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Application News

Differential Scanning Calorimeter/Simultaneous TG/DTA

Measurement of UV-Degraded Polymer Materials Using a Thermal Analyzer

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User Benefits

- The change due to UV degradation of polypropylene and polyethylene, which are typical polymer materials was measured. In thermal analysis, changes in thermal properties such as melting and decomposition temperature can be evaluated.
- The degraded part caused by ultraviolet irradiation is the sample surface layer, but the difference can be confirmed without sampling only the surface.

■ Introduction

Generally, resin and polymer materials are known to deteriorate due to heat and ultraviolet rays. Resin products used outdoors, in particular, must be resistant to ultraviolet rays.

This article introduces the data measured by differential scanning calorimeter (DSC), differential thermal/thermogravimetric analyzer (DTG), and Fourier transform infrared spectrophotometer (FTIR) regarding the effect of ultraviolet irradiation (UV irradiation) on polypropylene (PP) and polyethylene (PE), which are typical polymer materials.

■ Degradation of Polymer Materials by Ultraviolet Rays

The chemical structure, molecular weight, melting point, and decomposition temperature of polymer materials change when they deteriorate due to ultraviolet rays or heat. As a result, various properties of the material are affected, such as strength, elongation, and impact resistance.

In FTIR, changes in the chemical structure can be measured as changes in the infrared spectrum.

On the other hand, thermal analysis equipment can evaluate thermal properties such as melting point and decomposition temperature. This article describes the chemical structural changes measured using FTIR, and changes in thermal properties measured using a thermal analyzer (DSC, DTG). The differences in data measured with each model are introduced.

■ Measurement of Polypropylene

As a measurement sample, approximately 1 mm thick plate-like PP was cut into 3 cm squares and irradiated with UV light for 0, 50, 100, and 550 hours (samples irradiated for 50 hours were not used for FTIR).

Fig. 1 shows the results of FTIR measurement of PP. When the UV irradiation time is prolonged, significant differences are observed in absorption due to hydroxyl group (O-H), carbonyl group (C=O), and ether bond (C-O-C) due to oxidation degradation.

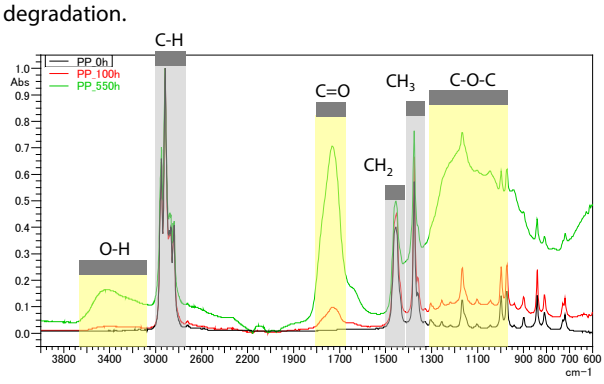

Fig. 1 Infrared Spectra of PP with Different UV Irradiation Times

Fig. 2 shows DSC measurement data, and Table 1 shows the measurement conditions. The samples used for DSC were obtained by further cutting the sample mentioned above into 1 mm^3 or less.

In the 1st and 2nd heating, the melting peaks measured at around 150 to 170 °C are shifted to the lower temperature side due to degradation, and it can be seen that the peak shape of 2nd heating is broader than that of 1st heating.

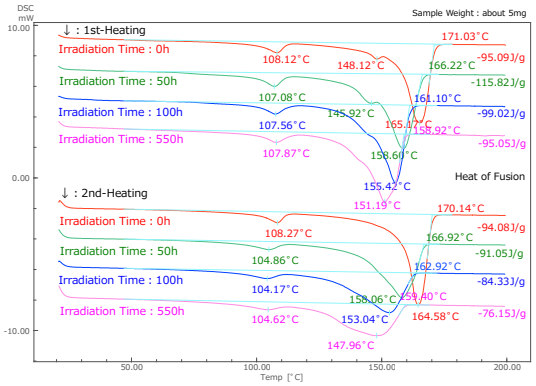

Fig. 2 DSC Measurements of PP with Different UV Irradiation Times

Table 1 DSC Measurement Conditions

Device	:	Differential Scanning Calorimeter (DSC-60Plus) Electric cooling device (TAC-60i)
Temperature Range	:	20 °C → 200 °C → 20 °C → 200 °C
Heating/Cooling Rate	:	10 °C/min
Sample Weight	:	Approx. 5 mg
Atmospheric Gas	:	N_2

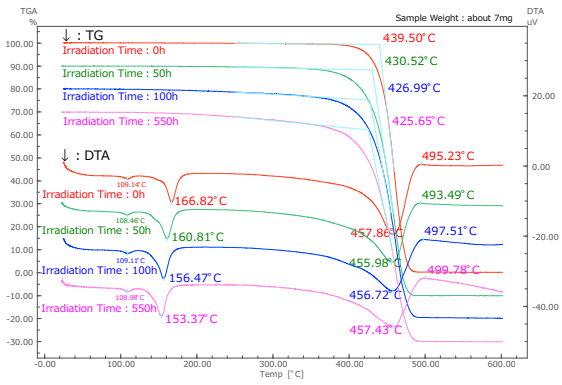

Fig. 3 DTG Measurements of PP with Different UV Irradiation Times

Fig. 3 shows the results of same samples measured with DTG (TG-DTA), and Table 2 shows the measurement conditions.

