APPLICATIONS

Both analyzers come with Hitachi's intuitive and advanced NEXTA TA software, which gives you options for how you need to operate the instrument. New users are able to get reliable and accurate results and experienced operators can use these instruments for more advanced analysis. All modules are included with the instruments, so if you decide to expand your use into new applications, you won't have to purchase additional modules. The software includes three modes of operation:

- Guidance mode for step by step measurement and analysis including a calibration wizard.
- Simple mode for more experienced users carrying out routine analysis that requires a simple interface. All important features are available on the main screen.
- Standard mode where all modules are included, and more complex analysis can be set up.

PERFORMANCE AND RESULTS

The NEXTA DSC200 and NEXTA STA200 were used to evaluate the crystallinity and heat resistance of different types of polylactic acid material.

Four samples of PLA bioplastic were analyzed: a, b, c and c'. They had different D/L ratios and molecular weights as shown below:
a, b, c: same molecular weight, but different L/D ratios (L ratio was the smallest for a and the most for sample c)
c': has the same L/D ratio as sample c, but lower molecular weight.

DSC methodology
Sample weight : 10mg
Heating rate : 10ºC / min to 200ºC
Atmosphere : Nitrogen

STA methodology
Sample weight : 10mg
Heating rate : various, see results
Atmosphere : Nitrogen

DSC results for all samples at a cooling rate of 0.1ºC/min

Figure 1 shows the results for all four samples when they were heated to above melting point to 200ºC and then cooled. The glass transition temperature (Tg) can be seen at around 60ºC for all samples. Endothermic peaks indicating melting can be seen at 150ºC and 170ºC for samples b and c/c' respectively. From these results, we can see that the higher the L ratio, the easier it is for crystallinity to occur. Crystallization did not occur at all for sample a. We can also see that the melting temperature and heat of fusion for samples c and c' were about the same, implying that molecular weight doesn't affect crystallinity under these conditions.

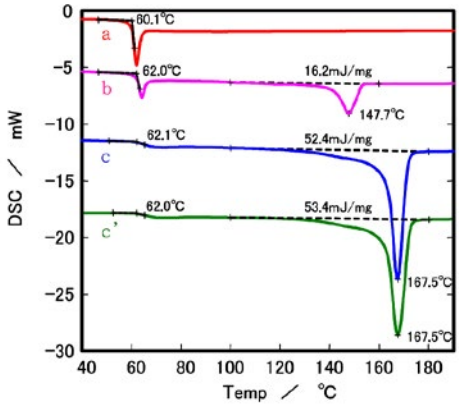


Figure 1 DSC results for cooling at 0.1ºC/min

DSC results for all samples when quench cooling

Comparing the melting peaks in figure 2 with figure 1, we can see that sample b has no melting peak at all. This illustrates the importance of cooling rate on isomeric ratio during PLA molding manufacturing. We can also see differences in c and c' for cold crystallization at around 140ºC and at the melting peak in the quench cooling scenario. This implies that when the L ratio is the same (as is samples c and c') the sample with the lower molecular weight has higher crystallinity.

