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Qualitative Profiling of Co-polymer Polyethylene Terephthalate through Multifunctional Pyrolyzer-GC/MS by various Thermal Treatment Techniques

ASMS 2017 TP-279

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Introduction

Polyethylene terephthalate (PET) is the most common thermoplastic polymer resin of the polyester family that is extensively used for packaging applications due to its barrier properties, recyclability and compatibility with food applications. It can be synthesized through condensation of ethylene glycol and terephthalic acid. To improve the properties of PET, modifications can be made to create PET co-polymer (co-PET).[1] Multi-functional pyrolyzer coupled with gas chromatography/mass spectrometry (GC/MS) is a powerful technique for distinguishing different types of co-PETs. However, the chromatogram obtained from conventional flash pyrolysis (Py) of polyester can be complicated as further degradation of the polymer can occur to produce smaller molecules such as benzene and benzoic acid.[2] To simplify data interpretation of the pyrogram for qualitative profiling, the samples were subjected to thermochemolysis, also known as reactive pyrolysis (RxPy) in the presence of tetramethylammonium hydroxide (TMAH). In this study, a combination of evolved gas analysis (EGA)-MS, thermal desorption (TD)-GC/MS, Py-GC/MS and RxPy-GC/MS techniques were applied to study the components of different co-PETs.

Method and Materials

Work Flow and Sample Preparation

A thermogram was first acquired by EGA-MS to determine the suitable desorbtion temperature of additives and, the Py and RxPy temperatures of the polymer backbone. A summary of analytical workflow is shown in Figure 1.

Determination of temperature profile for polymer

0.3mg of sample was weighed into an eco cup

↓

0.5mg deactivated silica wool was added into eco cup

↓

EGA-MS analysis

Qualitative profiling of additives

0.2mg of sample was weighed into an eco cup

↓

0.5mg deactivated silica wool was added into eco cup

↓

TD-GC/MS analysis

Qualitative profiling of co-PET backbone

0.5mg of sample was weighed and dissolved in 1mL of dichloromethane

↓

10µL of the solution was added into eco cup and evaporated to dryness

↓

Py-GC/MS analysis

Qualitative profiling of co-PET backbone

0.5mg of sample was weighed and dissolved in 1mL of dichloromethane

↓

10µL of the solution was added into eco cup and evaporated to dryness

↓

2µL of TMAH was into eco cup

↓

RxPy-GC/MS analysis

Figure 1. Work flow for analysis of co-PET samples

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Analysis Conditions

A single quadrupole GC/MS, GCMS-QP2020 (Shimadzu Corporation, Japan) coupled with an automated multi-functional pyrolyzer, AS-1020E/PY-3030D (Frontier Lab, Japan) were used in this study (Figure 2). Dimensions of Ultra-alloy columns, UADTM 2.5N and ultra-alloy 5HT columns (Frontier Lab, Japan); together with the analysis conditions for all profiling studies are listed in Table 1.

Table 1. Analytical conditions for automated multi-functional pyrolyzer-GC/MS

	EGA/MS	TD-GC/MS	Py-GC/MS	RxPy-GC/MS
Pyrolyzer				
Furnace Temperature	100°C → 20°C/min to 700°C	100°C → 20°C/min to 340°C	600°C	Sample A, 400°C Samples B, C, 360°C
Interface Temperature	300°C			
Gas Chromatography				
Column	Ultra alloy UADTM 2.5N (2.5m length, 0.15mm ID)	Ultra-alloy 5HT (30m Length, 0.25mm ID, 0.25μm df)		
Injection Mode	300°C, Split mode, Split ratio 50	300°C, Split mode, Split ratio 100		
Carrier Gas	Helium	Helium		
Flow Control Mode	Linear velocity	Linear velocity		
Linear Velocity	138.0cm/sec	36.1cm/sec		
Oven Temperature	300°C (35min)	40°C (2min) 20°C/min to 320°C (14min)		
Mass Spectrometer				
Ion Source Temperature	200°C			
Interface Temperature	300°C			
Acquisition Mode	Scan mode (35-700amu), scan			

