Application News

IRTracer™-100 Fourier Transform Infrared Spectrophotometer, AGX™-V Autograph Precision Universal Testing Machine, DUH™-210 Dynamic Ultra Micro Hardness Tester, DSC-60 Plus Differential Scanning Calorimeter, UV-2600i UV-VIS Spectrophotometer, MALDI-8020 Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometer

Multifaceted Evaluation of Plastics: Differences due to Kneading Conditions

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User Benefits

◆ Multifaceted evaluation by instrumental analysis can provide a more detailed understanding of changes in properties due to differences in molding conditions such resin material kneading conditions, and the data obtained are effective for studying the optimum molding conditions.

◆ Use of the MALDI-TOF MS makes it possible to analyze changes in the molecular structure of resin materials during molding.

■ Introduction

It is necessary to study the optimum conditions for injection molding of resin because various molding conditions, such as temperature, pressure, and time, affect the properties of molded products. In particular, when using blended resins, changes in property due to differences in kneading during molding are a concern. In this experiment, multifaceted measurements of the properties of samples prepared under different kneading conditions (differences with/without kneading treatment by a kneading machine) were carried out using a polycarbonate (PC)/acrylonitrile-butadiene-styrene (ABS) blended resin to confirm the effects of kneading conditions.

■ Test Specimens

Here, the material properties of two types of specimens were compared, Sample A with PC : ABS = 50 : 50, which was prepared by injection molding with kneading only in the molding machine without kneading treatment by the kneading machine, and Sample B with the same PC : ABS compounding ratio, which was injection molded after kneading treatment with the kneading machine. Table 1 shows the molding conditions, and Fig. 1 shows a photograph of the samples.

Table 1 Molding Temperature and Kneading Time

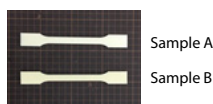|	Kneading machine treatment	Heating conditions
Sample A	Without kneading	Kneaded in molding machine, 260 ˚C, 250 s (approx.)
Sample B	With kneading	Kneading machine treatment, 260 ˚C, 120 s + Kneaded in molding machine, 260 ˚C, 250 s (approx.)

Sample A
Sample B

Fig. 1 Photograph of Samples

■ Confirmation of Compositional Homogeneity

Differences in the compositional homogeneity of the blended resins in Sample A and Sample B were confirmed by using a Fourier transform infrared spectrophotometer (FTIR). The single reflection ATR method was used in the measurements, which were performed at three locations (center and near the two ends) of the dumbbell-shaped specimens (see Fig. 1).

Table 2 Measurement Conditions

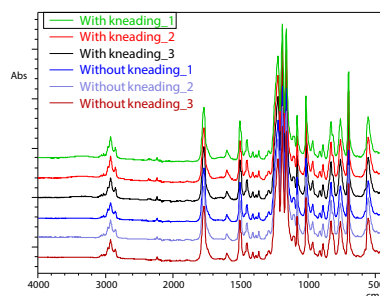|	
Instruments	: IRTracer-100, QATR™10 (diamond prism)
Wavelength range	: 400 - 4000 cm⁻¹
Resolution	: 4 cm⁻¹
Accumulation	: 40 times
Apodization function	: Happ-Genzel
Detector	: DLATGS

Fig. 2 IRTracer™-100

Fig. 3 Infrared Spectra

From Fig. 3, the spectral shapes at the total of six locations on the two samples were in good agreement. Based on these infrared spectra, there are considered to be no compositional differences between the samples due to differences in the kneading conditions of this experiment.

■ Thermal Analysis

Measurements were carried out by differential scanning calorimeter (DSC). Fig. 5 shows the DSC curves. The glass transitions of the ABS and PC resins were measured at around 110 ˚C and 140 ˚ C, respectively. The glass transition temperature is an index of heat resistance. No significant differences were seen between Sample A and Sample B.

Fig. 4 DSC-60 Plus

Table 3 Measurement Conditions

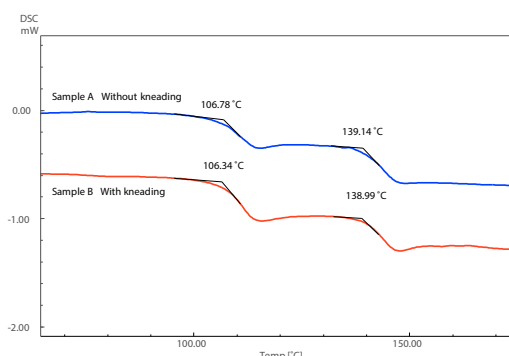|	
Instrument	: DSC-60Plus
Heating rate	: 20 ˚C/min
Specimen weight	: 8 mg
Atmosphere	: Nitrogen

Fig. 5 DSC Curves

■ Yellowness Index Measurement

Comparing the appearances of the two molded specimens, the colors of Sample A and Sample B were different. Therefore, yellowness index was evaluated with an ultraviolet-visible spectrophotometer (UV). Yellowness index was obtained by calculation from reflectance, and was higher in Sample B, which received kneading treatment by the kneading machine.

