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Application News

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Spectrophotometric Analysis

Analysis of Thermally Degraded Plastics Using Thermally Degraded Plastics Library

-Applications to Contaminant Analysis-

Introduction

In daily life, we encounter a variety of natural products and manufactured goods. In fields such as food products, pharmaceuticals, and machinery, effort is put into quality assurance, striving to prevent the incorporation of contaminants. However, the incorporation of contaminants does inadvertently occur due to unforeseen factors and problems.

While there are many types of contaminants, the plastic parts used in production line, specific environments, and the vicinity become brittle due to aging and thermal degradation, making their incorporation in part a possibility.

FTIR is optimal for the analysis of such plastic contaminants. However, the infrared spectrum of degraded plastic differs from the spectral pattern before degradation. Accordingly, in searches using commercially available plastics libraries, even if a search result has top ranking, it can inadvertently consist of the spectral pattern for a different substance, making identification and qualification difficult.

In this article, we introduce an example of the changes to the infrared spectrum of a plastic degraded by heat, and a sample search using a library containing data created by changing the heating temperature and time beforehand.

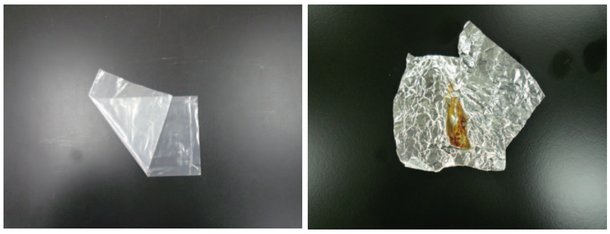
Changes to the Spectrum of a Polyethylene Film Due to Thermal Degradation

A polyethylene film was wrapped in aluminum foil, and then heated on a hot plate. As it was heated in air, the polyethylene film was subject to oxidative degradation.

Fig. 1 is a photograph of the polyethylene film before heating, and then after heating at 200 °C for two hours. Before heating, it was transparent. After heating, however, it evidently turned brown.

Fig. 2 (top) shows the respective infrared spectra. The measurements were performed using the single bounce ATR method. Polyethylene has a repeating $-(CH_2)_n-$ structure, so before heating, peaks due solely to this structure are visible near 3000 cm^{-1}, 1400 cm^{-1}, and 700 cm^{-1}.

As a result of heating, in addition to the original peaks, there are peaks in the 1700 cm^{-1} to 1750 cm^{-1} range due to -C=O, and peaks in the 1100 cm^{-1} to 1200 cm^{-1} range due to -C-O-. These are likely due to oxidative degradation. Fig. 2 (bottom) shows the spectra for polystyrene film before and after an identical heat treatment. Identical changes are visible here as well.



Before Heating　　After Heating

Fig. 1 Polyethylene Film Before Heating, and After Heating at 200 °C for 2 Hours

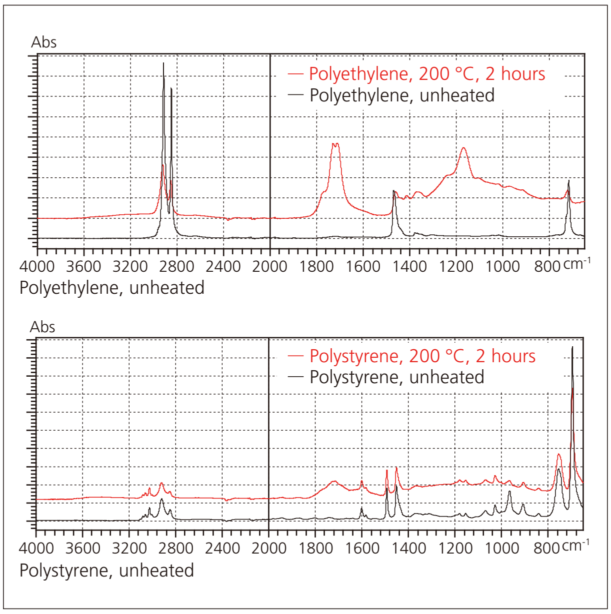


Fig. 2 Top: Infrared Spectra of Polyethylene Film Before Heating (Black) and After Heating at 200 °C for 2 Hours (Red). Bottom: Polystyrene Film Before Heating (Black) and After Heating at 200 °C for 2 Hours (Red)

Analysis of a Contaminant on a Plated Part

A semi-transparent light brown contaminant was visible on a plated product. This area was measured, and the spectrum in Fig. 3 was obtained. A search of the spectrum was performed using a standard library directly, but no equivalent spectra were found.
As shown in Fig. 2, a portion is similar to heated plastic, so it is presumed to be plastic that had been changed by heating.