PY-3030D with autosampler AS-1020E

GCMS-QP2020
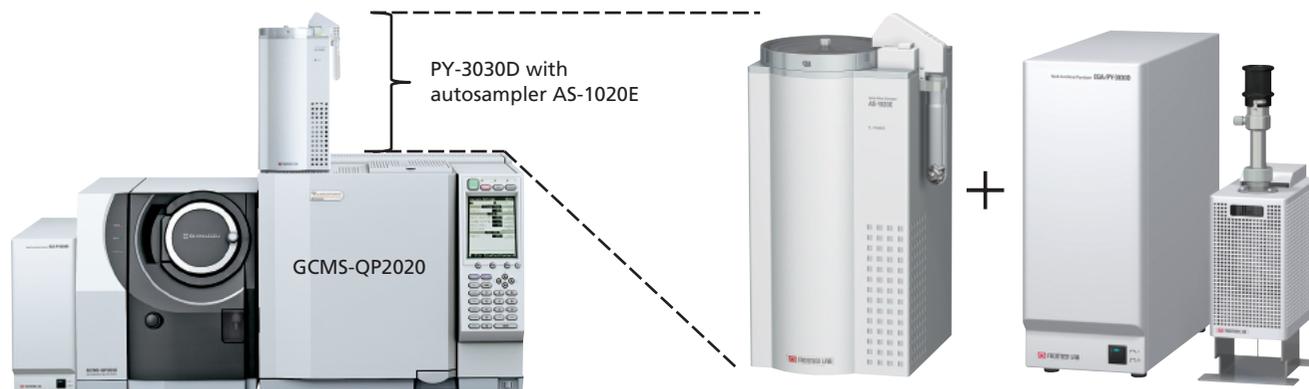
Figure 2. GC/MS with automated multi-functional pyrolyzer

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Results

EGA-MS

EGA-MS analysis is to provide an overall profile of each polymer sample under a range of heating temperature. The thermograms of the three co-PETs (Samples A, B and C) are shown in Figure 3. All samples displayed a broad peak between 370°C to 540°C, which indicates that the co-PETs decomposed during this temperature range. An additional small hump was observed in Sample B (at a lower temperature region, ≤340°C) which indicates possible

presence of additives, and other volatiles/semi-volatiles. From the result of the thermograms, different thermal treatments were applied to different samples. TD-GC/MS was applied for Sample B only. Py-GC/MS was applied for all samples at 600°C to obtain the polymer backbone profiles. In order to collect more comprehensive information of the polymer backbones, RxPy-GC/MS was done at 360°C for Samples B & C and 400°C for Sample A.
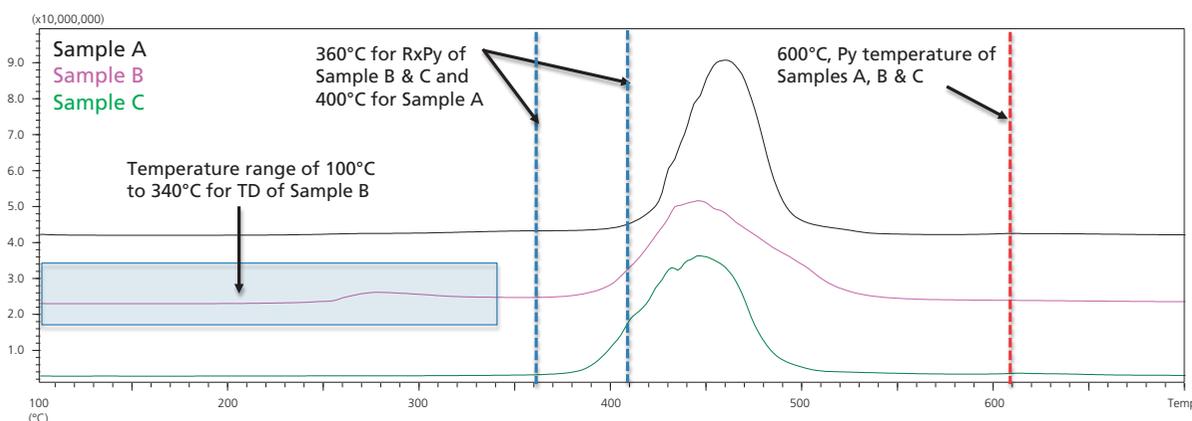
Figure 3. Overlay of thermograms for co-PET samples A (black), B (pink) and C (green) with baseline shifts

