An Innovative Identification and Degradation Evaluation of Elastomers Using TDP/DART-MS

Derek Gonzales*, Chikako Takei, Kenichi Yoshizawa
The world is confronted with the environmental pollution.
What’s 4R (Reduce, Reuse, Recycle, Renew)?
We can do for 4R

- Innovative separation method, before Reusing, Renewing and Recycling
- Innovative evaluation method of degradation degree for develop of new materials
We can do for 4R

- Innovative separation method, before Reusing, Renewing and Recycling
- Innovative evaluation method of degradation degree for development of new materials
In order to Reuse, Renew and Recycle, separation method is necessary

How to separation…
- Specific gravity difference
- Solvent fractionation
- Electrostatic sorting
Mass spectrometry is also helpful for separation

Although py-GC/MS could be a helpful separation way, it require much analysis time, because of the separation column.
If thermal desorption for extraction of additives is needed, this method require about 120 mins or more.

Therefore, py-GC/MS isn’t suitable for rapid separation.
DART-MS enables analysis of solid and liquid materials without sample pretreatment. So, DART-MS is a powerful separation method.
In order to expand the ability of DART-MS...

Thermal desorption and pyrolysis (TDP) device for DART®-MS

TDP/DART-MS system

1. Excitation of He

2. Linear temperature gradients from ambient to 600°C. Vaporized sample rises into the DART® gas stream

3. Detected by MS

Miligram (mg) samples are sufficient. Many kinds of samples are easily reproducibly thermally desorbed from the copper sample pot: liquids, solids, powders, and viscous samples.
An example of using TDP/DART-MS

Sample: nylon-6
Temperature cond.: RT to 600°C, 100°C/min

Fig. TIC of nylon-6 using TDP/DART-MS

Additives
DBP
Trimethylolpropane
Tris (2-chloropropyl) phosphate

TDP/DART-MS enables analysis both additives and polymer matrix.
An example of identification of polymers using TDP/DART-MS

![Graphs of different polymers showing mass spectra and temperature conditions.]

**PE**

**PP**

**PET**

**PVC**

**PA (nylon-6)**

Fig. Mass spectra of polymers using TDP/DART-MS at 400°C

Easy to identify

Fig. TDP/DART-MS Temperature condition

-100°C/min

600°C

113

BioChromato
Identification among similar structural polymers using FT-IR

Sample: PET, PTT
Analysis method: FT-IR

PET
Repeat structure: C_{10}H_{8}O_{4} (Mw 192)

PTT
Repeat structure: C_{11}H_{10}O_{4} (Mw 206)

Fig. FT-IR spectra

In case of similar structural polymer, FT-IR disables identification among them
Identification among similar structural polymers **using TDP/DART-MS**

**Sample:** PET, PTT  
**Analysis method:** TDP/DART-MS

**PET**  
Repeat structure:  
\[ C_{10}H_8O_4 \text{ (Mw 192)} \]

**PTT**  
Repeat structure:  
\[ C_{11}H_{10}O_4 \text{ (Mw 206)} \]

**Fig. TIC of PET and PTT using TDP/DART-MS**

**Fig. Mass spectra of PET and PTT using TDP/DART-MS at 450°C**

*In case of similar structural polymer, TDP/DART-MS enables identification among them*
Identification among same polymer materials using TDP/DART-MS

Sample: PET
Analysis method: TDP/DART-MS

Even with the same polymer materials, TDP/DART-MS enables identification among them using additives or pyrolysis patterns as their marker.
TDP/DART-MS is powerful method for separating before Reuse, Renew and Recycle
- Innovative separation method, before Reusing, Renewing and Recycling

- Innovative evaluation method of degradation degree for development of new materials
In order to reduce, high durability materials are necessary.

To develop high durability materials:
- High functional additives
- High functional polymer matrix
In order to develop a high durability materials

Various evaluation technology are necessary.

**Durability** e.g. heat resistance, solvent resistance, oil resistance…

**Degradation**

For durability, physical property evaluation are usually used.

On other way, in order to clarify the degradation mechanism, chemical analysis are also usually used. However, these evaluation method are required long testing time.

![Sample: PBT
Heat treatment cond.: 300 °C, up to 72 h
Analysis method: FT-IR](image)

![Fig. FT-IR spectra of PBT after heat treated](image)

As the result of FT-IR, no significant differences were detected at up to 2h. To evaluate more sensitively, TDP/DART-MS were examined.
Analysis of heat-treated PBT using TDP/DART-MS

Sample: heat-treated PBT, 300°C, up to 2h
Analysis method: TDP/DART-MS

Sample pot

Just cut into the Pot!
Sample size: 0.5 mm square

Fig. FT-IR spectra of PBT after heat treated
Analysis of heat-treated PBT using TDP/DART-MS

Sample: heat-treated PBT, 300°C, up to 2h
Analysis method: TDP/DART-MS

PBT, \([C_{12}H_{12}O_4]_n\)

Mw (repeat unit) 220

Heat-treated PBT
300°C × 2hr

- As adding the temperature gradient heating, the thermal desorption and pyrolysis reaction were detected, since the intensity was changed.
- For the mass spectrum, the monomer and dimer units of PBT were detected.
Analysis of heat-treated PBT using TDP/DART-MS

Sample: heat-treated PBT, 300°C, up to 2h
Analysis method: TDP/DART-MS

PBT, \([\text{C}_{12}\text{H}_{12}\text{O}_4]_n\)
Mw (repeat unit) 220

For the TIC, it was no significant differences were detected.

EIC of the PBT monomer \((m/z\ 221.08, \ [\text{C}_{12}\text{H}_{12}\text{O}_4+\text{H}]^+)\) were shown on the right. The temperature that the PBT monomer was detected were shifted to lower, and the amount of PBT monomer were increased with heat-treated length.

It was confirmed that TDP/DART-MS enable evaluation the degradation degree at initial degradation stage by using the temperature that the PBT monomer was detected or the amount of PBT monomer as a degradation maker.
Analysis of heat-treated PBT using TDP/DART-MS

Sample: heat-treated PBT, 300°C, up to 2h
Analysis method: TDP/DART-MS

PBT, \([C_{12}H_{12}O_4]_n\)

\(M_w(\text{repeat unit})\ 220\)

- TDP/DART-MS enable evaluation the degradation degree at initial degradation stage which hasn’t been detected using FT-IR by using the temperature that the PBT monomer was detected and the amount of PBT monomer as degradation makers.

Fig. 12 Results of FT-IR
No significant difference

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

- For the purpose of recycling and waste reduction, we suggested quick separation of polymer materials before reusing and development of new products using TDP/DART-MS and development study of new products.

- Since TDP/DART-MS enables identification more detailed than FT-IR, it is expected to contribute greatly in rapid separation before reusing.

- Since TDP/DART-MS enable detection the degradation more sensitive than FT-IR, it is expected to contribute to reduction of durability test. That is, it can be contribute to reduction.
Thank you for your attention!!