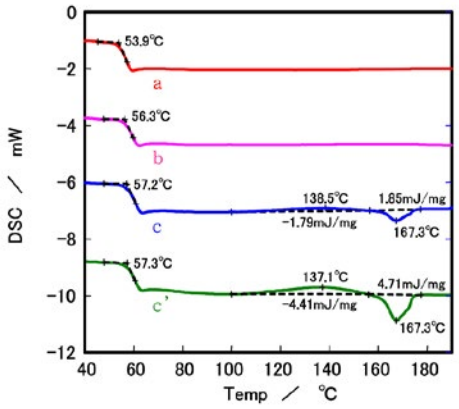


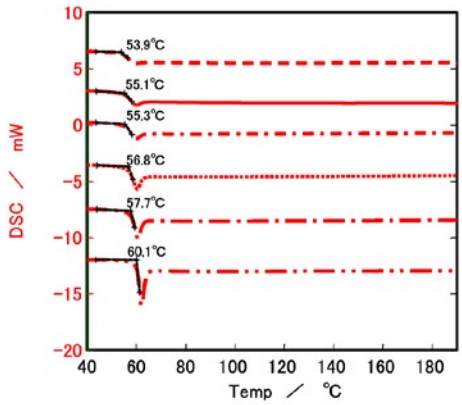
Figure 2 DSC results for quench cooling

DSC results for samples a, b, c and c' under various cooling conditions

Figures 3 to 6 show DSC results for each sample under different cooling rates. We can see that sample a did not show a melting peak under any cooling rate and we can conclude that this sample is nearly amorphous. Sample b shows a melting peak when the cooling rate was 1ºC / min or lower, implying that to increase the crystallinity of this sample, the cooling rate must be at this level or lower.

A comparison of samples c and c' shows that there was no difference in crystallinity at a cooling rate of 0.1ºC/ min, however when the cooling rate was 0.5ºC or greater, sample c' had a large heat of fusion. This shows that the crystallinity of sample c' is higher.

Figure 3-6: DSC results for samples a, b, c and c' for the following conditions:



Quench cooling
Cooling at 10ºC/min
Cooling at 5º/min
Cooling at 1ºC/min
Cooling at 0.5º/min
Cooling at 0.1º/min

Figure 3

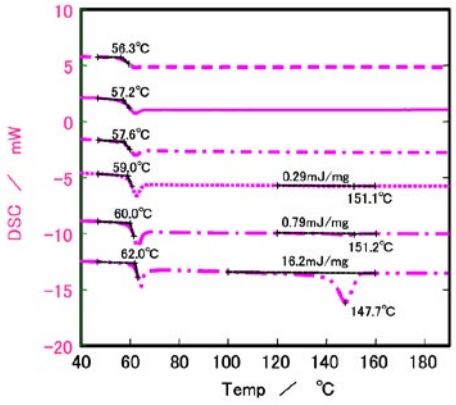


Figure 4

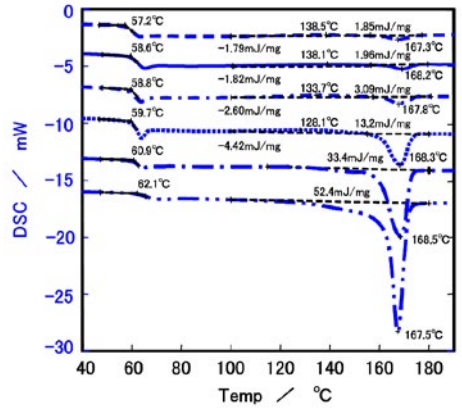


Figure 5

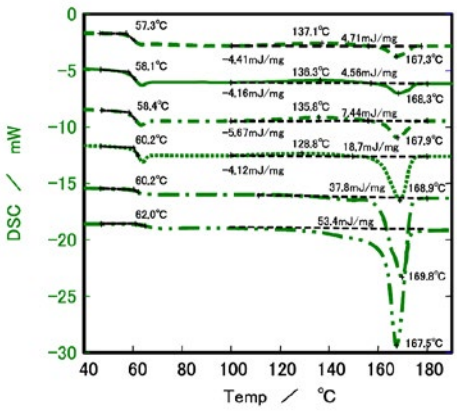


Figure 6

Comparison of relative crystallinity by cooling rate

	0.1	0.5	1	5	10	Quench cooling
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

Table 1: comparison of relative crystallinity by cooling rate (ºC/min)

Relative crystallinity can be calculated from the heat of fusion. This is done by normalizing the heat of fusion of sample c' which was cooled at a rate of 0.1ºC/min to one. The table above presents the results from this calculation.

We can see from the table that the higher the L ratio, the higher the crystallinity. Comparing results for c and c' gives us the impact of the molecular weight. We can see that molecular weight has an influence on crystallinity that is dependent on the cooling rate.

STA results for samples b and c at different heating rates

Figure 7 presents the results from STA measurements of samples b and c at four different heating rates. There is little difference in thermal decomposition, implying little difference in heat resistance between the samples.

