

Evaluation of thermal history of thermoplastic resins by thermal desorption and pyrolysis combined with DART-MS (TDP/DART-MS)



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Introduction

- Recycled thermoplastic resins are regarded as important materials for realizing a sustainable society. However, thermoplastic resins are weakened by thermal history addition in physical properties such as strength and elongation.
- Therefore, it is important to control and grasp the thermal history of polymer recycle. However, when the recycle times were a little, it is difficult to detect the differences between virgin and recycled.
- Thermal Desorption and Pyrolysis/Direct Analysis in Real Time-Mass Spectrometry (TDP/DART-MS) is useful method for qualitative and quantitative analysis for additives or polymer matrix into the plastic products.

The purpose of this work :
To evaluate the thermal history, directly and rapidly.

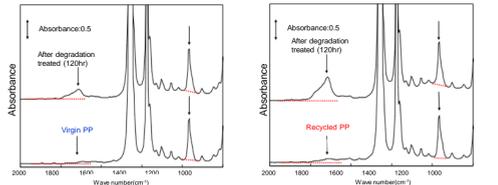


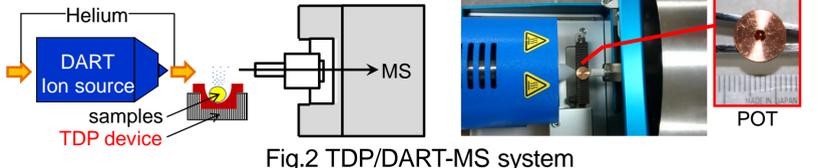
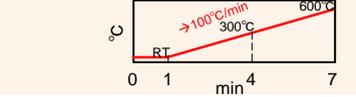
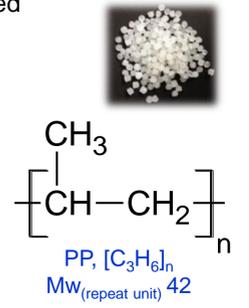
Fig.1 FT-IR spectra of virgin and recycled PP

Explanation on methods for research on recycled plastics formulation, Ministry of the Environment
https://www.env.go.jp/policy/hozen/green/trust/guideline/attach/guideline_2mat-3.pdf

Materials and Methods

- PP samples**
Virgin pellets
3x recycled pellets
- Analytical methods** : TDP/DART-MS (Fig.2)
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

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



Results

- Regarding the total ion current gram (TIC) of the virgin PP pellet and 3x recycled PP pellet from ambient temperature to 600°C (Fig.3), no significant difference was detected between the samples, and similar thermal decomposition reaction were mainly observed.
- Heat maps of the compounds were recorded, as shown in Fig.4. A part where the intensity increased locally and a part where the intensity increased periodically were detected respectively. It was presumed that one is the additives contained in PP pellets, and the other is the pyrolysed products of PP. The difference of the intensity of additives were detected between the samples.
- For a detailed comparison, the mass spectra of the thermal decomposition reaction of polypropylene seemed to begin at 260 °C were shown in Fig.5. Tris(2,4-di-tert-butylphenyl) phosphite, an antioxidant additive called Irgafos168 with the chemical formula $C_{42}H_{63}O_3P$, and its oxidized compound (tris(2,4-di-tert-butylphenyl) phosphoric acid, $C_{42}H_{63}O_4P$) were detected (Fig.5 and Fig.6). In comparing the intensity ratios of the oxidized Irgafos168 and pure Irgafos168 between the samples, the ratio of the 3x recycled PP pellet was higher than that of the virgin PP pellet (Fig.5 and Fig.7). This confirmed that the oxidized Irgafos168 were derived from the recycle process. Therefore, it was presumed that TDP/DART-MS enables evaluation the degree of thermal history using the intensity ratio of oxidized Irgafos168 and pure Irgafos168 as a marker.
- In this work, it was confirmed that TDP/DART-MS can be a useful way to evaluate the thermal history, by using the antioxidants contained in the thermoplastic resins as a "thermal history marker".

