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Application News

AGX™-V2 AUTOGRAPH Precision Universal Testing Machine
HITS™-TX High Speed Tensile Testing Machine DUH™-210 Dynamic Ultra Micro Hardness Tester
DSC-60 Plus Differential Scanning Calorimeter SPM-Nanoa™ Scanning Probe Microscope
AIRsight™ Infrared and Raman Microscope

Multifaceted Evaluation of Changes in Physical Properties of Recycled Plastics by Advanced Recycling Process and Influencing Microstructural Changes (Part 2): Example of Application to Simulated Degraded Polypropylene

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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 previously-published Application News article "Multifaceted Evaluation of Changes in Physical Properties of Recycled Plastics by Advanced Recycling Process and Influencing Microstructural Changes (Part 1)," it was found that the microscopic physical structure of recycled polyethylene (PE) was controlled by applying a new advanced recycling process, and as a result, the strain at break and the impact property improved. That study also demonstrated that a multifaceted evaluation combining the elastic modulus, indentation hardness (H_{IT}), crystallization start temperature, and orientation and structural information in the micro region is an effective approach for understanding the changes in the microscopic physical structure. Here, the same multifaceted evaluation was carried out for simulated degraded polypropylene (PP), and the changes in the physical properties and the microscopic physical structure were analyzed.

■ Test Pieces

Virgin homopolypropylene was used as the material. Pellets prepared by applying the advanced recycling process to virgin homopolypropylene after simulated degradation by shearing multiple times in a kneading machine, and pellets of the same material without the advanced recycling process were used as the samples. These two types of pellets were molded to the ISO 527-2 1A and ASTM D1822 Type L test piece shapes by injection molding. Table 1 shows the test piece shapes and the types of evaluations conducted.

Table 1 Test Piece Shapes and Evaluations Conducted

Test piece shape	Evaluations conducted
ISO 527-2 1A	Tensile test, hardness test, DSC, FTIR, SPM
ASTM D1822 TYPE L	High speed tensile test

(The test pieces used in DSC, FTIR and SPM were cut and processed to the corresponding size and state.)

■ Evaluations

First, in order to confirm the effects of the advanced recycling process on the physical properties of the plastic, strain at break and the elastic modulus of the samples were investigated by a static tensile test, and the impact property was investigated by a high speed tensile test. Next, to discuss the factors in changes in the strain at break and impact property, the following evaluations were conducted.

- Dynamic ultra micro hardness tester (DUH): Hardness
- Differential scanning calorimeter (DSC): Crystallization start temperature
- Scanning probe microscope (SPM): Orientation
- Fourier transform infrared spectrophotometer (FTIR): Ratio of helical structure and parallel structure

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

The tensile test was conducted using the Autograph precision universal testing machine. A TRViewX non-contact digital video extensometer was used as the extensometer. Fig. 1 shows the appearance of the testing machine, Fig. 2 shows the appearance during a test, and Table 2 shows the instrument configuration and test conditions. Fig. 3 shows the stress-strain curves to break, Fig. 4 shows the stress-strain curves in the elastic region, and Table 3 shows the measured results of the strain at break. Strain at break increased in the test pieces with the advanced recycling process in comparison with those without the process. Table 4 shows the measured results of the elastic modulus. The elastic modulus with the advanced recycling process was lower than that without the process.

Fig. 1 AGX™-V2

Fig. 2 Appearance during Test

Table 2 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 break)
Gauge length	: 75 mm
Number of tests	: n = 7
Test piece width	: 10 mm
Test piece thickness	: 4 mm
Grip distance	: 115 mm

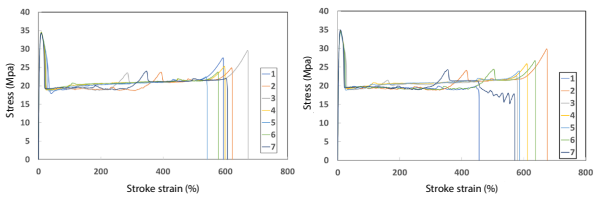

Fig. 3 Stress-Strain Curves to Break
(Left: With Advanced Recycling Process,
Right: Without Advanced Recycling Process)

