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Application News

IRSpirit™-TX Fourier Transform Infrared Spectrophotometer
DSC-60 Plus Differential Scanning Calorimeter
DTG-60 Simultaneous Thermogravimetric and Differential Thermal Analyzer

Discriminating between Microsamples of Similar Resins with a Combination of FTIR and Thermal Analysis Instruments

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User Benefits

- Using the ATR method with FTIR spectroscopy enables simple and rapid qualitative analysis of polymers.
- DSC analysis may be able to reveal differences in polymer thermal histories that cannot be confirmed by FTIR alone.
- TG-DTA can be used to confirm the content level of inorganic additives in polymers.

■ Introduction

A wide range of polymer resins is used in modern society for diverse applications, resulting in increasing demand for qualitative analysis of resin microsamples, such as identifying resin contaminants in products or qualitatively evaluating microplastics for environmental impact assessments. FTIR spectrophotometers are commonly used for qualitative analysis of polymers. In particular, the ATR (attenuated total reflectance) method is widely used because measurements can be performed simply and quickly by clamping a sample against a prism to ensure close contact.

While the ATR method makes it relatively easy to discriminate between different types of polymers, clear differences may not appear when analyzing similar polymers—for example, when there are only slight differences in the type or content of additives or the thermal histories during manufacturing. In such cases, differences may be confirmed by using thermal analysis instruments, such as a DSC or TG-DTA system.

This article describes an example in which three instruments—an IRSpirit-TX FTIR spectrophotometer, a DSC-60 Plus differential scanning calorimeter, and a DTG-60 simultaneous DTA-TG unit (Fig. 1)—were used to confirm differences among six microsamples of polypropylene (PP) resin.

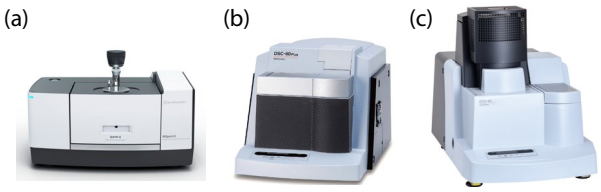

Fig. 1 External Views of the Instruments:
(a) IRSpirit™-TX, (b) DSC-60 Plus, (c) DTG-60

■ Samples

A photo of the six PP resin samples (1 to 6) measured is shown in Fig. 2. For each sample, one particle with a mass of 0.2 to 0.5 mg and an approximate size of 1 to 2 mm^2 was measured.

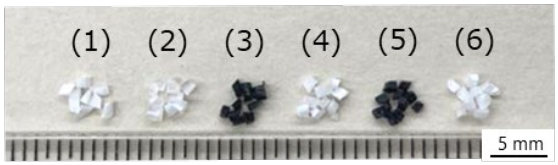

Fig. 2 Appearance of the Six PP Resin Samples Used for Measurement

■ FTIR Measurement

The six PP resin samples were measured using the ATR method with FTIR spectroscopy. The measurement conditions are shown in Table 1 and the result is shown in Fig. 3.

Table 1 FTIR Measurement Conditions

Instrument:	IRSpirit-TX, QATR™-S (Diamond)
Wavenumber Range:	4000 to 400 cm^{-1}
Resolution:	4 cm^{-1}
Number of Scans:	20
Apodization Function:	SqrTriangle

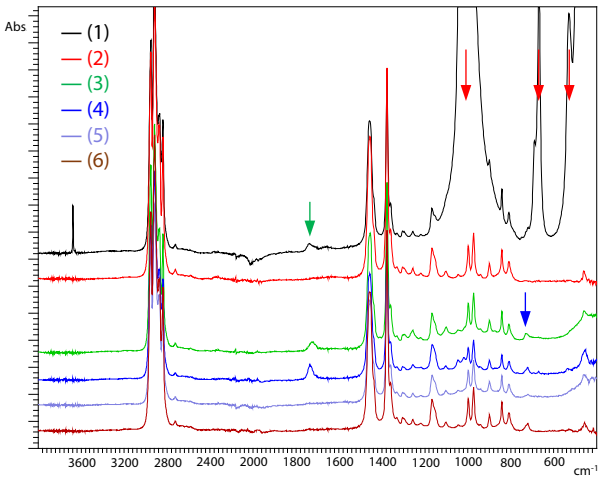

Fig. 3 Infrared Spectra of the Six PP Samples

As shown in Fig. 3, some PP spectra differed from the others. First, sample 1 shows relatively large peaks at around 1,000 cm^{-1}, 680 cm^{-1}, and 520 cm^{-1} (red arrows) compared to the other spectra. These peaks match the spectrum of talc, indicating that PP sample 1 contains talc as an additive.

