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Application News

AGX™-V2 AUTOGRAPH Precision Universal Testing Machine
DUH™-210 Dynamic Ultra Micro Hardness Tester DSC-60 Plus Differential Scanning Calorimeter
AIRsight™ Infrared and Raman Microscope

Multifaceted Evaluation of Changes in Physical Properties of Recycled Plastics by Advanced Recycling Process and Influencing Microstructural Changes (Part 3): Example of Application to Recycled Polypropylene Derived from Automotive Offcuts without Fillers

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User Benefits

- ◆ Evaluation of changes in the microscopic physical structures in plastic during molding is possible by multifaceted measurements using general-purpose instruments.
- ◆ It is possible to understand the physical properties of plastics and the factors that influence those properties.

■ Introduction

In the previous Application News article "Multifaceted Evaluation of Changes in Physical Properties of Recycled Plastics by Advanced Recycling Process and Influencing Microstructural Changes (Part 2)," we found that the microscopic physical structures of simulated degraded polypropylene (PP) were controlled by applying the new-developed advanced recycling process, and as a result, the strain at break and the impact property of the plastic were improved. We also showed that a multifaceted evaluation combining the elastic modulus, indentation hardness (H_{IT}), crystallization start temperature, proportion of the helical structure, and the orientation in the micro region is an effective approach for understanding changes in microscopic physical structures. In this article, we report the results of a study to determine whether this multifaceted evaluation approach is also effective for understanding the microscopic physical structures in actual recycled plastic, based on the practical application of the social implementation of recycled plastics. In this connection, in the automotive industry, active study on implementation of plastic recycling is also underway globally, beginning with a draft of regulations released by European Commission (EC) in July 2023. Based on this trend, recycled PP derived from automotive offcuts without fillers was used as the sample material in this study.

■ Test Pieces

The materials used in this study were pellets prepared by applying the advanced recycling process to polypropylene (PP) that did not contain talc or other fillers derived from offcuts in the automobile part production process, and pellets of the same material without the advanced recycling process. Both types of pellets were molded to the dumbbell test piece shape specified as ISO 527-2 1A by injection molding. For the thermal analysis and infrared analysis, the dumbbell test pieces were cut and processed to the proper size and shape.

■ Evaluation of Strain at Break and Elastic Modulus by Tensile Test

An Autograph precision universal testing machine was used in the tensile tests, and a TRViewX non-contact digital video extensometer was used in measurements of the elongation of the samples. Fig. 1 shows the appearance of the instrument, Table 1 shows the instrument configuration and test conditions, and Fig. 2 shows the appearance during a test. Fig. 3 shows the stress-strain curves to break, Fig. 4 shows the stress-strain curves in the elastic region, Table 2 shows the measured results of strain at break, and Table 3 shows the measured results of the elastic modulus. It was assumed that strain at break would increase as a result of the advanced recycling process. However, contrary to this expectation, strain at break was lower with the advanced recycling process. The elastic modulus with the advanced recycling process decreased in comparison with the result without the process.

Based on the fact that a spotted pattern appeared in the surface of the samples with the advanced recycling process during the test, it is possible that strain at break was reduced by the effect of foreign matter in the plastic. Therefore, the content of foreign matter was investigated by Fourier transform infrared spectrophotometer (FTIR).

Fig. 1 AGX™-V2

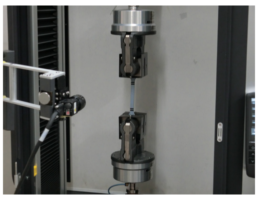


Fig. 2 Appearance during Test

Table 1 Instrument Configuration and Test Conditions

Instrument	: AGX-V2
Load cell	: 5 kN
Grip	: Pneumatic flat grip
Extensometer	: TRViewX 500D
Software	: TRAPEZIUM™X-V
Test speed	: 1 mm/min (measurement of elastic modulus) 50 mm/min (measurement to breaking)
Gauge length	: 75 mm
Number of tests	: n = 3
Test piece width	: 10 mm
Test piece thickness	: 4 mm
Grip distance	: 115 mm

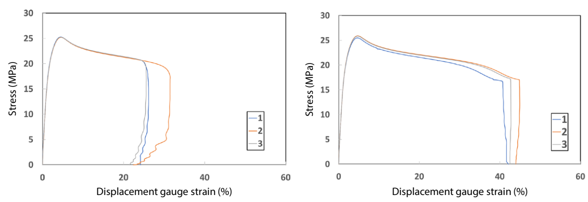


Fig. 3 Stress-Strain Curves to Break
(Left: With Advanced Recycling Process,
Right: Without Advanced Recycling Process)