Fig. 6 UV-2600i

Table 4 Measurement Conditions

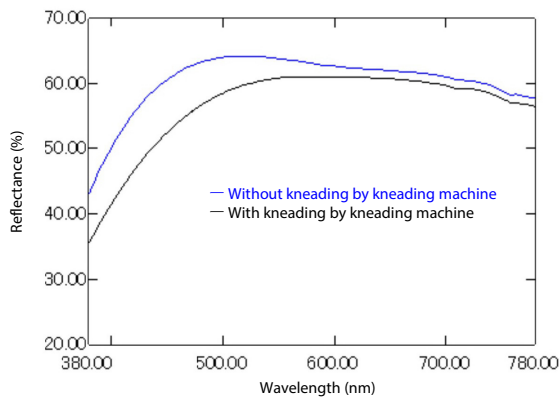|	
Instruments	: UV-2600i, ISR-2600Plus
Measured wavelength range	: 380 - 780 nm
Data interval	: 1.0 nm
Scan speed	: Medium
Slit width	: 5.0 nm

Fig. 7 Reflection Spectra of Specimens

Table 5 Results of Yellowness Index Measurements

	Kneading machine treatment	Yellowness
Sample A	Without kneading	3.44
Sample B	With kneading	12.99

■ Tensile Test

The following shows the results of a tensile test conducted with a precision universal testing machine.

Table 6 Instrument Configuration and Test Conditions

Precision universal testing machine	: AGX-V
Load cell	: 5 kN
Grip	: Pneumatic flat grip
Extensometer	: TRViewX240S
Software	: TRAPEZIUM™X-V
Test speed	: 1 mm/min 50 mm/min (switched at 0.3 % displacement)
Gauge length	: 75 mm
Number of tests	: n = 5
Specimen width	: 10 mm
Specimen thickness	: 4 mm
Grip distance	: 115 mm

Fig. 8 AGX™-V
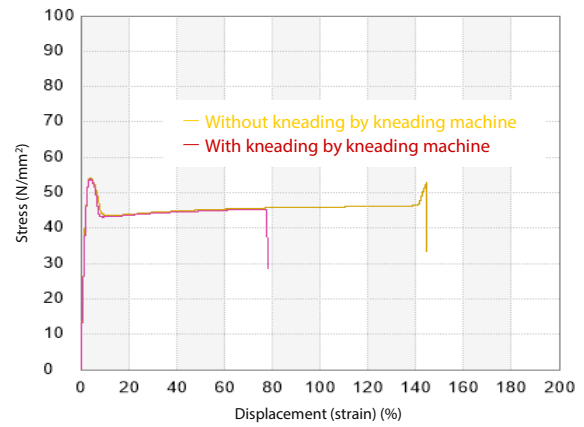

Fig. 9 Condition of Measurement

Fig. 10 Test Curves

Table 7 Test Results

	Kneading machine treatment	Tensile strength (MPa)	Elastic modulus (MPa)	Breaking elongation (%)
Sample A	Without kneading	54.23	2459.13	120.92
Sample B	With kneading	53.90	2492.45	71.75

No large differences were found in the tensile strength and elastic modulus of the two specimens. However, the breaking elongation of Sample B was smaller than that of Sample A.

■ Hardness Test

The hardness test was conducted using a dynamic ultra micro hardness tester (DUH).