Next, spectra of samples 3 to 6 show a peak at 720 cm^{-1} (blue arrow), but the spectrum of sample 2 does not. This peak is referred to as a CH_2 rocking-vibration peak, which appears when ethylene is copolymerized with PP. Therefore, PP samples exhibiting this peak are highly likely to be copolymers containing ethylene in their structure, whereas PP samples without this peak are highly likely to be homopolymers that do not contain ethylene in their structure. For details, refer to Application News No. 01-00710. Based on that information, sample 2 is predicted to be a homopolymer and samples 3, 4, 5, and 6 are predicted to be copolymers.

In addition, a peak at 1,730 cm^{-1} (green arrow) appears in the spectra of samples 1, 3, and 4 but not in the other PP spectra. That is a C=O stretching vibration peak that appears when a polymer undergoes oxidative degradation. That suggests that oxidative degradation presumably occurred in samples 1, 3, and 4 during manufacturing or storage. With the high-sensitivity IRSpirit-TX FTIR spectrophotometer, even minute changes due to oxidative degradation can be captured using the ATR method.

■ DSC Measurement

Based on the FTIR measurement results, it was predicted that sample 1 contained talc, sample 2 was a homopolymer, and samples 1, 3, and 4 were oxidatively degraded. However, FTIR measurements alone did not clearly reveal the differences between samples 3 and 4 or between samples 5 and 6. Therefore, DSC measurements were also performed for those samples.

Because FTIR spectroscopy is a nondestructive analysis technique, the same samples can be used as-is for DSC and TG-DTA measurements after FTIR analysis. The DSC measurement conditions are shown in Table 2 and results are shown in Fig. 4.

Table 2 DSC Measurement Conditions

Instrument:	DSC-60 Plus
Cell:	Aluminum cell
Heating Rate:	20 °C/min
Temperature Program:	0 °C → 200 °C
Atmosphere:	Nitrogen, 50 mL/min

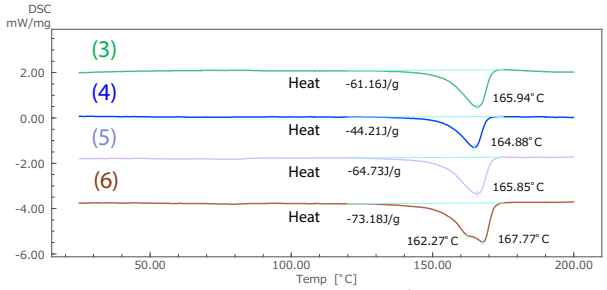

Fig. 4 DSC Measurement Results

As shown in Fig. 4, only sample 6 shows a shoulder on the melting peak, indicating a different melting peak shape from the other three samples. In addition, only sample 4 clearly shows a lower heat of fusion than the others.

To investigate the cause, after the FTIR analysis, sample 6 was measured again under the same DSC conditions. The result is shown in Fig. 5.

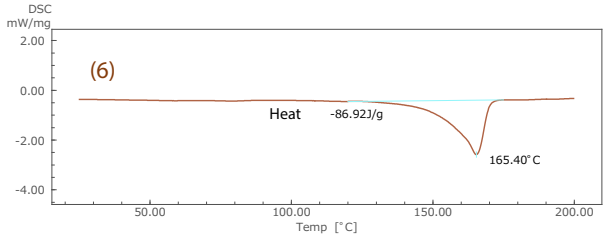

Fig. 5 Second DSC Measurement Result for Sample 6

As shown in Fig. 5, the shoulder peak disappeared in the second DSC measurement of sample 6 and the melting peak became a single peak. That suggests that the shoulder peak observed in the DSC curve of sample 6 in Fig. 4 was caused by the thermal history due to heat treatment during manufacturing. For details on resin thermal history, refer to Application News No. T159.

