AccuTOF-GCx Series

Identification and distribution analysis of additives in a molded NBR by PY/GCxGC/HRTOFMS

Introduction

The characteristics of polymeric materials vary depending on the additives. Consequently, a variety of additives can be added into the raw polymer resin in order to achieve the required characteristics for the product. PY/GC/MS is often used as an analytical method for the analysis of polymeric materials. However, PY/GC/MS is often insufficient for the chromatographic separation of additives and thermal decomposition products from the polymer. As a result, it is often difficult to assign compound identities.

On the other hand, comprehensive two-dimensional gas chromatography/high resolution time-of-flight mass spectrometry (GCxGC/HRTOFMS) is a well-known technique that provides high chromatographic separation by using two different polarity GC columns. Additionally, when this technique is used with high resolution mass measurements, it can be a powerful tool for estimating elemental compositions of analytes found within a complex mixture.

In this application note, the additives were identified within a commercially available molded polymer by using pyrolysis (PY)/GCxGC/HRTOFMS.

Experiment

A 1 mm thick piece of commercial nitrile rubber (NBR) X-ring was subdivided into smaller pieces of approximately 0.5mg. Each piece was then measured without further sample preparation by using PY/GCxGC/HRTOFMS which consisted of a JMS-T200GC "AccuTOF GCx" coupled with a Zoex ZX-1 GCxGC system and Frontier Lab PY-2020iD pyrolyzer. A BPX-5 and BPX-50 were connected as the 1st column and 2nd column, respectively. The additives were determined by using both EI and FI methods.

Results

The 2D total ion current chromatogram (TICC) maps of the sample by using EI and FI are shown in Figures 1 and 2, respectively. The horizontal axis indicates boiling point separation and the vertical axis shows polarity chromatographic separation. The EI and FI mass spectra

