

Evaluation of UV-Degraded Plastics by FTIR and Dynamic Ultra Micro Hardness Tester

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User Benefits

- ◆ It is possible to grasp the changes in the state of plastics due to ultraviolet (UV) irradiation and evaluate weathering resistance and other properties by an analysis using multiple instruments.
- ◆ Changes in the chemical structure of plastics by degradation can be confirmed by using the Plastic Analyzer plastic analysis system.
- ◆ Changes in the hardness of plastics by degradation can be evaluated by using the DUH-210 plastic hardness analyzer.

Introduction

Plastic products used outdoors in automotive parts, building materials, industrial products, and agricultural products are degraded over time as a result of exposure to sunlight (mainly ultraviolet radiation), rain, and temperature changes. Therefore, it is necessary to select appropriate materials which can be used safely, considering the use period, use environment, and weathering resistance. Understanding the condition and life of plastics that have been degraded by external factors (light and heat) is useful in the selection of additives (antioxidants and bulking agents) to be used in plastic products and in the development of high performance functional materials.

In this article, we evaluated the ultraviolet (UV) degradation of plastics that are frequently used in automotive parts. Changes in the chemical structure of the plastic surface under UV irradiation were evaluated by using a Fourier transform infrared spectrophotometer (FTIR), and changes in hardness were evaluated with a dynamic ultra micro hardness tester. The results are presented in the following.

Evaluation of Automobile Seat Material by Plastic Analyzer Plastic Analysis System

Plastic Analyzer is a specialized product for evaluation of degradation of plastics, and includes the Shimadzu IRSpirit Fourier transform infrared spectrophotometer, QATR™-S single-reflection ATR accessory, and Plastic Analyzer method package (UV-damaged plastics library, thermal-damaged plastics library, and analysis programs/method files for IR Pilot™). This system is a useful tool for correctly analyzing the presence/absence of degradation in plastic products and identifying the degradation process, and does not depend on the experience of the analyst. For product details and examples of use, please refer to Application News No. A647.

A polyurethane (PU) seat material which was used in an automobile was measured with IRSpirit, and the presence/absence of degradation was investigated by using the UV-damaged plastics library of Plastic Analyzer. The library contains infrared spectra obtained by UV irradiation of samples using a super accelerated weathering chamber manufactured by Iwasaki Electric Co., Ltd. for times from 0 h (no irradiation) to a maximum time of 550 h (equivalent to UV exposure for approximately 10 years). Table 1 shows the measurement conditions, and Fig. 1 shows the results of the analysis of the seat material.

Table 1 Measurement Conditions

Instruments	: IRSpirit QATR-S (diamond prism)
Resolution	: 4 cm ⁻¹
Accumulation	: 45 times
Wavelength range	: 4000 - 600 cm ⁻¹
Apodization function	: SqrTriangle
Detector	: DLATGS

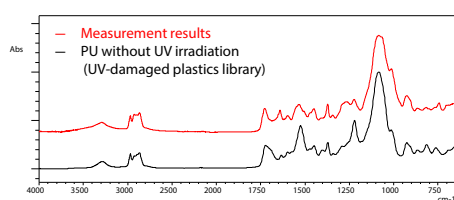


Fig. 1 Results of Analysis of Seat Material

A hit for PU without exposure to UV irradiation was obtained from the UV-damaged plastics library, and the results did not reveal peaks originating from O-H stretching vibration at around 3400cm⁻¹ or C=O stretching vibration at around 1700 cm⁻¹, which can be seen in the infrared spectrum of degraded PU. Based on these facts, it was clear that the seat material which was the target of this measurement was not degraded.

Change of Chemical Structure of Plastic Surface by UV Irradiation

Next, changes in the structures of polypropylene (PP) and polycarbonate (PC) by UV irradiation were investigated. PP is used in automobile bumpers, and PC is used in automobile roofs, headlamp lenses, and other parts. Fig. 2 and Fig. 3 show the infrared spectra of PP and PC, respectively, after UV irradiation for 0 h, 1 h, and 100 h using the above-mentioned super accelerated weathering chamber.

Focusing on the C=O stretching vibration at around 1750 cm⁻¹ (yellow boxes in the figures), when the samples were exposed to UV irradiation for 100 h, an increase in peak intensity was observed in the PP, and a change in the peak shape could be confirmed in the PC. These results clarified the fact that the surface of both plastics undergoes oxidative degradation under exposure to UV irradiation, and after 100 h, the structural changes associated with degradation have progressed to the point where changes in the peaks can be clearly detected.

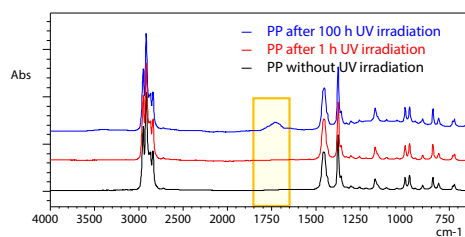


Fig. 2 Infrared Spectrum of Polypropylene (PP)

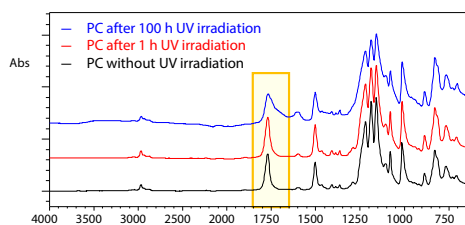


Fig. 3 Infrared Spectrum of Polycarbonate (PC)

■ Hardness Evaluation for UV Degradation by Plastic Hardness Analyzer

The DUH-210 plastic hardness analyzer is a specialized product for hardness evaluation of plastics, and can be used to conduct testing conforming to ISO/TS 19278: 2019^{*1}. Hardness testing is effective for evaluation of degradation of plastic materials, as simple measurement of the mechanical properties and physical properties of the materials is possible. Moreover, because the test conditions in the ISO standard are registered in the device in advance, hardness testing can be conducted without depending on the experience of the analyst.

