Analysis of degraded polybutylene terephthalate (PBT) products by thermal desorption and pyrolysis combined with DART®-MS (TDP/DART®-MS)

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Introduction

Polybutylene terephthalate (PBT), a thermoplastic engineering elastomer, is widely used in a variety of industrial fields. Due to its industrial applications, it is important to evaluate its degradation degree to facilitate the product development process. Although there are many methods to investigate degradation degree (ex. a Durometer, an Extensometer and FT-IR), it is difficult to detect the degradation degree during its initial degradation stage.

Recently, we have reported some polymer analysis results using Thermal Desorption and Pyrolysis combined with Direct Analysis in Real Time- Mass Spectrometry (TDP/DART-MS), and it is a useful method for complex mixtures such as degraded products.

The purpose of this work :

to evaluate the degradation degree during the initial degradation stage which hasn't been detected using FT-IR directly and rapidly.

Fig.1 FT-IR spectra:
Heat-treated pellets, PBT

Materials and Methods

◆ PBT samples
New products
Degraded products
Heat-treated pellets (300℃)

◆ Analytical methods :
TDP/DART-MS (Fig.3)

Small pieces (0.5 mm x 0.5 mm) of sample were put into the POT. Mass spectra were measured as the samples were heated

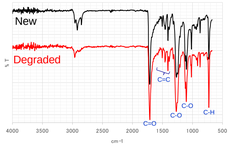
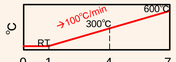
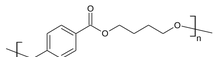


Fig.2 FT-IR spectra:
New/Degraded products, PBT

Mass Spec. : micrOTOF QIII (Bruker)
Mass range : *m/z* = 100-2000
Ion Source : DART-SVP (IonSense)
Ionization gas : Helium
Helium gas temperature : 400℃
TDP device : ionRocket (BioChromato)
Temperature program : RT → 600℃ (100℃/min)





PBT, $[C_{12}H_{12}O_4]_n$
$Mw_{(repeat\ unit)}$ 220

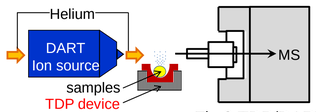
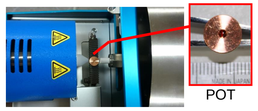


Fig.3 TDP/DART-MS system



Results

◆ Analysis results for new and degraded products

- As a results of FT-IR, no significant difference was detected between the new and degraded products (Fig.2).
- Total ion current gram (TIC) and mass spectrum at ca. 220℃ which is the melting point of PBT were shown in Fig.4. In the TIC, as adding the temperature gradient heating, thermal desorption and pyrolysis reactions were detected, as shown by the change in intensity. In the mass spectrum, the monomer and dimer units of PBT were detected.
- TICs of the new and degraded products were shown in Fig.5. The temperature at which thermal desorption products were detected were different between those two cases. For a detailed comparison, heat maps of the compounds were recorded, as shown in Fig.6. It was clear that the types and the intensity of detected ions differed considerably in the low temperature and low molecular weight region.
- Extracted ion current gram (EIC) of the PBT monomer (*m/z* 221.08, $[C_{12}H_{12}O_4+H]^+$) were shown in Fig.7. The PBT monomer were detected at a temperature much lower than the pyrolysis temperature of the PBT (ca. 400℃) between them. Moreover, for the degraded products, it was detected at much lower than the new products. It was presumed that PBT monomer was included as one of the degradation products.
- It was confirmed that TDP/DART-MS enables the detection of the degradation with more sensitivity than FT-IR spectroscopy.

