SHIMADZU APPLICATION NEWS

LA146-E007

● GASCHROMATOGRAPHY MASS SPECTROMETRY

No.M215

Analysis of Rubber by Evolved Gas Analysis Method

Pyrolysis GC or GC/MS methods (Pyr-GC or GC/MS), that are widely used to analyze polymers include instantaneous thermal decomposition (single-shot method) and thermal desorption. The former provides information about the polymers and the latter provides information about additives, etc. It is important for both methods, that the temperature be set to a level that provides the most useful information, where evolved gas analysis is also an efficient method for determining these temperature settings. This method consecutively heats the sample and directly detects the gas that is generated (Evolved Gas Analysis: EGA). It is possible to learn the gas generation status over a wide range of temperatures.

In this application note rubber was analyzed using the EGA method and the thermal desorption method.

■ EGA Curve of Rubbers

Fig. 1 shows the analysis results of two types of natural rubber (NR), Samples A and B, using evolved gas analysis. Peaks P-1 and P-2 are observed in the case of both samples. The mass spectra for P-1 and P-2 are shown in Fig. 2. These mass spectra do not clearly show the differences between these two types, but by performing a search we can assume the compounds are the following.

P-1 Antioxidant NOCRAC 6C from m/z 211, 268
P-2 Cycloparaffin from m/z 41, 43, 55, 69

Table 1 Analytical Conditions

Model	: GCMS-QP2010 (Shimadzu)
	: PY-2020D (FRONTIER LAB)
He	: 60kPa 60mL/min Split : 1/50
PYR. Temp.	: 50˚C-10˚C/min-500˚C
Column	: UADTM-2.5N (2.5m×1.5mm I.D)

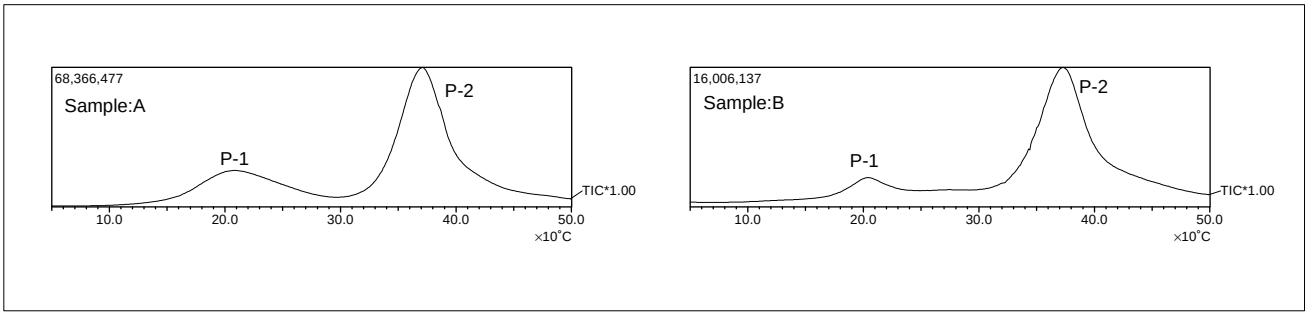

Fig.1 EGA Curve of Rubbers

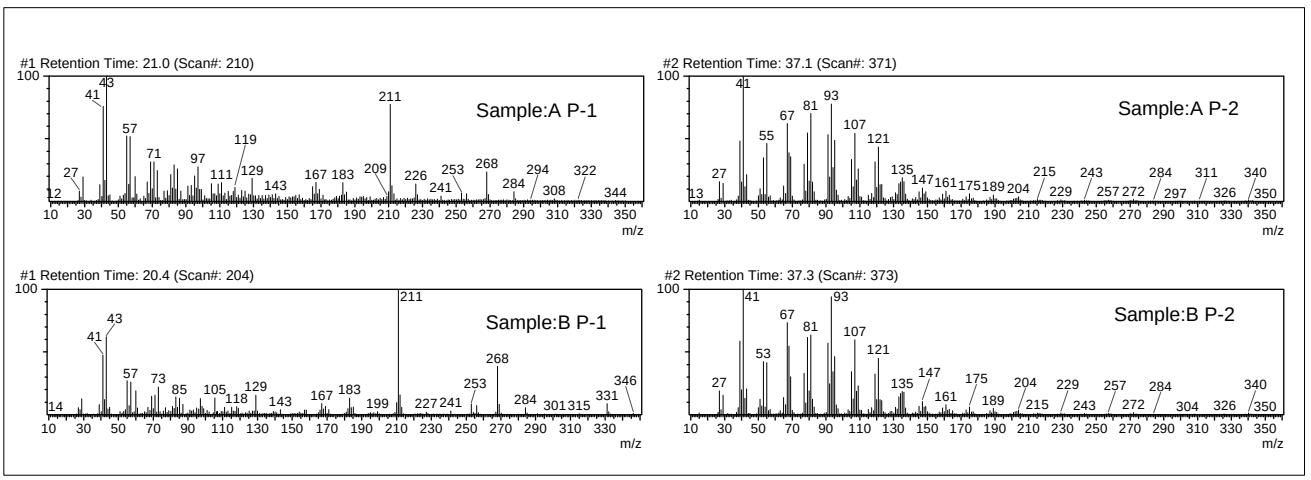

Fig.2 Mass Spectrum of P-1, P-2

■ GC/MS Analysis using Thermal Desorption Method

Fig. 3 shows GCMS data for thermal desorption at 300˚C. This thermal desorption temperature was determined from the EGA curve in Fig. 1. The identification results are shown in Table 2.