TD-GC/MS
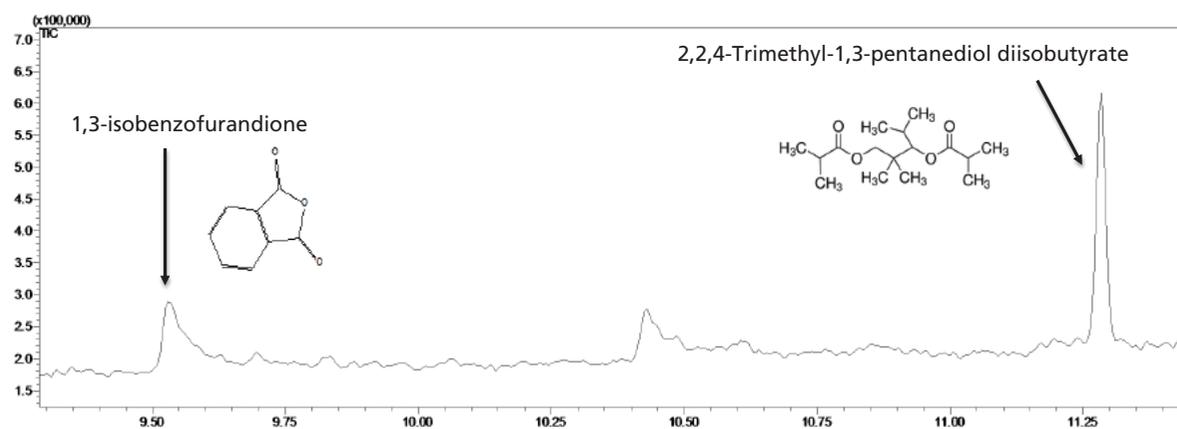
Figure 4. Chromatogram of Sample B analyzed via TD-GC/MS

Sample B was subjected to TD-GC/MS analysis from the range of 100°C to 340°C (highlighted in blue, Figure 3) to desorb any volatiles/semi-volatiles (additives or residual monomers/solvents) from the polymer. 1,3-isobenzofurandione and 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate were detected at 9.274 min and 11.285 min respectively in sample B (Figure 4). It is suspected that 1,3-isobenzofurandione was formed from thermal degradation of phthalates. Both additives identified in Sample B are plasticizer that are commonly doped into polymers.

PY-GC/MS

The expected monomers (ethylene glycol & terephthalate acid) of Co-PET were not found in pyrograms acquired from Py-GC/MS. Instead, common compounds such as benzene, biphenyl, vinyl benzoate and benzoic acid were present in all samples (Figure 5). Benzene, biphenyl and benzoic acid are possible degradation products of terephthalate acid through thermal cleavage on C-O bond adjacent to C=O with release of carbon dioxide release.[2] Thus, it is challenging to differentiate co-PET samples by Py analysis.
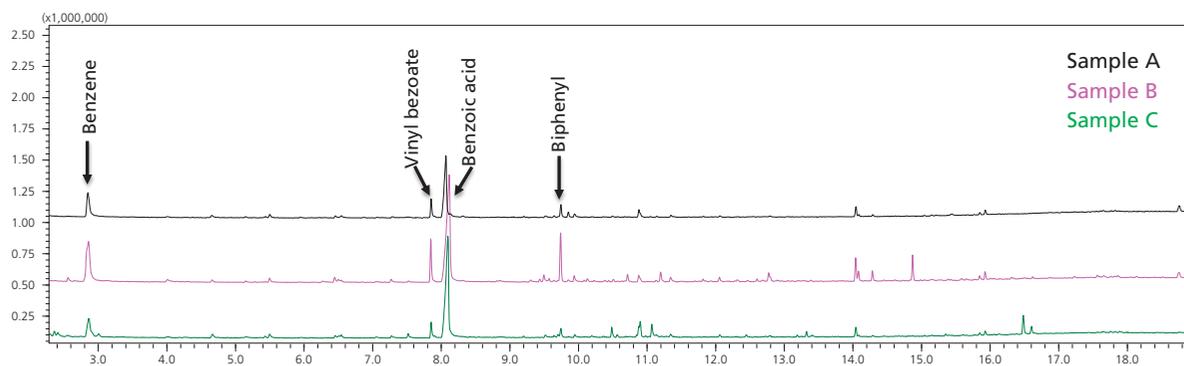
Figure 5. Overlay of pyrograms from Py-GC/MS for co-PET samples A (black), B (pink) and C (green) with baseline shifts

RxPy-GC/MS

The result of Py-GC/MS did not give conclusive information on the identity of the polymers. To aid the differentiation of co-PET samples, RxPx-GC/MS was conducted at a temperature slightly lower than the pyrolysis temperature, with addition of 25 wt.% TMAH in methanol. As an alkaline reagent, TMAH promotes specific hydrolysis of co-PET followed by methylation. As a result, the conventional thermal decomposition process of the polymer is suppressed.[3] Via this technique, expected monomers such as ethylene glycol and terephthalate acid could be identified in their derivatized forms (Figure 6). Additionally, the presence of derivatized neopentyl glycol and 1,4-butanediol glycol in Sample B, as well as derivatized 1,6-hexanediol and derivatized 3-methyl-1,5-pentanediol in Sample C were also identified. These details are essential for co-PETs identification and differentiating Sample A, B and C.