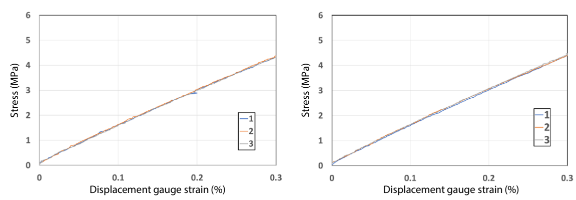


Fig. 4 Stress-Strain Curves in Elastic Region
(Left: With Advanced Recycling Process,
Right: Without Advanced Recycling Process)

Table 2 Measured Results of Strain at Break

Test piece	Strain at break (%)	Test piece	Strain at break (%)
W/ Advanced recycling process_1	25.98	W/o Advanced recycling process_1	40.71
W/ Advanced recycling process_2	31.46	W/o Advanced recycling process_2	44.85
W/ Advanced recycling process_3	25.51	W/o Advanced recycling process_3	42.68
Average	27.65	Average	42.75
Standard deviation	3.309	Standard deviation	2.070
Coefficient of variation	11.97 %	Coefficient of variation	4.84 %

Table 3 Measured Results of Elastic Modulus

Test piece	Elastic modulus (MPa)	Test piece	Elastic modulus (MPa)
W/ Advanced recycling process_1	1396.64	W/o Advanced recycling process_1	1418.87
W/ Advanced recycling process_2	1396.06	W/o Advanced recycling process_2	1415.35
W/ Advanced recycling process_3	1404.10	W/o Advanced recycling process_3	1429.03
Average	1398.93	Average	1421.08
Standard deviation	4.48	Standard deviation	7.10
Coefficient of variation	0.3 %	Coefficient of variation	0.5 %

■ Investigation of Foreign Matter by FTIR

Using the infrared mode of the AIRsight infrared and Raman microscope, foreign substances were measured by the transmission method. The appearance of the instrument is shown in Fig. 11. In the observation image (Fig. 5) using a 15x reflection objective mirror, a white spot-shaped substance that appears to be foreign matter could be seen. An infrared spectrum acquired in its neighboring area and the results of a spectrum search were overlaid, as shown in Fig. 6. The search indicated polyethylene (PE), suggesting this foreign matter could be a PE aggregate. It is assumed that the decrease in strain at break was caused by this aggregate of PE.

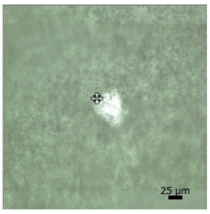


Fig. 5 Observation Image of Area Around Foreign Matter

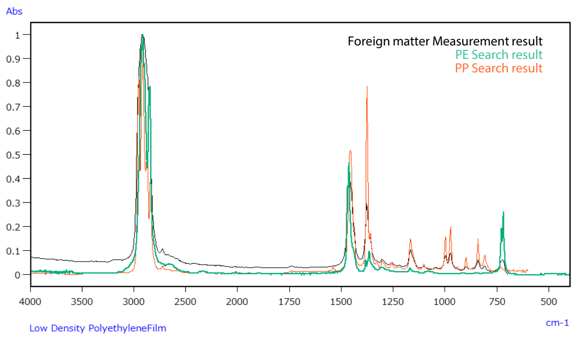


Fig. 6 Overlay of Spectrum of Foreign Matter and Search Result

■ Hardness Evaluation

Next, a hardness test was carried out using a dynamic ultra micro hardness tester (DUH). The test was conducted in the area near the center of the parallel part of the ISO 527-2 1A test piece. Fig. 7 shows the appearance of the instrument. Table 4 shows the test conditions, Fig. 8 shows the test force-indentation depth curves, and Table 5 shows the measured results of the indentation hardness H_{IT}. The H_{IT} with the advanced recycling process was lower compared to that without the process.

Table 4 Test Conditions
(Conforming to ISO/TS 19278)

Instrument	: 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
Room temperature	: 23 ± 2 °C
Grip distance	: 50 ± 10 %

Fig. 7 DUH™-210

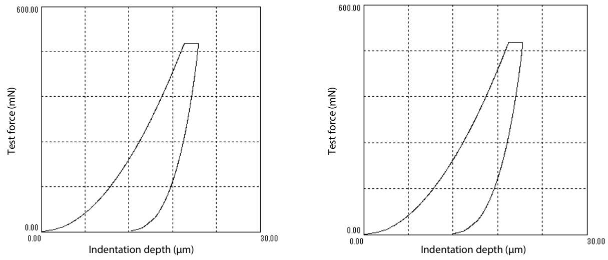


Fig. 8 Test Force-Indentation Depth Curves
(Left: With Advanced Recycling Process,
Right: Without Advanced Recycling Process)

Table 5 Measured Results of Indentation Hardness H_{IT} (N = 5)

Test piece	H_{IT} Average (MPa)	Standard deviation	Coefficient of variation (%)
With advanced recycling process	55.6	2.0	3.5
Without advanced recycling process	58.4	0.27	0.5