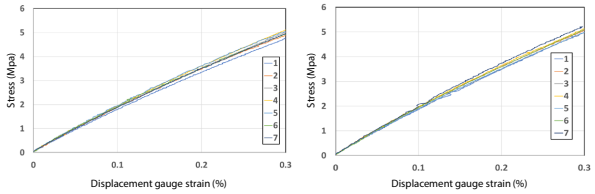

Fig. 4 Stress-Strain Curves in Elastic Region
(Left: With Advanced Recycling Process,
Right: Without Advanced Recycling Process)

Table 3 Measured Results of Strain at Break

Test piece	Strain at break (%)	Test piece	Strain at break (%)
W/ Advanced recycling process_1	594.1	W/o Advanced recycling process_1	448.1
W/ Advanced recycling process_2	622.5	W/o Advanced recycling process_2	676.0
W/ Advanced recycling process_3	673.2	W/o Advanced recycling process_3	579.6
W/ Advanced recycling process_4	599.2	W/o Advanced recycling process_4	612.3
W/ Advanced recycling process_5	539.8	W/o Advanced recycling process_5	586.8
W/ Advanced recycling process_6	578.0	W/o Advanced recycling process_6	638.3
W/ Advanced recycling process_7	604.9	W/o Advanced recycling process_7	449.8
Average	601.7	Average	570.1
Standard deviation	40.85	Standard deviation	88.86
Coefficient of variation	6.8 %	Coefficient of variation	15.6 %

Table 4 Measured Results of Elastic Modulus

Test piece	Elastic modulus (MPa)	Test piece	Elastic modulus (MPa)
W/ Advanced recycling process_1	1551	W/o Advanced recycling process_1	1622
W/ Advanced recycling process_2	1603	W/o Advanced recycling process_2	1642
W/ Advanced recycling process_3	1618	W/o Advanced recycling process_3	1613
W/ Advanced recycling process_4	1658	W/o Advanced recycling process_4	1668
W/ Advanced recycling process_5	1652	W/o Advanced recycling process_5	1625
W/ Advanced recycling process_6	1593	W/o Advanced recycling process_6	1653
W/ Advanced recycling process_7	1610	W/o Advanced recycling process_7	1723
Average	1612	Average	1649
Standard deviation	36.33	Standard deviation	37.64
Coefficient of variation	2.3 %	Coefficient of variation	2.3 %

■ Evaluation of Impact Property by High Speed Tensile Test

Next, the high speed tensile test was conducted using the high speed tensile testing machine (HITS-TX). Fig. 5 shows the appearance of the instrument, Table 5 shows the instrument configuration and test conditions, and Fig. 6 shows the stress-strain curves. Table 6 and Table 7 show the measured results of strain at break with and without the advanced recycling process, respectively. As in the static test, in comparison with the results without the advanced recycling process, the strain at break with the advanced recycling process increased in the high speed tensile test, and the break energy also increased.

Table 5 Instrument Configuration and Test Conditions

Instrument	: HITS-TX
Load cell	: 10 kN
Grip	: Flat grip for high speed tensile test
Extensometer	: Chuck displacement gauge
Software	: TRAPEZIUM HITS
Test speed	: 10, 1/s
Number of tests	: n = 5
Grip distance	: 40 mm

Fig. 5 HITS-TX

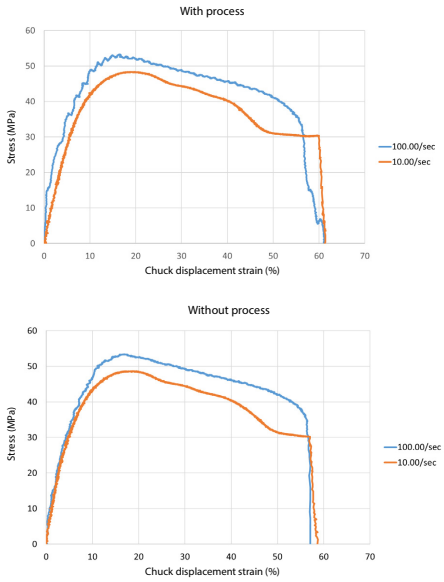

Fig. 6 Stress-Strain Curves to Break
(Top: With Advanced Recycling Process,
Bottom: Without Advanced Recycling Process)

Table 6 Measured Results of Strain at Break with Advanced Recycling Process (Average of N = 5)