We assume the C16 and C18 fatty acids at Peaks 2 and 4 are vulcanizing agents, Peaks 3 and 5 are antioxidants, and the hydrocarbons (Peaks 6 - 14) were added as softening agents. It was clear from Sample B that it contained few hydrocarbons.

If the characteristic ions from the identified compounds (m/z 57: hydrocarbons, 60: fatty acids, and 211: antioxidants) are incorporated into the EGA curve and the evolved gas substances are studied with respect to temperature, then you will be able to observe which substances appear at what temperatures (Fig. 4).

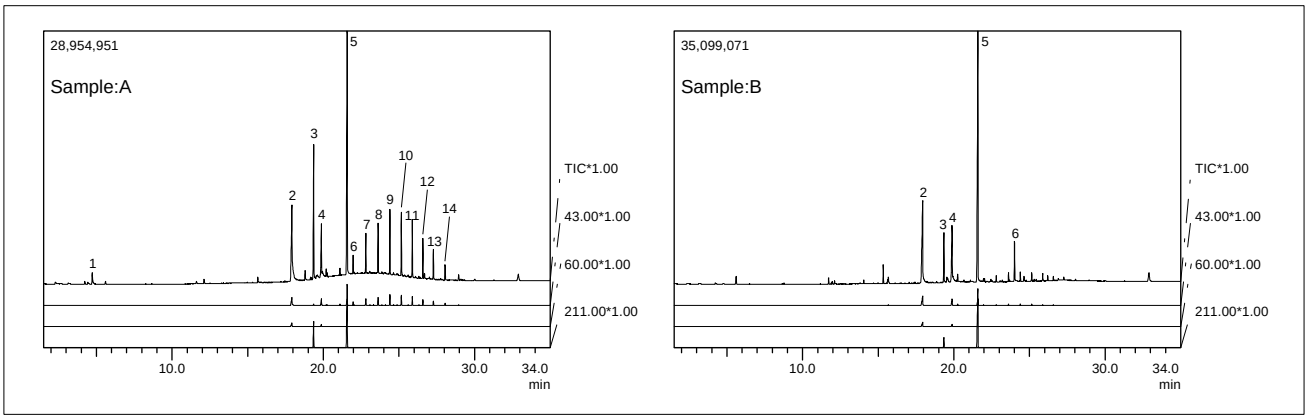

Fig.3 MC of Rubber (300°C)

Table 2 Identification Result

Peak No.	Component	Molecular Fomula	MW
1	Aniline	C6H7N	93
2	n-Hexadecanoic acid	C16H32O2	256
3	NOCRAC 810-NA	C15H18N2	226
4	n-Octadecanoic acid	C18H36O2	284
5	NOCRAC 6C	C18H24N2	268
6	n-C24	C24H50	338
7	n-C25	C25H52	352
8	n-C26	C26H54	366
9	n-C27	C27H56	380
10	n-C28	C28H58	394
11	n-C29	C29H60	408
12	n-C30	C30H62	422
13	n-C31	C31H64	436
14	n-C32	C32H66	450

Table 3 Analytical Conditions

Model	: GCMS-QP2010
	: PY-2020D (FRONTIER LAB)
GC	
Column	: DB-5ms (30m × 0.25mmI.D df=0.25μm)
Column Temp.	: 50˚C (2min)-10˚C/min-300˚C (20min)
Carriier Gas	: He 100kPa
Injection Temp.	: 300˚C
Split	: 1/50
MS	
Inetrface Temp.	: 280˚C
Ionsouce Temp.	: 200˚C
Scan Range	: m/z35-500
Interval	: 0.5sec

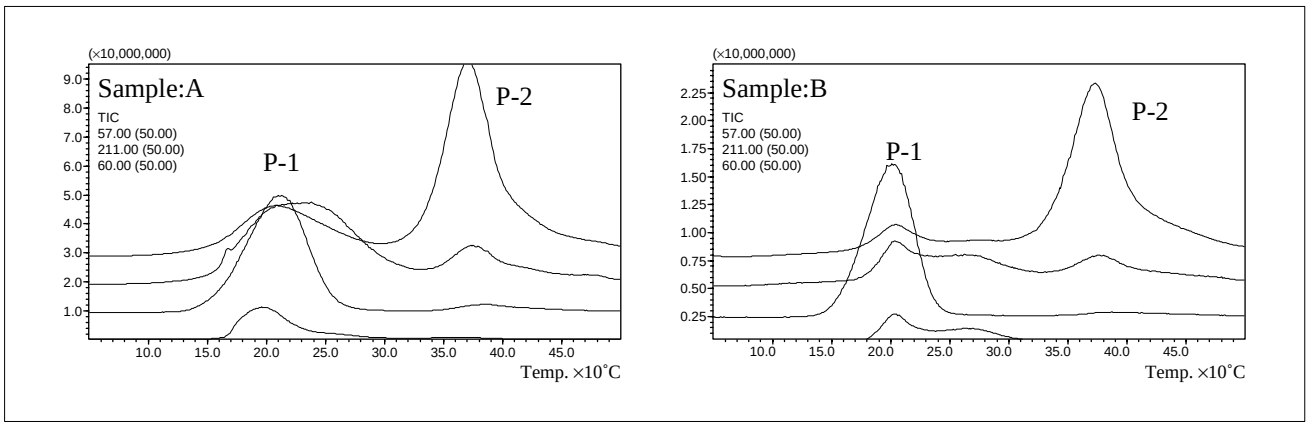

Fig.4 MC of Rubber (EGA)

SHIMADZU

SHIMADZU CORPORATION. International Marketing Division

3. Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan Phone: 81(3)3219-5641 Fax. 81(3)3219-5710
Cable Add.:SHIMADZU TOKYO

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