Generated gas analysis of styrene-butadiene rubber using high-resolution TG-TOFMS (1)

Product used: Mass Spectrometer (MS)

Introduction

Styrene-butadiene rubber (SBR) is used in a variety of products, including automotive tires, industrial products, and negative electrode binder materials for lithium batteries. Many synthetic rubber products, including SBR, contain various additives such as vulcanization accelerators, and information on the gases produced by heating is extremely important for evaluating product properties, quality, and safety. Thermogravimetric-Mass Spectrometry (TG-MS) is effective for the analysis of synthetic rubber because it is possible to correlate and obtain on the weight loss and qualitative information on the generated gas when heating is applied. On the other hand, since this method does not use chromatogram separation, many rubber pyrolysis products (mainly hydrocarbons) make it difficult to analyze trace components. Therefore, mass separation by high-resolution TOFMS JMS-T2000GC was performed and useful results were obtained. While this report presents the results of the EI method, MSTips 344 reports the results of the Electron Capture Ionization (ECI) method.

Experiment

Commercially available SBR rubber was used for the sample. A STA2500 Regulus manufactured by NETZSCH was used for TG, and the gas generated by heating was injected into the JMS-T2000G for analysis (Figure 1). The EI method was used as the ionization method for the JMS-T2000GC. Table 1 shows the TG-MS measurement conditions.

Table 1. Measurement conditions

Sample	1mg
TG	STA 2500 Regulus (NETZSCH)
Furnace temp.	45℃→10℃/min→600℃
Transfer-line temp.	300℃
Transfer-line column	Blank capillary tube, 3m, I.D.0.32mm
Atmosphere	He, 100mL/min
Split ratio	50:1
Furnace	600℃
MS	JMS-T2000GC (JEOL)
Ionization	EI, Ionization Energy 70eV
Mass range	*m/z* 10～800
Ion source temp.	300℃
GC-ITF temp.	300℃

Figure 1. JMS-T2000GC with TG

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Results and Discussion

Figure 2 shows the TG curve and TIC chromatogram of SBR rubber. Peak 1 and Peak 2 of the generated gas associated with weight loss were observed around 220℃ and 430℃, respectively.

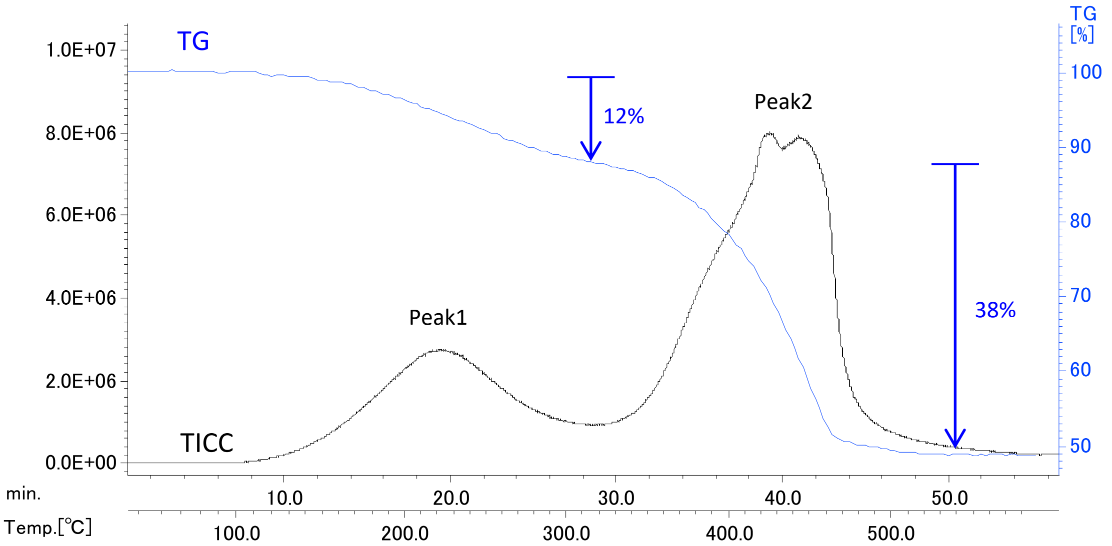

Figure 2. TG Curve and TIC chromatogram

Figure 3 shows the mass spectra of Peak 1 and Peak 2. Since a large number of ions as *m/z* 14 (CH2) interval are observed in both mass spectra, qualitative analysis by library search is difficult. However, qualitative analysis of particular ions is possible by using high-resolution TOFMS to estimate composition. It was estimated that major components were the additive DEHP in Peak 1 and toluene, a pyrolysis product of SBR, in Peak 2.