Strain rate (/s)		Yield stress (MPa)	Strain at break (%)	Break energy(J)
100	Average	53.327	57.006	2.335
	Standard deviation	0.541	2.075	0.086
	Coefficient of variation (%)	1	3.6	0.037
10	Average	48.158	59.747	2.105
	Standard deviation	098	1.239	0.042
	Coefficient of variation (%)	0.2	2	0.020

Table 7 Measured Results of Strain at Break without Advanced Recycling Process (Average of N = 5)

Strain rate (/s)		Yield stress (MPa)	Strain at break (%)	Break energy(J)
100	Average	53.814	55.286	2.297
	Standard deviation	0.493	2.649	0.097
	Coefficient of variation (%)	0.92	4.8	0.042
10	Average	48.636	56.639	2.051
	Standard deviation	0.028	3.523	0.123
	Coefficient of variation (%)	0.5	6.2	0.060

■ Hardness Evaluation

The hardness test was conducted using the dynamic ultra micro hardness tester (DUH). The test was carried out near the center of the parallel part of the ISO 527-2 1A test pieces. Fig. 7 shows the appearance of the instrument. Table 8 shows the test conditions, Fig. 8 shows the test force-indentation depth curves, and Table 9 shows the measured results of the indentation hardness H_{IT}. The H_{IT} with the advanced recycling process was lower than that without the process.

Table 8 Test Conditions

Instrument	: DUH-210
Indenter	: Berkovich indenter
Test mode	: Load/unload test
Test force	: 20 mN
Loading/unloading time	: 30 s
Load holding time	: 40 s
Number of tests	: 10
Room temperature	: 23 ± 2 ˚C
Humidity	: 50 ± 10 %

Fig. 7 DUH™-210

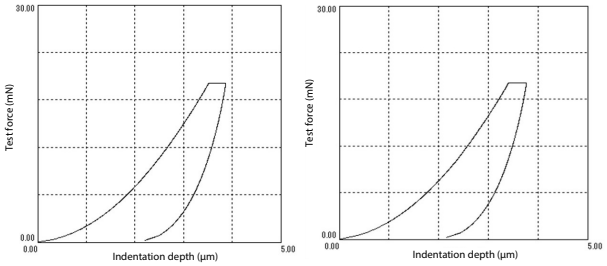

Fig. 8 Test Force-Indentation Depth Curves
(Left: With Advanced Recycling Process,
Right: Without Advanced Recycling Process)

Table 9 Measured Results of Indentation Hardness H_{IT} (N = 10)

Test piece	H_{IT}		
	Average (MPa)	Standard deviation	Coefficient of variation (%)
With advanced recycling process	70.3	2.1	3.0
Without advanced recycling process	74.0	1.9	2.6

■ Evaluation of Crystallization Start Temperature by Thermal Analysis

This section presents the results of measurements with the differential scanning calorimeter (DSC). Because a difference was observed in the crystallization process during cooling, the results with and without the advanced recycling process were compared, focusing on the crystallization start temperature. Fig. 9 shows the appearance of the instrument. Table 10 shows the measurement conditions, Fig. 10 shows representative DSC curves during cooling after heating (blue line: with advanced recycling process, red line: without advanced recycling process), and Table 11 shows the measured results of the crystallization start temperature. With the advanced recycling process, the crystallization start temperature was lower than that without the process. The cause of this difference is considered to be a delay in crystallization because the motion of molecule chains was suppressed by an increase in polymer entanglements due to the heat treatment in the advanced recycling process. Although not shown here, the heat of fusion in the heating process was compared, but no significant difference could be seen in the degree of crystallization with and without the advanced recycling process.