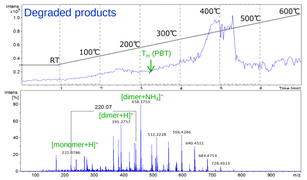


Fig.4 TIC and MS spectrum of degraded products

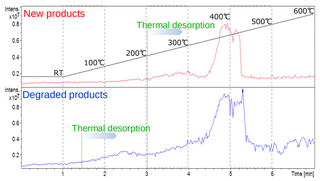


Fig.5 TIC

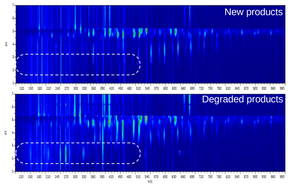


Fig.6 Heat map

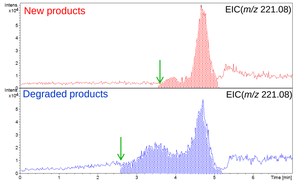


Fig.7 EIC of PBT monomer
(*m/z* 221.08, $[C_{12}H_{12}O_4+H]^+$)

◆ Analysis results for heat-treated PBT pellets

Heat-treated PBT pellets were prepared to evaluate the degree of degradation at the initial degradation stage, which wasn't detected by FT-IR,
Heat treatment conditions: heating temperature; 300℃, heating time; up to 72hr.
The FT-IR results indicated, no significant differences up to 2hr (Fig.1). Therefore, samples that were heat-treated for up to the 2hr were used for the analysis by TDP/DART-MS.

- As mentioned above, the TIC and mass spectrum at ca. 220℃ were shown in Fig.8. The monomer and dimer of PBT were detected.
- TIC and heat maps were shown in Fig.9 and Fig.10. While no significant differences were detected in the TICs, the heat maps showed that the type and the intensity of detected ions differed with the heat treatment time.
- The EIC of the PBT monomer (*m/z* 221.08, $[C_{12}H_{12}O_4+H]^+$) were shown in Fig.11. The temperature at which the PBT monomer was detected decreased, and the amount of PBT monomer increased with heat treatment time. Therefore, it was confirmed that TDP/DART-MS allows us to evaluate the degradation degree at initial degradation stage, using the temperature at which the PBT monomer is detected or the amount of the PBT monomer as a degradation marker.

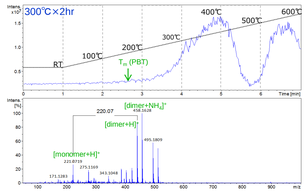


Fig.8 TIC and MS spectrum of heat-treated pellet

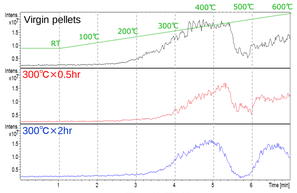


Fig.9 TIC

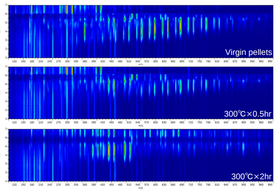


Fig.10 Heat map

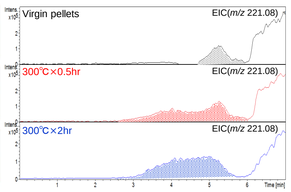


Fig.11 EIC of PBT monomer
(*m/z* 221.08, $[C_{12}H_{12}O_4+H]^+$)

Conclusion

◆ We adopted TDP/DART-MS to evaluate the degradation degree of PBT during the initial degradation stage, which has not been detected by FT-IR analysis.

◆ TDP/DART-MS enables evaluation of the degradation degree at initial degradation stage, which has not been detected by FT-IR analysis, using the temperature at which the PBT monomer is detected and the amount of PBT monomer as degradation markers.

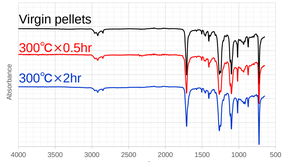


Fig.12 Results of FT-IR
No significant difference

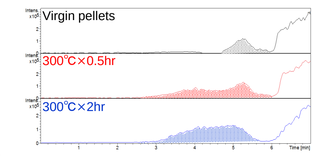


Fig.13 Results of TDP/DART-MS:
EIC(PBT monomer, a maker of degradation)

◆ TDP/DART-MS is expected to contribute to reduce of durability test at product development, and is applicable to polymer failure analysis, as well as research and development and quality control.

Acknowledgment

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