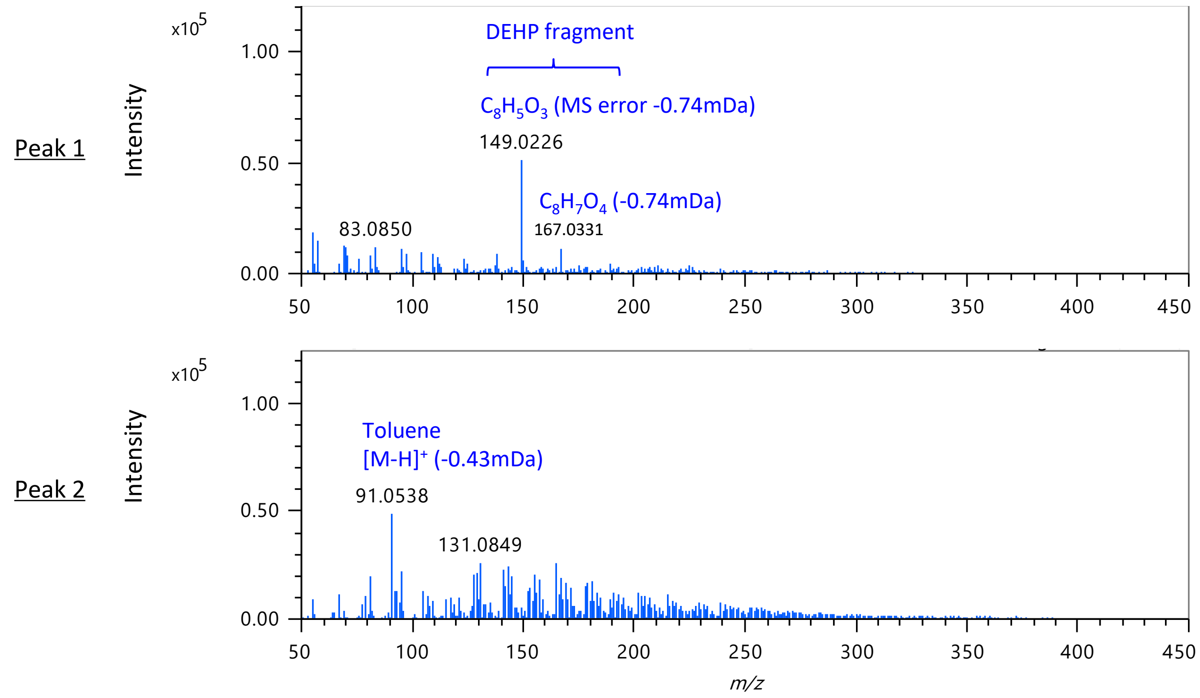

Figure 3. Mass spectra of Peak 1 and Peak 2 at TICC

Figure 4 shows the expanded mass spectrum of Peak 2 around both *m/z* 34 and *m/z* 64. *m/z* 33.9872 was estimated as H2S, *m/z* 63.9611 as SO2, and *m/z* 64.0303 as C5H4. Low-molecular-weight gases that are difficult to analyze with low-resolution MS due to ion interference can be separated and detected with high-resolution TOMS.