Fig. 11 DUH™-210

Table 8 Measurement Conditions (Conforming to ISO/TS 19278)

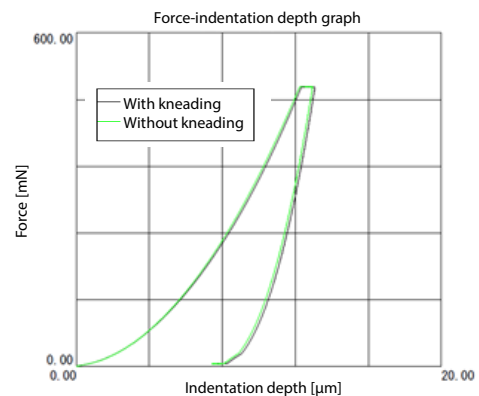|	
Instrument	: DUH-210
Indenter	: Berkovich indenter
Test mode	: Load-unload test
Force	: 500 mN
Loading time/ unloading time	: 30 s
Load holding time	: 40 s
Number of tests	: 5 (central 3 tests were extracted)
Ambient temperature	: 23±2 °C
Humidity	: 50±10 %

Fig. 12 Test Curves

Table 9 Test Results

	Kneading machine treatment	H_{IT} (MPa)
Sample A	Without kneading	166.46
Sample B	With kneading	160.36

No significant difference in the indentation hardness (H_{IT}) of the two specimens was seen.

◼ Measurement of Changes in Molecular Structure

In the results in the previous sections, differences in yellowness and breaking elongation were seen in Sample A and Sample B. These differences were assumed to occur due to changes in the chemical structure of the resin caused by the difference in the kneading condition. To confirm this assumption, the differences in the molecular structures of the two specimens were measured with a matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS). The results are shown in Fig. 14.

Fig. 13 MALDI-8020

Table 10 Measurement Conditions

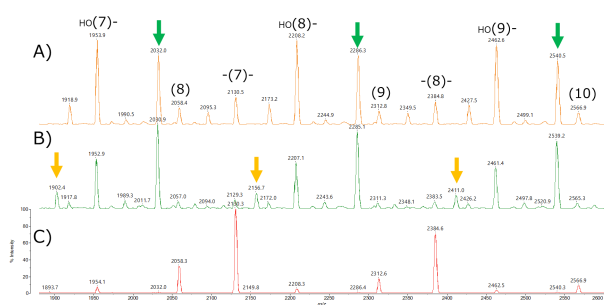|	
Instrument	: MALDI-8020
Laser source	: Solid-state laser (λ = 355 nm)
Matrix	: DCTB, NaI (cationization agent)
Mass range	: m/z 1-5000
Detection ion	: Positive ion mode
Flight mode	: Linear mode
Delayed extraction condition	: m/z 2500

Fig. 14 Comparison by MALDI-TOF MS
A) Without kneading, B) With kneading, C) PC

➡ : New signal due to kneading

➡ : Characteristic signal due to blending (molding)

Both-end capped; –(n)–

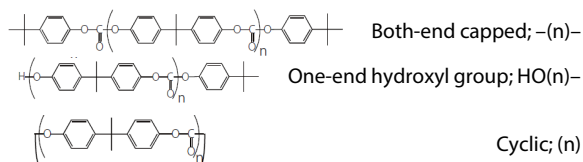One-end hydroxyl group; HO(n)–

Cyclic; (n)

Fig. 15 End Terminal Structures of Polycarbonate (PC)

Changes in the signal originating from PC in the blended product were observed, regardless of whether the material was treated with the kneading machine or not. In comparison with virgin PC, there was a relative decrease in both-end capped molecules in both Samples A and B, and the number of molecules having one end capped with a hydroxyl group increased. Furthermore, the number having a hydroxyl group at one end decreased in the specimen treated with the kneading machine. Although the chemical structure could not be estimated, new characteristic signals appeared, as indicated by the yellow arrows in Fig. 14. The possibility that the origin of these signals may be some type of reaction with the one-end hydroxyl groups due to the extended kneading time is conceivable.

A precise analysis extending to the cause of the changes in yellowness and breaking elongation was not possible. However, it was at least possible to confirm that changes occur in the end groups of PC as a result of a chemical reaction during kneading. Thus, in addition to analytical methods to understand the physical properties of the material, such as strength, analysis of chemical structure at the molecular level is considered to be effective for ensuring proper molding.

◼ Conclusion

In this evaluation, there were no differences in the compositional homogeneity, tensile strength, elastic modulus, hardness, or glass transition temperature of the specimens prepared under the different kneading conditions. Thus, no effect of kneading on these properties was observed. On the other hand, when kneading treatment was conducted, deterioration of the yellowness index and breaking elongation properties could be seen, and progress of changes in the molecular structure due to kneading treatment was also confirmed. Multifaceted evaluation like that introduced here can provide a detailed understanding of the changes in material properties that occur as a result of differences in overall molding conditions, not limited simply to kneading. Therefore, this is considered to be an effective approach for study of the optimum molding conditions.

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