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Application News

AGX™-V Autograph Precision Universal Tester, DUH™-210 Dynamic Ultra Micro Hardness Tester, DSC-60 Plus Differential Scanning Calorimeter, IRTracer™-100 Fourier Transform Infrared Spectrophotometer

Multifaceted Evaluation of Plastics: Difference of Heat Treatment Conditions

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User Benefits

- Changes in physical properties due to heat treatment can be evaluated by using a tensile testing machine and hardness tester.
- Multifaceted evaluation by thermal analysis, FTIR, and other techniques is effective for study of the cause of changes in physical properties.
- Data from tensile tests and hardness tests can be accumulated and is a useful tool for quality control.
- In hardness testing, hardness can be evaluated simply by applying a load to a partial area of the specimen, making it possible to evaluate hardness with the actual shape of the part.

■ Introduction

As a plant-derived plastic material, polylactic acid resin (PLA) is expected to reduce environmental loads, including global warming and depletion of petroleum resources. Although PLA was originally developed as an alternative to acrylonitrile-styrene-butadiene resin (ABS), which is widely used in automobiles and electrical products, its durability and heat resistance are inferior to those of ABS, and high temperature crystallization treatment (annealing treatment) is necessary to achieve comparable performance. However, an accurate understanding of the material properties resulting from annealing treatment is essential for obtaining the targeted properties in PLA.

In this article, the difference in material properties due to annealing treatment was evaluated by tensile testing and hardness testing, and the state of crystallization in the respective specimens was then evaluated by differential scanning calorimetry (DSC) and Fourier transform infrared spectrophotometry (FTIR). Annealing was carried out at 100 ˚C for 30 minutes.

■ Tensile Test

The tensile test was conducted by mounting a Shimadzu TRViewX non-contact digital video extensometer on an AGX-V Autograph precision universal tester. Fig. 1 shows the condition of the test, Table 1 shows the instrument configuration, and Table 2 gives the conditions used in the tensile test and information concerning the test piece. As one example of the test results, Fig. 2 shows the stress-strain curve of PLA with and without annealing. Fig. 3 shows the results for tensile strength, elastic modulus, and breaking elongation. According to Fig. 3(a) and (b), the tensile strength and the elastic modulus were improved by annealing, while breaking elongation decreased substantially after annealing and became about half the value without annealing, as shown in Fig. 3 (c).

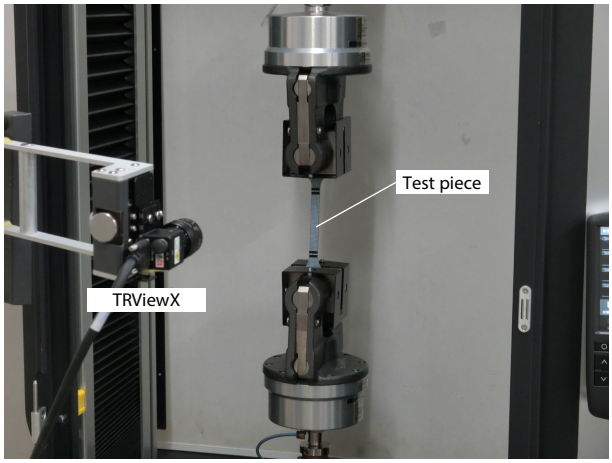

Fig. 1 Condition of Test

Table 1 Instrument Configuration

Precision universal tester	: AGX-V
Load cell	: 5 kN
Grip	: Pneumatic flat grip
Extensometer	: TRViewX240S
Software	: TRAPEZIUM™ X-V

Table 2 Test Conditions and Test Piece Information

Test speed	: 1 mm/min
Gauge length	: 75 mm
Number of tests	: n = 5
Annealing temperature	: 100 ˚C
Annealing time	: 30 min