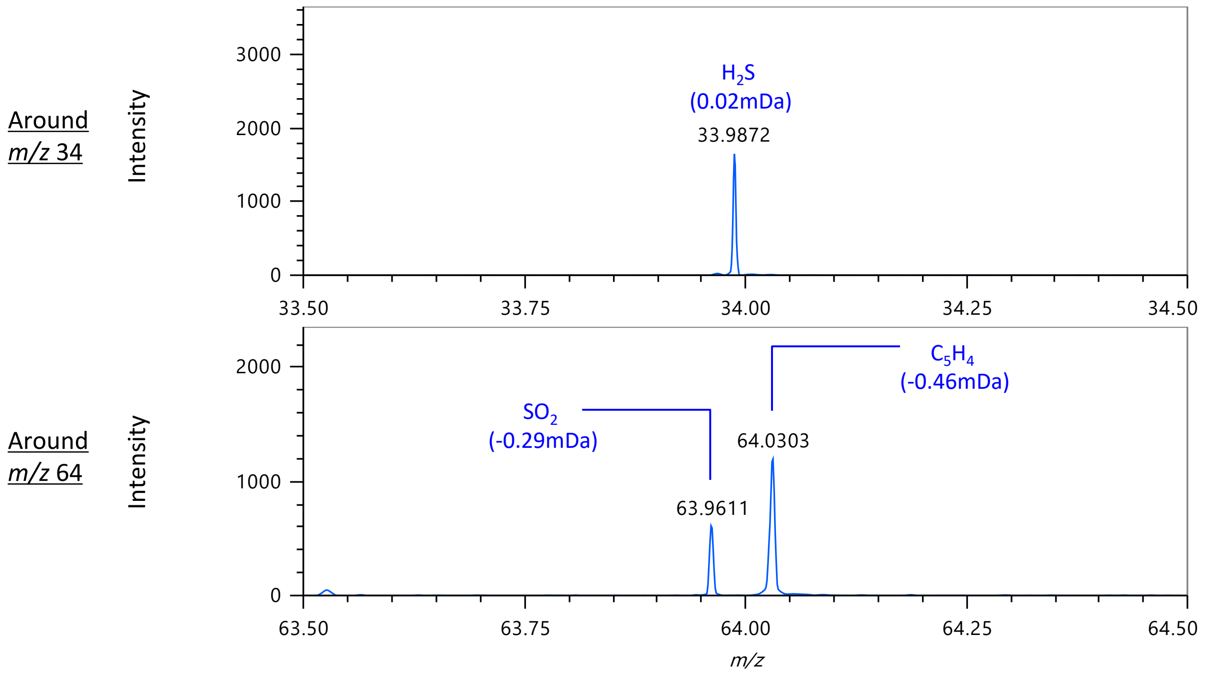

Figure 4. Mass spectra around both *m/z* 34 and *m/z* 64 of peak 2 at TICC

Figure 5 shows the mass spectra around both 300°C and 400°C. From the mass spectra around 300°C, they were estimated to be Dehydroabietic acid, a rosin component used as an emulsifier, and Tri-styrenated phenol (=2,4,6-Tris(1-phenylethyl)phenol) used as an anti-aging agent. From the mass spectra at around 400°C, 2-Mercaptobenzothazole, used as a vulcanization accelerator, and benzothiazole, its pyrolysis product, were estimated.

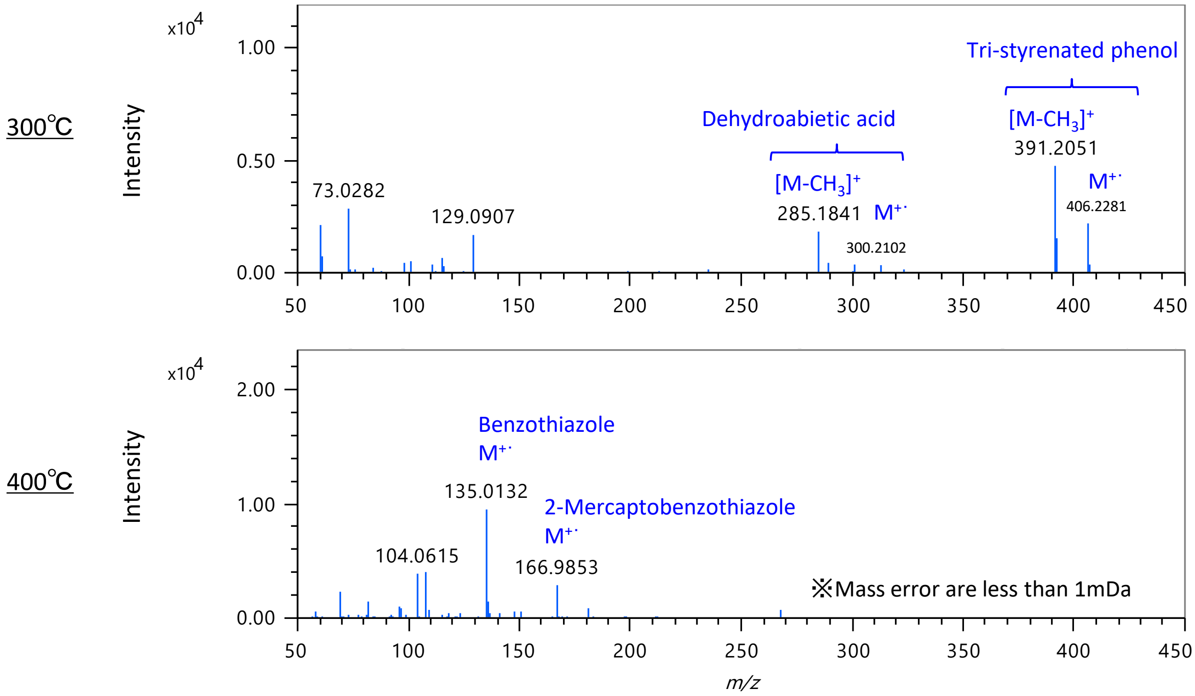

Figure 5. Mass spectra around both 300℃ and 400℃

Figure 6 shows the TIC chromatogram and the extracted ion chromatogram (EIC) in the monitored ions of the particular components. The generation temperatures of each component, including trace components, were confirmed.