■ TG-DTA Measurement

DSC measurements indicated that only sample 6 had a melting peak shoulder due to thermal history effects, unlike samples 3, 4, and 5. However, the reason why sample 4 had a lower heat of fusion was still not clear, so TG-DTA measurements were performed for those samples.

Note that TG-DTA measurements are destructive. Fig. 6 shows TG curves and includes the weight loss (%) due to heating from room temperature to 500 °C. The measurement conditions are indicated in Table 3 and results are shown in Fig. 6.

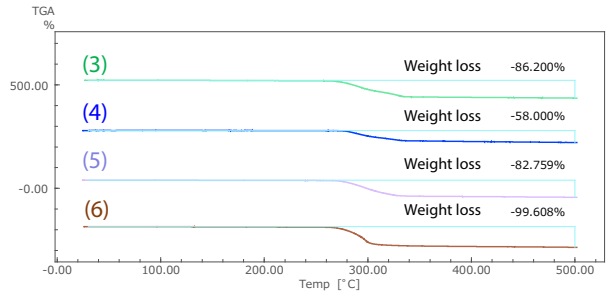

Fig. 6 TG-DTA Measurement Results (TG Curves Only)

Table 3 TG-DTA Measurement Conditions

Instrument:	DTG-60
Cell:	Aluminum cell
Heating Rate:	20 °C/min
Temperature Program:	Room temperature → 500 °C
Atmosphere:	Air, 100 mL/min

Based on these results, the weight loss at 500 °C differs from the other samples. Sample 6 shows nearly 100 % weight loss, whereas samples 3, 4, and 5 do not reach 100 % weight loss. Because fibrous residues remained in the cell after measurement, that indicates that no additives that underwent thermal decomposition or combustion up to 500 °C were present. In addition, sample 4 shows less weight loss and a larger amount of residue than samples 3 and 5, suggesting a higher additive content. This is considered to be the same underlying cause as the lower heat of fusion observed for sample 4 in the DSC results. Finally, to investigate the components in those residues, FTIR-ATR measurements were performed for each residue under the conditions in Table 1. The results are shown in Fig. 7.

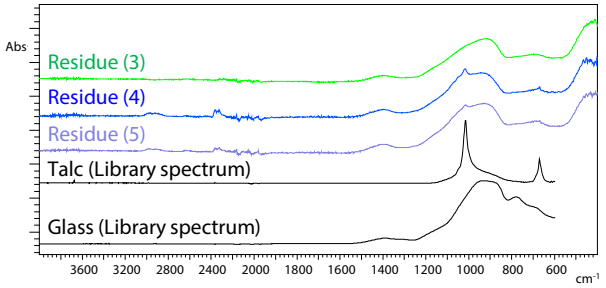

Fig. 7 Infrared Spectra of Residues for Samples 3, 4, and 5

Based on Fig. 7, the residue of sample 3 is identified as glass fiber, and residues of samples 4 and 5 are identified as glass fiber and talc. These additives were not evident in the FTIR results in Fig. 3, which is attributed to the glass fiber not being exposed on the PP surface during measurement and the talc being present only in trace amounts.

■ Conclusion

Details of the six types of PP resin identified from the above measurement results are shown in Table 4. The results indicate that by using an FTIR spectrophotometer in combination with thermal analysis equipment, such as DSC and TG-DTA systems, it is possible to distinguish between minute amounts of the same type of resin with various different properties.

Table 4 Details of the Six PP Samples

PP	Details
(1)	Contains a relatively large amount of talc and is oxidatively degraded.
(2)	Probably a homopolymer.
(3)	Contains glass fiber and is oxidatively degraded. Probably a copolymer.
(4)	Contains a trace amount of talc and glass fiber and is oxidatively degraded. Glass fiber content is higher than in samples 3 and 5. Probably a copolymer.
(5)	Contains trace amounts of talc and glass fiber. Probably a copolymer.
(6)	Heat-treated. Probably a copolymer.

Related Applications

1. Distinction of Polyethylene and Polypropylene by Infrared Spectrum, Application News No. 01-00710
2. Estimation of Thermal History of Polymer Using DSC-60 Plus Differential Scanning Calorimeter, Application News No. T159

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