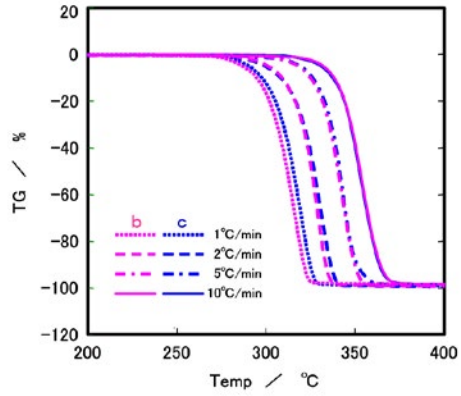


Figure 7 STA results for samples b and c for the following heating rates:
1ºC/min
2ºC/min
5ºC/min
10ºC/min

Kinetics analysis for sample c

Kinetics analysis (using the Ozawa method) was then performed on samples b, c and c' at different heating rates. The results for sample c is illustrated in figure 8. These results were used to table the activation energy results for samples b, c and c'. These are presented in table 2.

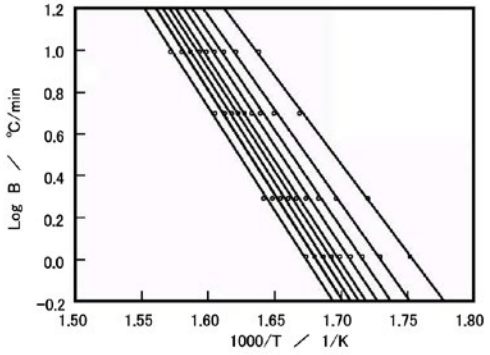


Figure 8 Results of kinetics analysis for sample c

Sample	ΔE (kJ/mol)	Constant temperature degradation time (lifetime) (hr)
b	144	15.4
c	155	21.6
c'	136	10.9

Table 2: calculation results for activation energy

The results presented in table 2 show that sample c' (low molecular weight) reacts quickly. Also, at the same molecular weight, samples with a lower L ratio react fastest. These results confirm that heat resistance changes with molecular weight and L ratio.

SUMMARY

The **NEXTA STA200** and the **NEXTA DSC200** can be used in tandem to reliably offer precise analysis of polylactic acid. Excellent baseline performance and high sensitivity provides a reliable basis for crystallization and heat resistance investigations of samples of different isomeric ratios. With intuitive, easy-to-use software within robust instruments, manufacturers and research teams can use the NEXTA STA and NEXTA DSC to confidently determine the essential performance characteristics of PLA bioplastic.

Many applications have been optimized for Hitachi High-Tech Analytical Science's thermal analyzers. For more information on other applications, please contact our experts at **contact@hitachi-hightech.com**.

NEXTA STA: COMPLETE QUANTITATIVE THERMAL ANALYSIS

Designed for complete thermal analysis of materials, including thermal resistance, decomposition temperature, melting point and specific heat testing, the NEXTA STA combines DSC and TGA to deliver TGA applications and more within a single analyzer.

The NEXTA STA range offers:

- Ultimate accuracy and precision even when measuring trace amounts of material
- Superior heating technology that meets the most advanced applications of TGA
- Cp measurement in a wide temperature range
- Unique, Real View camera system for viewing material behaviour on screen
- Easy to use with automated features, intuitive software and simple report creation

NEXTA DSC: HIGH ACCURACY MATERIALS CHARACTERIZATION

Designed for accurate determination melting point, glass transition and crystallisation temperatures, our range of differential scanning calorimeters deliver excellent sensitivity and baseline flatness.

The NEXTA DSC range offers:

- High sensitivity and baseline performance, with unique furnace design for accuracy
- Real View camera system that allows you to watch material behaviour on screen
- Intuitive, easy to use software, with advanced functionality for specific applications
- Reliable auto-sampler testing and auto analysis function for faster testing
- High degree of flexibility, allowing for addition of options after installation

Visit **www.hitachi-hightech.com/hha** for more information.