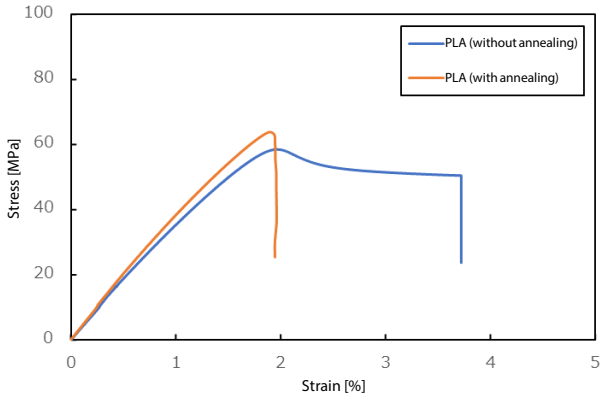

Fig. 2 Example of Stress-Strain Curves of PLA with/without Annealing Treatment

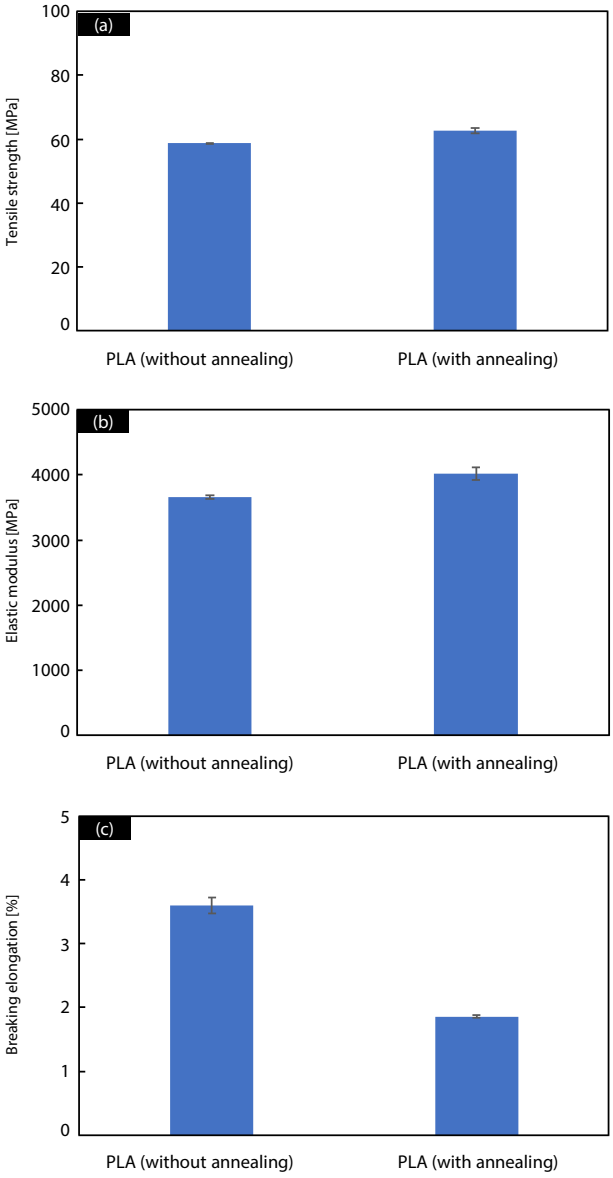

Fig. 3 Test Results
(a) Tensile Strength, (b) Elastic Modulus, (c) Breaking Elongation
* Error bars show standard deviation.

■ Hardness Test

In the hardness test, a DUH-210 analyzer for measurement of the hardness of plastics was used. The test was carried out referring to ISO/TS 19278, which was issued in 2019 as an indentation hardness measurement technique for plastics. Table 3 shows the instrument configuration and test conditions.

As an example of the hardness test, Fig. 4 shows the test force-indentation depth curves for PLA with and without annealing. Table 4 shows the test results, which indicated that indention hardness H_{IT} is increased by annealing.

Table 3 Instrument Configuration and Test Conditions

Testing machine	: DUH-210
Indenter	: Berkovich indenter
Test mode	: Load-unload test
Test force	: 500 mN
Loading-unloading time	: 30 s
Load holding time	: 40 s
Number of tests	: 5 (take 3 central points)
Ambient temperature	: 23 ± 2 ˚C
Humidity	: 50 ± 10 %

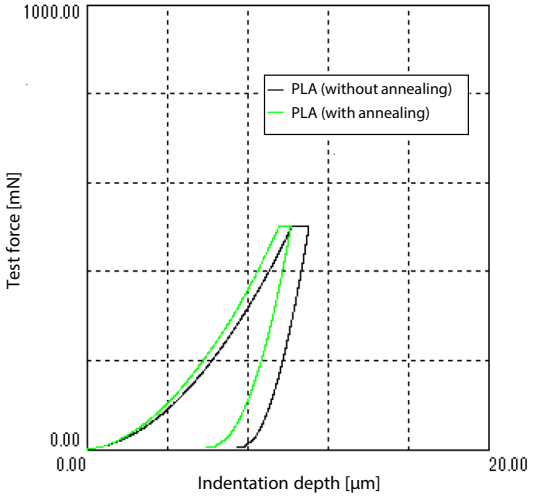

Fig. 4 Test Force-Indentation Depth Curves

Table 4 Test Results

Specimen	H_{IT} [MPa]
PLA (without annealing)	221.5
PLA (with annealing)	277.6

■ Thermal Analysis

DSC measurements were carried out to confirm the cause of the difference in mechanical properties depending on the annealing condition of the specimens in the tensile test and hardness test. Table 5 shows the measuring instrument configuration and the measurement conditions, and Fig. 5 shows the DSC curve. Comparing the 1st run measurement results, in the measurement of the unannealed PLA, a glass transition point of 55.96 ˚C and a peak of crystallization at 114.08 ˚C were detected. In the measurement of the annealed PLA, these features did not appear in the DSC curve, and it was found that crystallization proceeded with annealing treatment. In addition, there was no large difference in the melting point. Table 6 summarizes the measurement results of the 1st run. For your reference, following the 1st run, the specimens were rapidly cooled, and a 2nd run was conducted. In this case, the glass transition and crystallization peaks appeared in the curves for both specimens, and the specimens displayed an amorphous property.