■ Evaluation of Crystallization Start Temperature by Thermal Analysis

This section presents the results of measurements by the differential scanning calorimeter (DSC). Fig. 9 shows the appearance of the instrument. Table 6 shows the measurement conditions, Fig. 10 shows representative DSC curves during cooling after heating (blue line: with advanced recycling process, red line: without process), and Table 7 shows the measured results of the crystallization start temperature. In comparison with the result without the advanced recycling process, the crystallization start temperature decreased with the advanced recycling process. This decrease is thought to be caused by a delay in crystallization resulting from suppression of motion of polymer chains due to an increase in polymer entanglements. Although not shown here, the heat of fusion in the heating process was also compared, but no significant difference was seen in the degree of crystallization with and without the advanced recycling process.

Fig. 9 DSC-60Plus

Table 6 Measurement Conditions

Instrument	: DSC-60Plus
Heating/cooling rate	: 10 °C/min
Sample amount	: 6 mg
Atmosphere	: Nitrogen

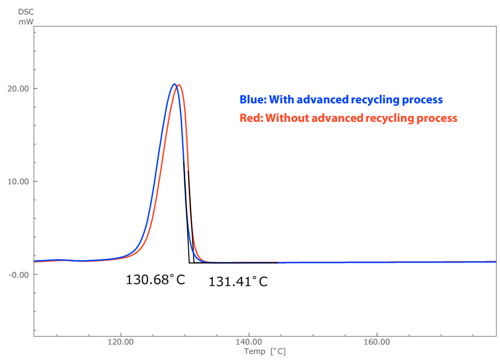


Fig. 10 DSC Curves for Crystallization (Cooling Process)

Table 7 Measured Results of Crystallization Start Temperature (N = 5)

Test material	Crystallization start temperature (°C) Average	Standard deviation
With advanced recycling process	130.66	0.064
Without advanced recycling process	131.45	0.080

■ Evaluation of Polymer Structure Ratio by FTIR

As noted above, differences in mechanical properties were observed with and without the advanced recycling process, and from the decrease in the crystallization start temperature, which is one thermal property, polymer entanglements are thought to increase. Based on these two points, it is considered possible that the microscopic physical structures in the plastic were altered by the advanced recycling process. In evaluating the change in the microscopic physical structures, we focused on the proportion of helical structures, which are considered to be closely related to polymer entanglements.

The polymer structures of PP are the helical structure and the parallel structure, and it is possible to detect peaks originating from these structures by FTIR. Here, ratios of the two structures with and without the advanced recycling process were evaluated. Using a microtome, test slices with a thickness of 15 µm were taken from the parallel part of the ISO 527-2 1A test pieces, and area mapping measurements were carried out by the transmission method using the infrared mode of the AIRsight infrared and Raman microscope. Fig. 11 shows the appearance of the instruments, and Table 8 shows the measurement conditions.

Fig. 12 shows the spectra of each of the two sample materials with and without the advanced recycling process. Peaks originating from the helical structure at 998 cm^{-1} and from the parallel structure at 971 cm^{-1} were detected, and chemical images (Fig. 13) were prepared based on the height ratio (helical/parallel) of the two peaks. For comparison, the vertical axes of the chemical images were unified at 0.71 to 0.85 AU. The results confirmed that the material with the advanced recycling process had a higher in-plane average value of the helical/parallel ratio than the material without the process.

Fig. 11 IRXross™ and AIRsight™

Table 8 Measurement Conditions

Instruments	: IRXross™, AIRsight™ (infrared mode)
Resolution	: 8 cm^{-1}
Accumulation	: 10 times
Apodization function	: SqrTriangle
Aperture size	: 30 µm × 30 µm
Step width	: 30 µm
Mapping range	: 150 µm × 330 µm (with advanced recycling process) 40 µm × 260 µm (without advanced recycling process)
Detector	: T2SL

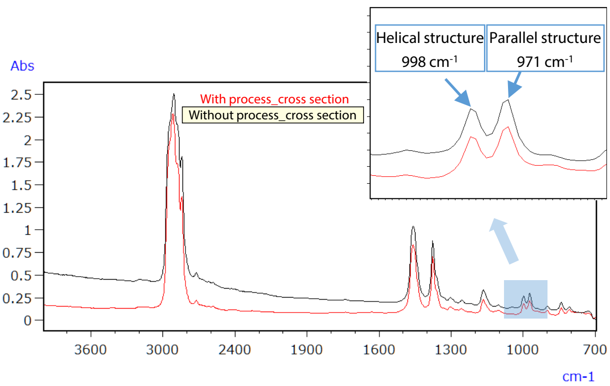
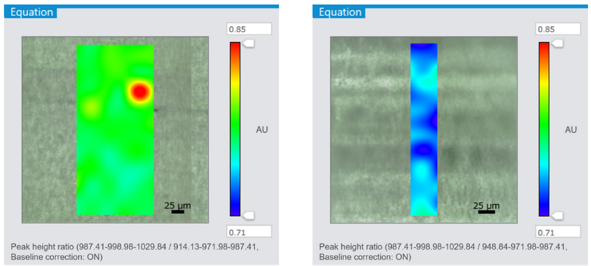