In this experiment, changes in the hardness of polypropylene (PP) and polycarbonate (PC) by UV irradiation were evaluated. Table 2 shows the measurement conditions, and Table 3 and Fig. 4 to Fig. 6 show the results of hardness measurements of PP and PC after UV irradiation for 0 h (no irradiation), 1 h, and 100 h. It can be understood that the surfaces of both the PP and PC samples became harder as a result of UV irradiation. In the FTIR measurements, the structural changes in the samples became remarkable after 100 h, but in the hardness test, a clear difference in the hardness of the samples could be observed after only 1 h. These results suggest that the intrinsic flexibility of resins decreases due to oxidative degradation of the sample surface by UV radiation, and as a result, cracking may occur more easily.

*1 ISO/TS 19278: 2019 was issued in 2019 as a technique for measuring the indentation hardness H_{IT} of plastics. Details concerning the measurement method and examples of application may be found in Application News No. i274.

Table 2 Measurement Conditions

Instrument	: Plastic hardness analyzer DUH-210
Room temperature	: 23±2 °C
Humidity	: 50±10 %
Upper pressure indenter	: Berkovich indenter (diamond)
Test mode	: Load/unload test
Test force	: 500 mN
Loading time	: 30 s
Holding time	: 40 s
Unloading time	: 30 s
No. of test cycles	: 5

Table 3 Difference of Indentation Hardness H_{IT} [N/mm²]

Sample name	UV irradiation 0 h	UV irradiation 1 h	UV irradiation 100 h
PP	61.3	84.2	85.3
PC	116.6	149.6	161.4

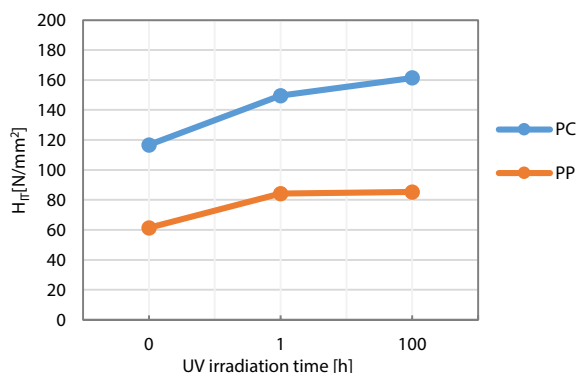


Fig. 4 Change of Hardness with Irradiation Time

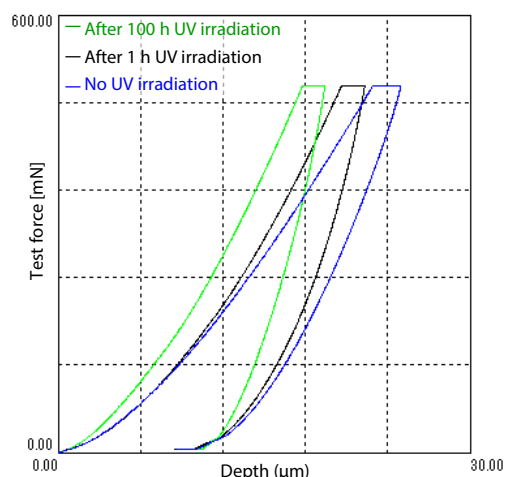


Fig. 5 Measurement Results of Hardness Test of Polypropylene (PP)

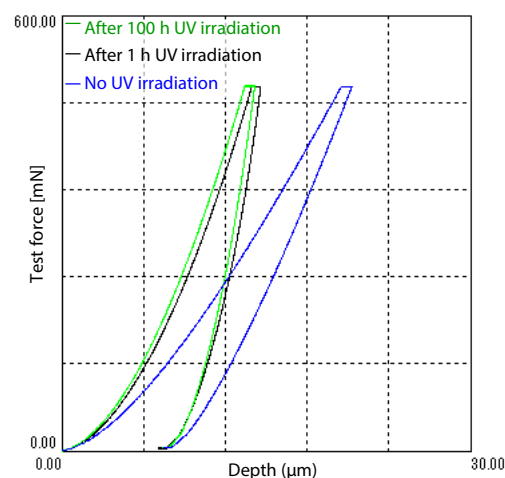


Fig. 6 Measurement Results of Hardness Test of Polycarbonate (PC)

■ Conclusion

In order to evaluate the weathering resistance of plastics which are frequently used in automotive parts, changes in the structure of the plastics were analyzed by FTIR, and changes in hardness were analyzed by using a dynamic ultra micro hardness analyzer. As a result, it was found that structural changes due to oxidation occurred at the surface of the plastics under UV irradiation, and hardness tended to increase. These evaluation data are useful for selection of additives to be added to plastics and improvement of functionality.

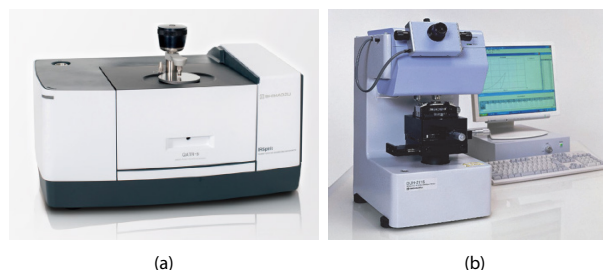


Fig. 7 (a) IRSpirit™ Fourier Transform Infrared Spectrophotometer, (b) DUH™-210 Plastic Hardness Analyzer

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