Searches Using Thermally Degraded Plastics Library

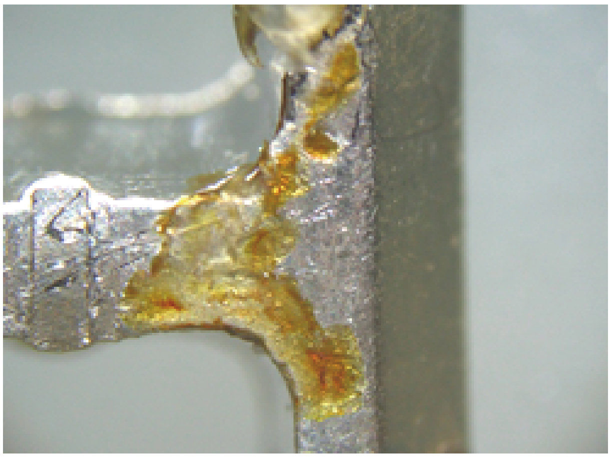
As in Figs. 2 and 3, with heating, the infrared spectral pattern is changed due to oxidation. Typical search libraries contain the infrared spectra for plastic samples measured in an unheated state. As a result, if a search is performed directly, there is a risk that the results obtained will be different than for plastic samples after heating.
This article introduces the Thermally Degraded Plastics Library, a proprietary library compiled by Shimadzu. It consists of spectra obtained by measuring samples at the Industrial Research Institute of Shizuoka Prefecture's Hamamatsu Technical Support Center. The library contains 13 plastics, both unheated and thermally degraded at temperatures from 200 °C to 400 °C.
Fig. 4 shows the results of a search utilizing these. It is evident that the heated plastics have top ranking.
In addition, this library contains infrared spectra changed by heating temperature and heating time, which will be useful for estimating the thermal history of a plastic.
Note that this library is not intended for searches of heating time and heating temperature, but is considered for investigating the thermal history of a sample.

Conclusion

It is evident that qualitative analysis of plastics that have undergone thermal changes can easily be performed by searching the Thermally Degraded Plastics Library.
This library will prove useful in contaminant analysis.

Table 1 FTIR Analysis Conditions

Instrument	: IRTracer-100 MIRacle10
Resolution	: 4.0 cm^{-1}
Accumulation	: 100
Apodization	: Happ-Genzel
Detector	: DLATGS



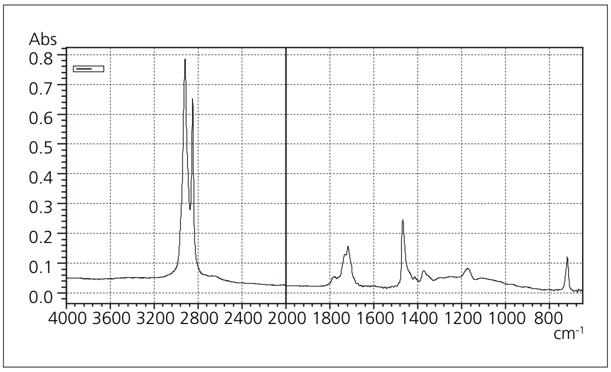
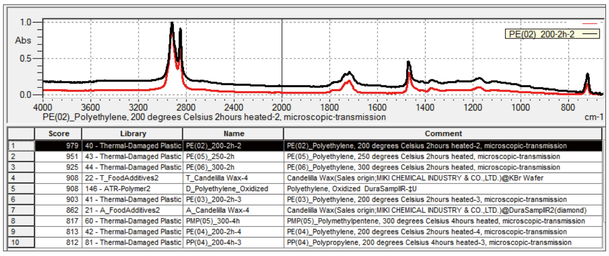


Fig. 3 Photograph of a Contaminant on a Plated Part (Top); Measured Infrared Spectrum (Bottom)



	Score	Library	Name	Comment
1	979	40 - Thermal-Damaged Plastic	PE(02)_200-2h-2	PE(02)_Polyethylene, 200 degrees Celsius 2hours heated-2, microscopic-transmission
2	951	43 - Thermal-Damaged Plastic	PE(05)_250-2h	PE(05)_Polyethylene, 250 degrees Celsius 2hours heated, microscopic-transmission
3	925	44 - Thermal-Damaged Plastic	PE(06)_300-2h	PE(06)_Polyethylene, 300 degrees Celsius 2hours heated, microscopic-transmission
4	908	22 - T_FoodAdditives2	T_Candelilla Wax-4	Candelilla Wax(Sales origin;MIKI CHEMICAL INDUSTRY & CO.,LTD.)@KBr Wafer
5	908	146 - ATR-Polymer2	D_Polyethylene_Oxidized	Polyethylene, Oxidized DuraSamplIR-‡U
6	903	41 - Thermal-Damaged Plastic	PE(03)_200-2h-3	PE(03)_Polyethylene, 200 degrees Celsius 2hours heated-3, microscopic-transmission
7	862	21 - A_FoodAdditives2	A_Candelilla Wax-4	Candelilla Wax(Sales origin;MIKI CHEMICAL INDUSTRY & CO.,LTD.)@DuraSamplIR2(diamond)
8	817	60 - Thermal-Damaged Plastic	PMP(05)_300-4h	PMP(05)_Polymethylpentene, 300 degrees Celsius 4hours heated, microscopic-transmission
9	813	42 - Thermal-Damaged Plastic	PE(04)_200-2h-4	PE(04)_Polyethylene, 200 degrees Celsius 2hours heated-4, microscopic-transmission
10	812	81 - Thermal-Damaged Plastic	PP(04)_200-4h-3	PP(04)_Polypropylene, 200 degrees Celsius 4hours heated-3, microscopic-transmission

Fig. 4 Search Results Using the Thermally Degraded Plastics Library

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