Fig. 9 DSC-60Plus

Table 10 Measurement Conditions

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

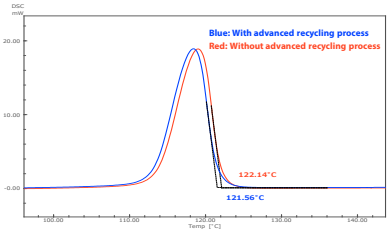

Fig. 10 DSC Curves for Crystallization (Cooling Process)

Table 11 Measured Results of Crystallization Start Temperature (N = 5)

Test piece	Crystallization start temperature (˚C)	
	Average	Standard deviation
With advanced recycling process	121.64	0.067
Without advanced recycling process	122.06	0.117

Based on the two points that (1) differences in mechanical properties were observed with and without the advanced recycling process, and (2) entanglements of polymers are thought to increase due to a decrease in the crystallization start temperature, which is one thermal property, it is conceivable that the microscopic physical structures in the plastic may change as a result of the advanced recycling process. Therefore, in evaluating the changes in the microscopic physical structures, this study focused on the proportion of the helical structure to the parallel structure and orientation, which is closely related to polymer entanglements.

■ Evaluation of Ratio of Polymer Structures by FTIR

The polymer structures of PP are the helical structure and the parallel structure, and it is possible to detect the peaks originating from these structures by using FTIR. Here, the difference in the ratio of these two structures with and without the advanced recycling process was evaluated.

Test slices with a thickness of 15 µm were taken from the parallel part of the ISO 527-2 1A test pieces with a microtome, and area mapping measurements by the transmission method were carried out using the infrared mode of the AIRsight infrared and Raman microscope. Fig. 13 shows the appearance of the instrument and Table 12 shows the measurement conditions.

Fig. 11 shows spectra of both the samples with and without the advanced recycling process at each point. Peaks originating from the helical structure at 998 cm^{-1} and from the parallel structure at 971 cm^{-1} were confirmed, and chemical images were prepared based on the height ratio (helical/parallel) of these two peaks in the samples with and without the advanced recycling process, as shown in Fig. 12. For comparison, the vertical axes of the chemical images were unified at 0.78 to 0.84 AU. The results confirmed that the sample with the advanced recycling process has a higher in-plane average value of the helical/parallel ratio than the sample without the advanced recycling process.

Table 12 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	: 330 µm × 270 µm
Detector	: T2SL

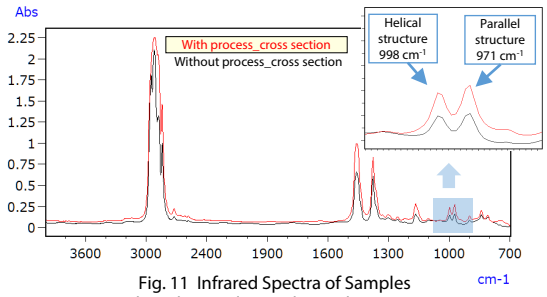

Fig. 11 Infrared Spectra of Samples with/without Advanced Recycling Process

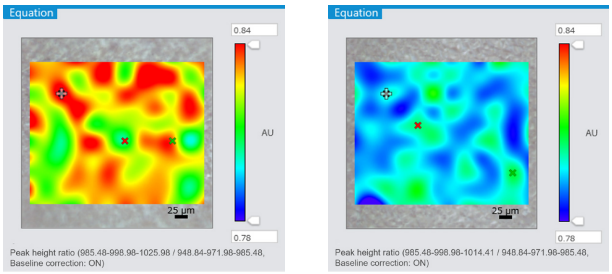

Fig. 12 Chemical Images of Test Slices (Left: With Advanced Recycling Process, Right: Without Advanced Recycling Process)

Fig. 13 IRXross™ and AIRsight™

■ Evaluation of Orientation by SPM

The difference in orientation with and without the advanced recycling process was evaluated. With SPM, it is possible to measure the distribution of diverse physical quantities according to the selection of the measurement mode, and micron-level regions can be evaluated. Here, the adhesion distribution was used, as this is effective for evaluating the uniformity of a sample.

Cross sections of the parallel part of the ISO 527-2 1A test pieces were taken with a cryomicrotome, and the cross sections were measured using the SPM. Fig. 14 shows the appearance of the instrument, and Table 13 shows the measurement conditions. Fig. 15 and Fig. 16 show the topography images and adhesion images with and without the advanced recycling process, respectively.

Without the advanced recycling process, a striped structure could be observed in the adhesion image with a 1 µm field of view, which is the micron-level region. This striped structure is considered to indicate orientation, and is thought to show the effect of shearing in the molding process. On the other hand, with the advanced recycling process, a uniform distribution can be seen in the field of view, suggesting that the effect of shearing is moderated by the advanced recycling process.