The melting peak at around 150 to 170 °C in the DTA curve shows decrease of melting temperature similar to the 1st heating data in DSC. The TG curve also shows that the decomposition start temperature, which is seen in the vicinity of 420 to 440 °C, shifts to the lower temperature side.

Table 2 DTG Measurement Conditions

Device	:	Simultaneous TG/DTA (DTG-60)
Temperature Range	:	R.T. → 600 °C
Heating Rate	:	10 °C/min
Sample Weight	:	Approx. 7 mg
Atmospheric Gas	:	N_2

■ Measurement of Polyethylene

Like PP, PE was prepared by cutting a plate-like specimen approximately 1 mm thick into 3 cm squares and irradiating it with ultraviolet rays for 0, 50, 100, and 550 hours. (Samples irradiated for 50 hours were not used in FTIR and for 100 hours were not used in thermal analysis.)

Fig. 4 shows the results of FTIR measurement of the PE. As with PP, when the UV irradiation time was prolonged, significant differences can be seen in the absorption of O-H groups, C=O groups, and C-O-C bonds due to oxidation. However, the difference is small compared with PP, with little difference between unirradiated and 100-hour irradiated samples.

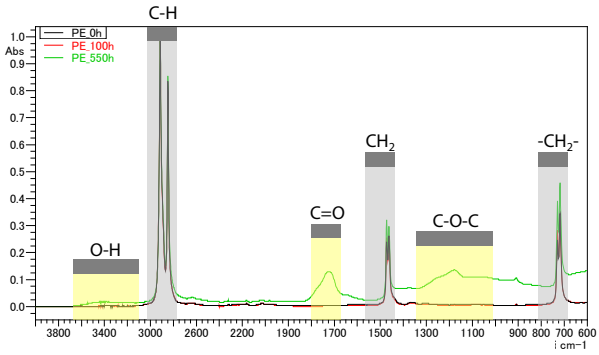

Fig. 4 Infrared Spectra of PE with Different UV Irradiation Times

Fig. 5 shows the results measured by DSC, and Table 3 shows the measurement conditions. As with PP, the sample used was a 3 cm square sample that had been cut into 1 mm^3 or less.

In PE, unlike the PP data above, there was little difference in the melting peak detected in the 1st heating. On the other hand, the endothermic peak of melting observed in the 2nd heating was different.

Fig. 6 shows the results of DTG (TG-DTA) on the same PE, and Table 4 shows the measurement conditions. In this data, the area around the start temperature of the weight loss is enlarged.

As with DSC, the melting peak of the DTA curve corresponding to the 1st heating was not affected by the irradiation time, but the TG curve showed that the decomposition start temperature decreased as the irradiation time increased.

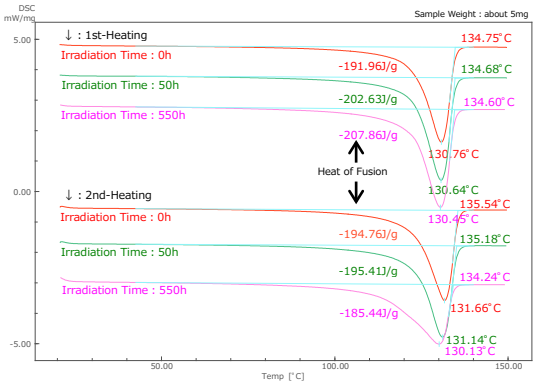

Fig. 5 DSC Measurements of PE with Different UV Irradiation Times

Table 3 DSC Measurement Conditions

Device	:	Differential Scanning Calorimeter (DSC-60Plus) Electric Cooling Device (TAC-60i)
Temperature Range	:	20 °C → 150 °C → 20 °C → 150 °C
Heating/Cooling Rate	:	10 °C/min
Sample Weight	:	Approx. 5 mg
Atmospheric Gas	:	N_2

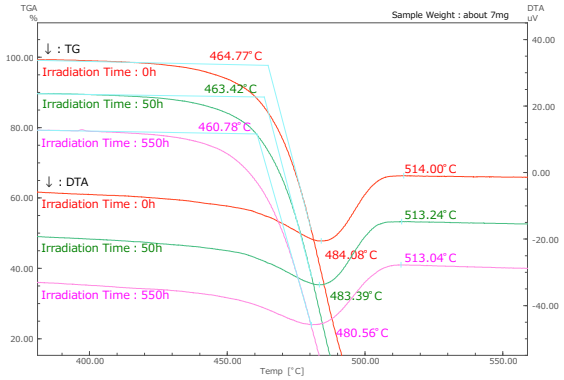

Fig. 6 DTG Measurements of PE with Different UV Irradiation Times (Enlarged View)

Table 4 DTG Measurement Conditions

Device	:	Simultaneous TG/DTA (DTG-60)
Temperature Range	:	R.T. → 600 °C
Heating Rate	:	10 °C/min
Sample Weight	:	Approx. 7 mg
Atmospheric Gas	:	N_2

■ Conclusion

The melting point and decomposition temperature of polymer materials degraded by ultraviolet rays were measured using thermal analysis. In order to evaluate deterioration in detail, various methods are required, but it is necessary to select an appropriate method according to the purpose. FTIR is effective for the evaluation of chemical structural changes, and thermal analysis is one of the effective options for the evaluation of physical properties.

The infrared spectrum data presented in this report is taken from Shimadzu's proprietary UV deterioration plastic library. It is a very useful library for molecular structure analysis, and more useful information can be obtained by comprehensive analysis with thermal analysis data.

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