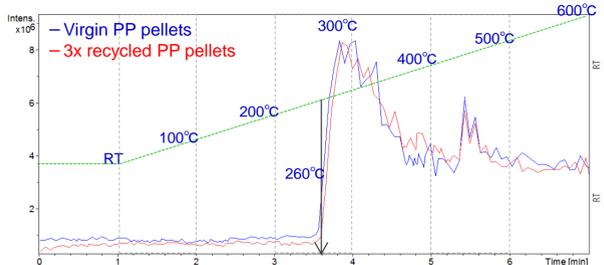


Fig.3 TIC by TDP/DART-MS: virgin and recycled PP pellets

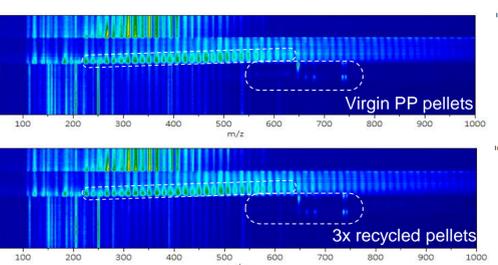


Fig.4 Heat map by TDP/DART-MS: virgin and recycled PP pellets

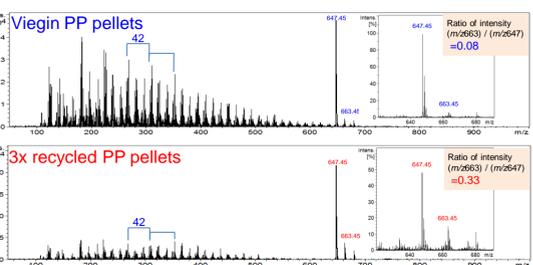


Fig.5 Mass spectra at 260°C: virgin and recycled PP pellets

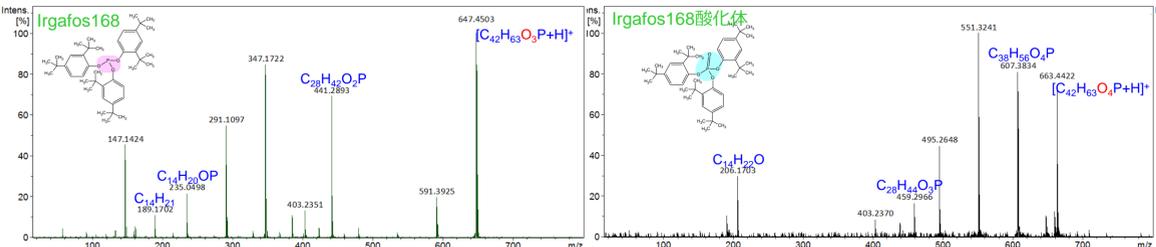


Fig.6 MS/MS spectra of m/z 647 and m/z 663

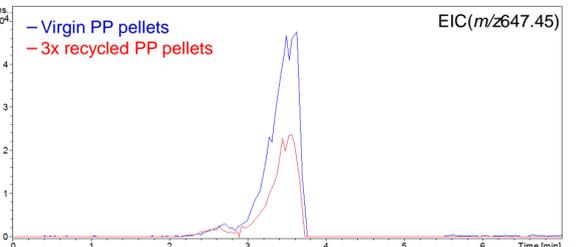
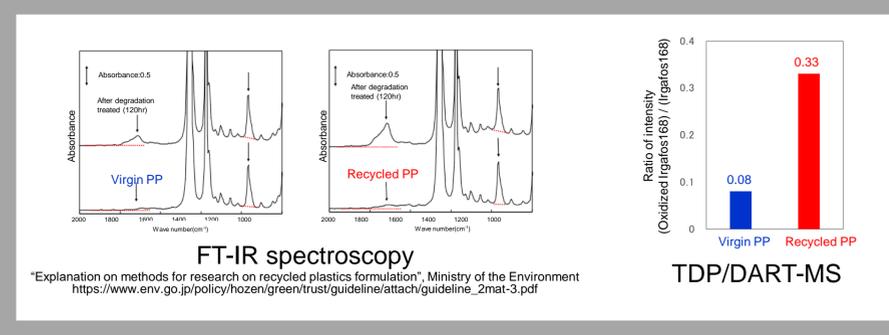


Fig.7 EIC of m/z 647 (protonated Irgafos168) virgin and recycled PP pellets

Conclusion

- We adopted TDP/DART-MS evaluate the thermal history, directly and rapidly.
- By using a TDP/DART-MS analysis method, additives contained in the PP pellet and the PP polymer matrix were detected independently and directly by gradient thermal heating.
- TDP/DART-MS analysis method can be a useful way to evaluate the thermal history of recycled thermoplastic resins quickly and easily, by using the antioxidants contained in the thermoplastic resins as a "thermal history marker".



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



Acknowledgment

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