Fig. 14 SPM-Nanoa™

Table 13 Measurement Conditions

Instrument	: SPM-Nanoa
Scanner	: Medium-range scanner (XY: 30 µm, Z: 5 µm)
Observation mode	: Nano 3D Mapping™ Fast
Observation field of view	: 1 µm × 1 µm
Pixel	: 256 × 256

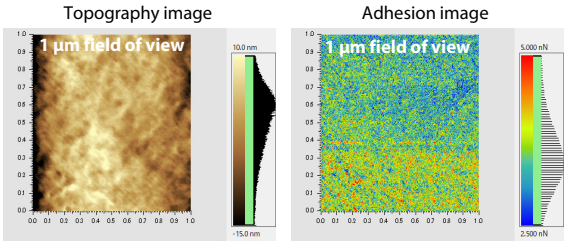

Fig. 15 Topography Image and Adhesion Image with Advanced Recycling Process

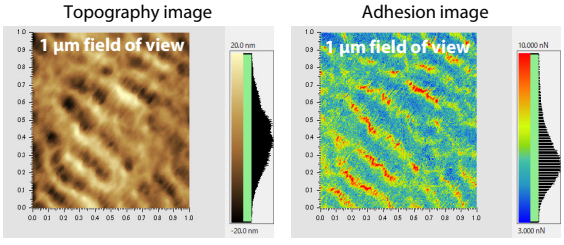

Fig. 16 Topography Image and Adhesion Image without Advanced Recycling Process

■ Study of Changes in Microscopic Physical Structure by Multifaceted Evaluation

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

First, this section considers the existence of intermediate layers containing tie molecules, which are expected to have a strong influence on the improvement of the impact property and strain at break of plastics. Both the elastic modulus and H_{IT} were reduced by the advanced recycling process. The cause of this change is considered to be either a decrease in the degree of crystallization, or an increase in the intermediate layers containing tie molecules. In this evaluation, the DSC analysis showed that there was no difference in the heat of fusion, confirming that there is 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. The image of the tie molecules and intermediate layers is shown in Fig.17.

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

In the section, the increase in tie molecules is considered, changing the perspective from the macroscopic physical properties of the elastic modulus, H_{IT}, and the degree of crystallization to the microscopic viewpoint. It is suggested that the increase in polymer entanglements during melting in the advanced recycling process contributes to the formation of intermediate layers containing tie molecules. The condition of polymer entanglements during melting is estimated from the polymer structure in 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. When the ratio of the parallel structure and the helical structure was investigated by FTIR, it was found that the helical structures had increased. Based on this, it is thought that relaxation proceeds as a result of the advanced recycling process. Moreover, the evaluation of the orientation in the micro region by SPM showed that the distribution becomes more uniform as a result of the advanced recycling process, which also supports the conclusion that the effect of shearing was moderated by the advanced recycling process. As mentioned previously, the crystallization start temperature during cooling in the DSC measurements decreased as a result of the advanced recycling process, which also suggests that polymer entanglements increased.

Based on the multifaceted evaluation described above, it is though that relaxation of the polymer during melting was promoted by the advanced recycling process, leading to an increase in polymer entanglements and an accompanying increase in the intermediate layers containing tie molecules, and as a result, the impact property and strain at break of the recycled plastic improved.

■ Conclusion

It was found that the impact property and strain at break of PP were improved by the advanced recycling process.

This study also demonstrated that the multifaceted evaluation described in this article is an effective tool for evaluating changes in the microscopic physical structure.

■ Reference: Image of Entaglements 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 increase.

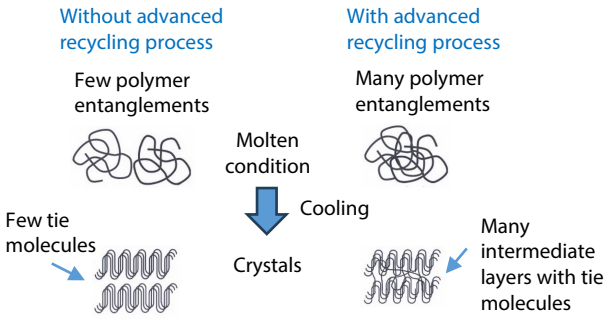

Fig. 17 Image of Aggregation State of Polymers

<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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