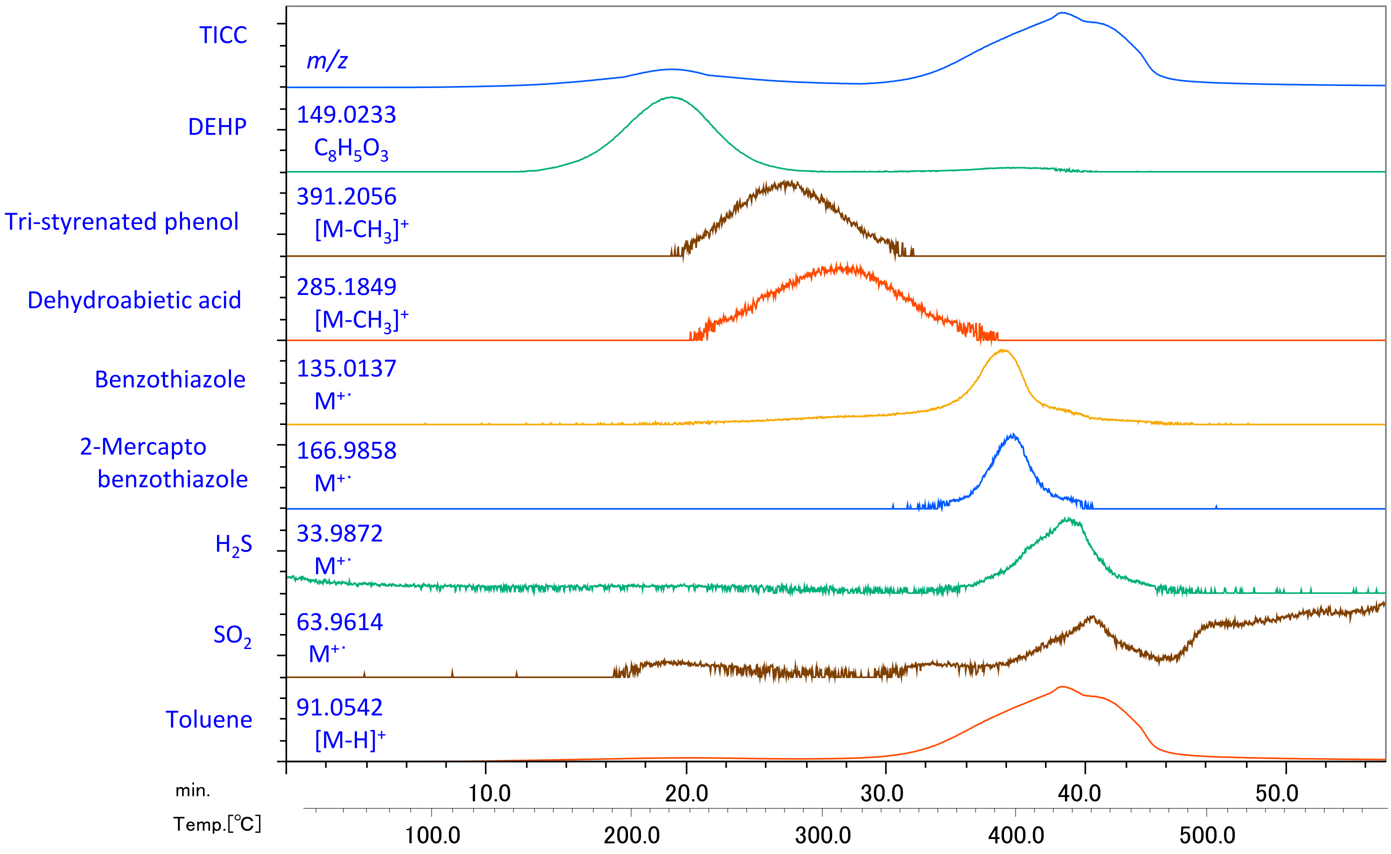

Figure 6. TICC and EIC (*m/z*±0.01Da)

Conclusions

TG-TOFMS with its high mass resolution capability and composition estimation was confirmed to be effective in analyzing trace gas components generated from synthetic rubber, which had been difficult with the TG-MS method.

Reference

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