Fig. 12 Infrared Spectra of Samples with/without Advanced Recycling Process



With Advanced Recycling Process　　Without Advanced Recycling Process

Fig. 13 Chemical Images of Test Slices

■ Study of Changes in Microscopic Physical Structure by Multifaceted Evaluation

(1) Verification of increase in tie molecules and intermediate layers from the macro viewpoint

In this evaluation, improvement of strain at break was not seen, but differences were observed in the elastic modulus, H_{IT}, crystallization start temperature, and ratio of helical structures. Although the microscopic physical structures are considered to be altered by the advanced recycling process, we concluded that improvement in strain at break was not seen due to the effect of foreign matter. As in the previous Application News article mentioned in the Introduction, an increase in tie molecules is considered as a change in the microscopic physical structure. The image of the aggregation state of the polymer is shown in Fig. 14.

Both the elastic modulus and H_{IT} decreased as a result of the advanced recycling process. The cause of this decrease is considered to be either a decrease in the degree of crystallization, or an increase in the intermediate layers containing tie molecules. However, in this evaluation, there was no difference in the heat of fusion in the DSC measurements, indicating that there was no difference in the degree of crystallization with and without the advanced recycling process. Based on these facts, it can be thought that the intermediate layers containing tie molecules are increased by the advanced recycling process.

(2) Consideration of changes in the physical structure from the micro viewpoint

In this section, we consider the increase in tie molecules from the microscopic viewpoint, rather than the macroscopic physical properties of the elastic modulus, H_{IT}, and the degree of cystallization. It is thought that the increase in polymer entanglements during melting contributes to the formation of intermediate layers containing tie molecules. Therefore, the condition of polymer entanglements during melting is estimated from the polymer structure of the solid state after molding. In the molding process from the molten state, it is thought that the polymer is elongated to the parallel structure when shearing is applied, and the probability that the polymer will become a helical structure increases as polymer relaxation proceeds. From the investigation of the ratio of the helical structures and parallel structures by FTIR, it is found that the helical structures increased. Based on this, it is thought that polymer relaxation proceeds when the advanced recycling process is applied. As mentioned above, based on the fact that the crystallization start temperature in the cooling process is decreased by the advanced recycling process in the DSC measurement, it is thought that polymer entanglements increase.

From the above, it is thought that polymer entanglements also increase due to polymer relaxation during melting by the advanced recycling process in PP without fillers derived from offcuts in the automobile manufacturing process, and as a result, the intermediate layers containing tie molecules also increase. However, unlike the evaluation of the samples of virgin homo PP with simulated physical degradation, in this study, it is thought the effect of the increased polymer entanglements on strain at break was cancelled out by the effect of foreign matter in the actual recycled plastic.

■ Conclusion

This study demonstrated that an evaluation combining the elastic modulus, H_{IT}, the crystallization start temperature, and the proportion of helical structures is also an effective index for understanding the changes in microscopic physical structure even in samples that contain foreign substances.

FTIR was effective for evaluation of the foreign matter in this study. However, if the object of the evaluation is an inorganic material, it is suggested that an energy dispersive X-ray fluorescence spectrometer (EDX) or similar instrument may be used.

■ Reference: Image of Entanglements during Melting of Polymers and Crystal Structure after Cooling [1)]

As reference, the following diagram shows the image of the aggregation state of polymers explained in the main text. If entanglements of the molecules are increased by heat treatment in the advanced recycling process, the number of tie molecules after crystallization will also increase.

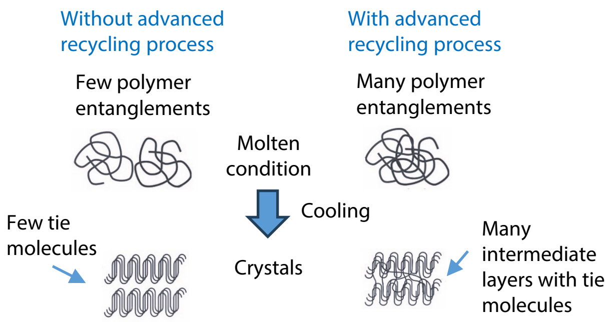


Fig. 14 Image of Aggregation State of Polymers

<Acknowledgement>

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<Reference>

1) Present and future of waste plastics: plastic resource circulation in sustainable society, The Japan Institute of Energy, p. 147

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