Table 5 Instrument Configuration and Measurement Conditions

Measuring instrument	: DSC-60Plus
Heating rate	: 10 ˚C/min
Specimen weight	: 8 mg
Atmosphere	: Nitrogen

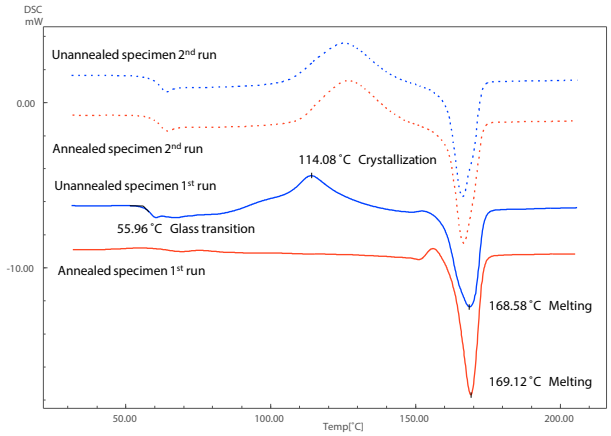

Fig. 5 DSC Curves

Table 6 Results of 1st Run of Thermal Analysis

Specimen	Tg [˚C]	Crystallization [˚C]	Melting [˚C]
PLA (without annealing)	55.96	114.08	168.58
PLA (with annealing)	-	-	169.12

■ FTIR Analysis

A FTIR analysis was conducted, as this is an effective technique for analyzing the molecular structures of plastics. Table 7 shows the instrument configuration and measurement conditions.

Fig. 6 (a) shows the analysis results, and Fig. 6 (b) shows an enlarged view of the spectra around 1000 to 800 cm^{-1}. Crystallization proceeded with annealing treatment, and the amorphous peak at around 955 cm^{-1} decreased. Conversely, the peak originating from C-C skeletal stretching vibration in the α crystal increased at around 921 cm^{-1}. Thus, the FTIR analysis results revealed that the amorphous property decreases and crystallization proceeds with annealing, and the crystal form changes to the α crystal [(1)].

Table 7 Instrument Configuration and Measurement Conditions

Measuring instruments	: IRTracer™-100, QATR™10 (diamond)
Resolution	: 4 cm^{-1}
Accumulation	: 20 times
Apodization function	: Happ-Genzel
Detector	: DLATGS

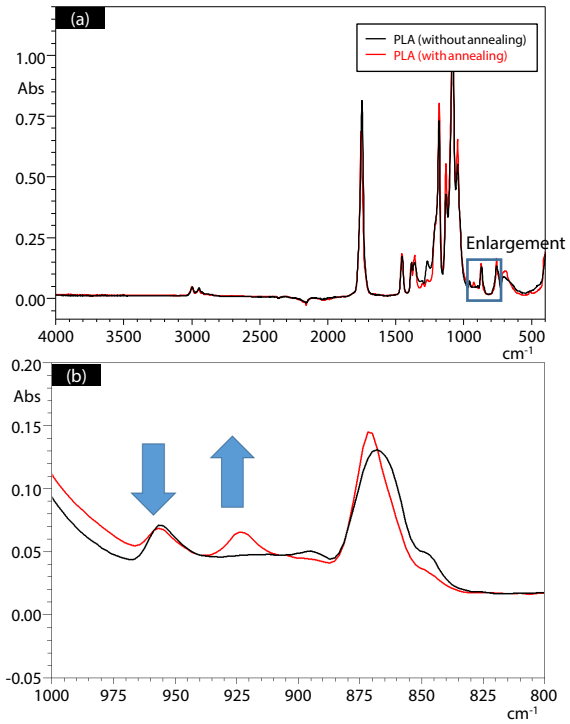

Fig. 6 (a) Results of FTIR Analysis, (b) Partial Enlargement of (a)

■ Conclusion

This experiment showed that annealing treatment of PLA resin increases the tensile strength, elastic modulus, and indention hardness H_{IT} and decreases breakage elongation. The results of a thermal analysis and FTIR revealed that these changes in mechanical properties are related to the crystallization induced by annealing. This type of multifaceted evaluation is considered to be an effective approach for evaluating the effect of forming conditions on mechanical properties and its cause.

Normally, strength evaluations of plastic materials are conducted by destructive testing such as tensile tests and bending tests using a specimen with a test-piece geometry which is specified by the standard. However, when evaluating the effect of forming with the actual part shape, it may not be possible to cut test pieces from the part, depending on its shape and dimensions. For this reason, there are sometimes cases where tensile tests and bending tests cannot be conducted. Since it is possible to evaluate mechanical properties from the hardness of the specimen merely by partial loading of the specimen, the test can be performed without causing significant damage of the specimen, and simple testing is possible with the actual part shape. Therefore, if these data are accumulated and the correlation between hardness and the values of the respective mechanical properties is clarified, it is thought that this approach can contribute to improved efficiency not only in material evaluations as such, but also in quality control work, in which it is necessary to evaluate the material properties of parts having the actual product shape.

<Reference>

(1) J.M. Zhang, Y.X. Duan, H. Sato, H. Tsuji, I. Noda, S. Yan, and Y. Ozaki, Macromolecules, 38, 8012 (2005)

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