Table 1. Measurement conditions

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Instruments	JMS-T200GC *"AccuTOF GCx"* (JEOL Ltd.)
	ZX-1 (GCxGC module：ZOEX Corporation)
	PY-2020iD (Frontier Laboratories Ltd.)
Pyrolysis conditions	
PY temp.	600˚C
PY-GC-ITF temp.	350˚C
GCxGC conditions	
Inlet temp.	350˚C
Inlet mode	Split mode (200 :1)
1st column	BPX-5 (30 m x 0.25 mm, firm thickness 0.25 μm)
2nd column	BPX-50 (2 m x 0.1 mm, firm thickness 0.1 μm)
Oven temp. program	50˚C (3min) => 5˚C/min => 360˚C (3min)
Carrier gas flow	1.33mL/min (He, Constant flow)
Modulation period	10 sec
MS conditions	
Ionization method	EI(+): 70 eV, 300 μA FI(+): -10 kV, Carbon emitter
Interface temp.	300˚C
Ion source temp.	EI: 280˚C FI: OFF
Spectrum recording interval	50 Hz (0.02 sec/spectrum)
m/z range	30 ～ 600
Drift compensation	*m/z* 207.0329 ($C_7H_{21}O_4Si_4$)
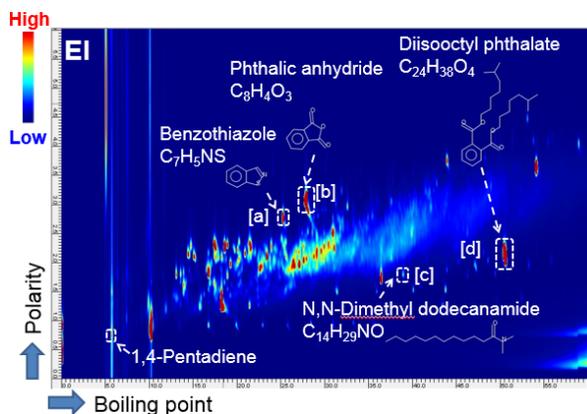
Figure 1. 2D map (EI, TICC) for x-ring
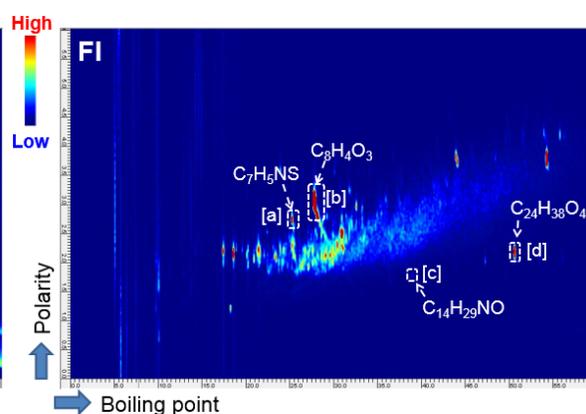
Figure 2. 2D map (FI, TICC) for x-ring
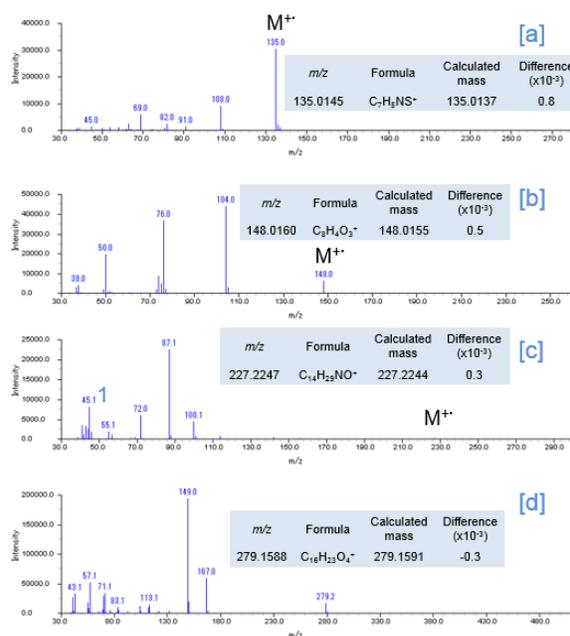
Figure 3. Mass spectra for the observed additives.
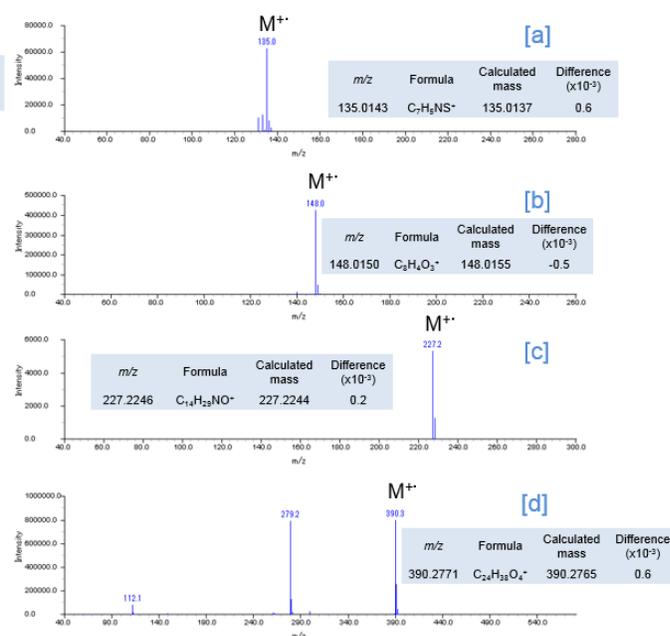
Figure 4. Mass spectra for the observed additives.

of the additives are shown in Figures 3 and 4, respectively. The additives benzothiazole (Fig. 3 [a]), phthalic anhydride (Fig. 3 [b]), N,N-dimethyl dodecanamide (Fig. 3 [c]) and diisooctyl phthalate (Fig. 3 [d]) were assigned in the results by using a NIST library search of the EI mass spectra. It should be noted here that when a single GC column is used, the identification of benzothiazole is very difficult because this compound completely coelutes with an NBR thermal decomposition compound. To further complicate this situation, the abundance of this compound is very low relative to the interfering thermal decomposition product. However, the benzothiazole was easily separated chromatographically by the addition of a 2nd column (GCxGC conditions). The EI spectrum of diisooctyl phthalate showed only fragment ions (Fig. 3[d]).

On the other hand, the FI spectrum showed the molecular ion with a relatively high intensity (Fig. 4[d]) which allowed for the estimation of its elemental composition. The composition result was consistent with the library search result by EI. Furthermore, the results of the elemental composition estimations for the fragment ions by EI were also consistent with the assigned composition of the molecular ion.

Conclusion

The additives such as benzothiazole in the polymer material were easily separated chromatographically by using 2D GC. Using the EI mass spectra for library searches and the FI mass spectra for molecular ion elemental composition estimations are effective for the qualitative identification of the additives. Therefore, PY/GCxGC/HRTOFMS with EI and FI is a reliable technique for qualitative analysis of additives in polymer material.