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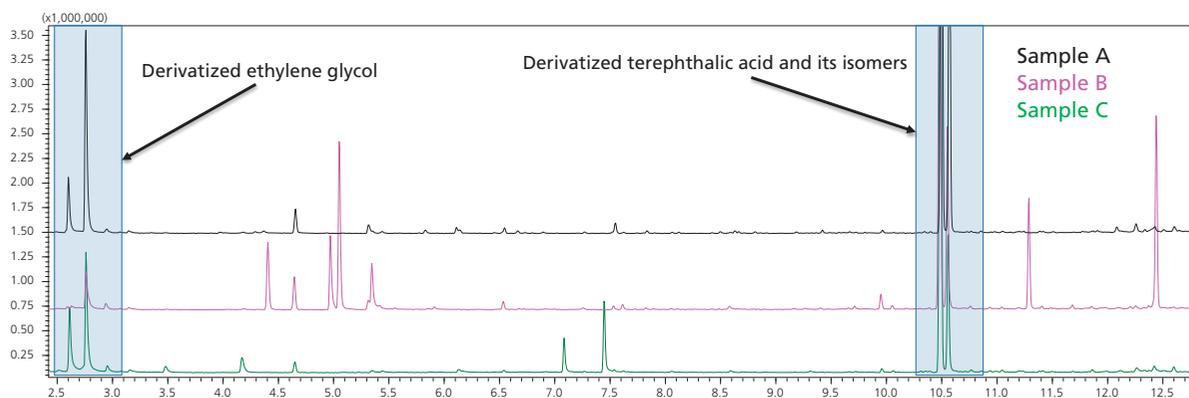
Figure 6. Overlay of pyrograms from RxPy-GC/MS ofco-PET samples A (black), B (pink) and C (green) with baseline shifts

To test the robustness of the RxPy process, the mean area ratio of identified pyrolyzates were calculated (area ratio was calculated by area of target pyrolyzate against area summation of all identified pyrolyzates in each sample, Table 2). The repeatability of the mean area ratio of every pyrolyzate is expressed as %RSD. Except for the branching agent, derivatized 1,2,4-benzenetricarboxylic acid), the relative standard deviation (%RSD, n=4) of the area ratio of target pyrolyzates were well within 4.0%, therefore demonstrating the robustness of this developed RxPy for polymeric qualitative profiling.

Table 2. Mean retention time, area ratio and %RSD (area ratio) for the identified pyrolyzates of co-PETs

Sample	Compound name	Mean retention time in min (n=4)	Mean area ratio[a] (n=4)	%RSD (n=4)
A	Partially derivatized ethylene glycol*	2.600	0.1712	3.6
	Derivatized ethylene glycol*	2.759		
	Derivatized terephthalic acid	10.500	0.5608	1.2
	Derivatized terephthalic acid isomer	10.570	0.2680	1.5
B	Derivatized ethylene glycol	2.765	0.0252	1.4
	Derivatized neopentyl glycol*	4.406	0.1662	4.0
	Neopentyl glycol*	5.053		
	Derivatized 1,4-butanediol*	4.973	0.0786	3.1
	Partially derivatized 1,4-butanediol*	5.348		
	Derivatized terephthalic acid	10.481	0.4319	1.2
	Derivatized terephthalic acid isomer	10.552	0.1187	1.2
	Derivatized decanedioic acid	11.289	0.0672	0.6
	Derivatized 1,2,4-benzenetricarboxylic acid	12.441	0.1122	10.4
C	Partially derivatized ethylene glycol*	2.604	0.1656	3.9
	Derivatized ethylene glycol*	2.759		
	Derivatized 1,6-hexanediol	7.079	0.0460	2.5
	Derivatized 3-methyl-1,5-pentanediol	7.443	0.0418	1.8
	Derivatized terephthalic acid	10.483	0.6392	1.4
	Derivatized terephthalic acid isomer	10.552	0.1075	3.6

* Peak area of the same compound in different derivatized forms were summed up before calculating the mean area ratio
[a] Area ratio was calculated by area of target pyrolyzate against area summation of all identified pyrolyzates in each sample.

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Conclusion

Using a combination of EGA-MS, TD-GC/MS, Py-GC/MS and RxPy-GC/MS, the major components and the additives of co-PET samples were successfully identified. We have herein presented a simple and convenient work-flow, whereby four different thermal treatment techniques can be achieved by a single hyphenated, multi-functional pyrolyzer-GC/MS system for comprehensive qualitative profiling of co-PETs.

References

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