Multifaceted analysis of styrene butadiene rubber (SBR) product using FD and Pyrolysis-GC-MS method of JMS-T2000GC

Product used: Mass Spectrometer (MS)

Introduction

SBR is a synthetic rubber made from a copolymer of styrene and 1,3-butadiene. It is used in many products, such as automobile tires, because it is easy to process and can be supplied at a low cost and of high quality. When used as a product, it is common to blend it with other polymers and add additives to improve physical properties and vulcanization speed.

In this MSTips, we will introduce an application of SBR analysis using FD and Pyrolysis-GC-MS method of the JMS-T2000GC. In the FD method, the sample is applied to the emitter and directly introduced into the ion source, and then detected by soft ionization. It is possible to detect molecular ions peak in less than one minute. When measuring polymers such as SBR, a complex mass spectrum containing multiple peaks from oligomers is obtained. Even in this case, qualitative information can be easily obtained by KMD analysis. The main component styrene-butadiene copolymer can be visually evaluated the molecular weight distribution due to the difference of end group and degree of polymerization, and other ion peaks can be qualitatively analyzed by composition estimation. Although it is difficult to obtain the structural formula using the FD method alone, it is possible to obtain it efficiently using the Pyrolysis-GC-MS method in combination. Furthermore, these two methods can complement the range of measurable mass (= boiling point), making multifaceted analysis possible.

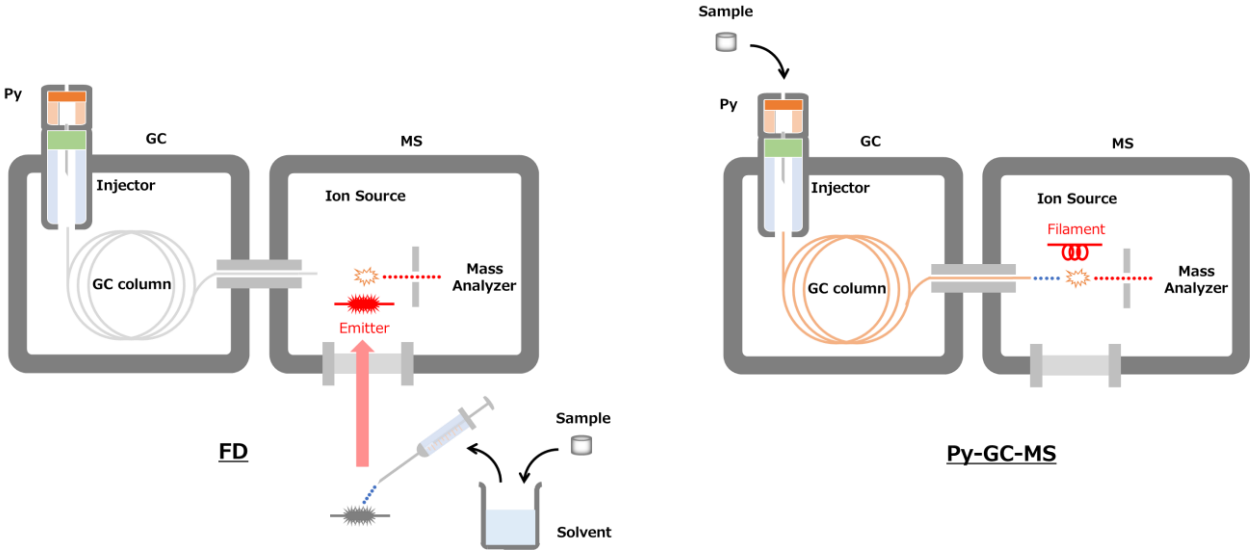

Figure 1 Schematic diagram of FD and Pyrolysis-GC-MS method

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Experiment

As the sample, commercially available SBR product (rubber sheet) was used. In FD method, 10 mg was immersed in 1 mL of tetrahydrofuran (THF), and then 1 µL of this was applied to the emitter and measured. In Pyrolysis-GC-MS method, 0.5 mg was weighed and measured. EI and FI (field ionization) methods were used for ionization in Pyrolysis-GC-MS method. The obtained data were analyzed using msRepeatFinder and msFineAnalysis AI. Table 1 shows details of the measurement conditions.

Table 1 Measurement conditions

Pyrolyzer : EGA/PY-3030D (Frontier Lab)	
Sample amount	0.5mg
Furnace Temperature	600°C
Gas Chromatograph : 8890A GC (Agilent Technologies)	
Column	ZB-5MSi (Phenomenex)
	30m x 0.25mm, 0.25µm
Oven Temperature	40°C(2min)-10°C/min -320°C(30min)
Split ratio	100 : 1
Carrier gas	He, 1mL/min

Mass Spectrometer : JMS-T2000GC (JEOL)	
Ion Source	EI/FI combination ion source
Ionization	EI : 70eV
	FI : FI emitter, Flashing 12mA 30msec
	FD: FD emitter, 0-50mA@51.2mA/min
IS Temperature	EI : 250°C, FI and FD : No heating
GC-ITF Temperature	EI and FI : 250°C, FD : No heating
Mass Range	EI and FI : *m/z* 10-800, FD : *m/z* 35-1600
Drift compensation	EI : *m/z* 281.05, column bleed at end time
	FI : *m/z* 281.05, reservoir every 15min
	FD : None

Results ① - FD method

Figure 2 shows the TIC chromatogram and mass spectrum of FD method. A sample introduced into the MS ion source was ionized and detected in about 20 seconds. Because it was a soft ionization method without chromatographic separation, multiple molecular ions were detected in one mass spectrum. In the FD method, it was difficult to detect low mass (low boiling point) compounds due to volatilization in the ion source. But it was possible to detect high mass (= high boiling point) compounds which were difficult to detect by Pyrolysis-GC-MS method.

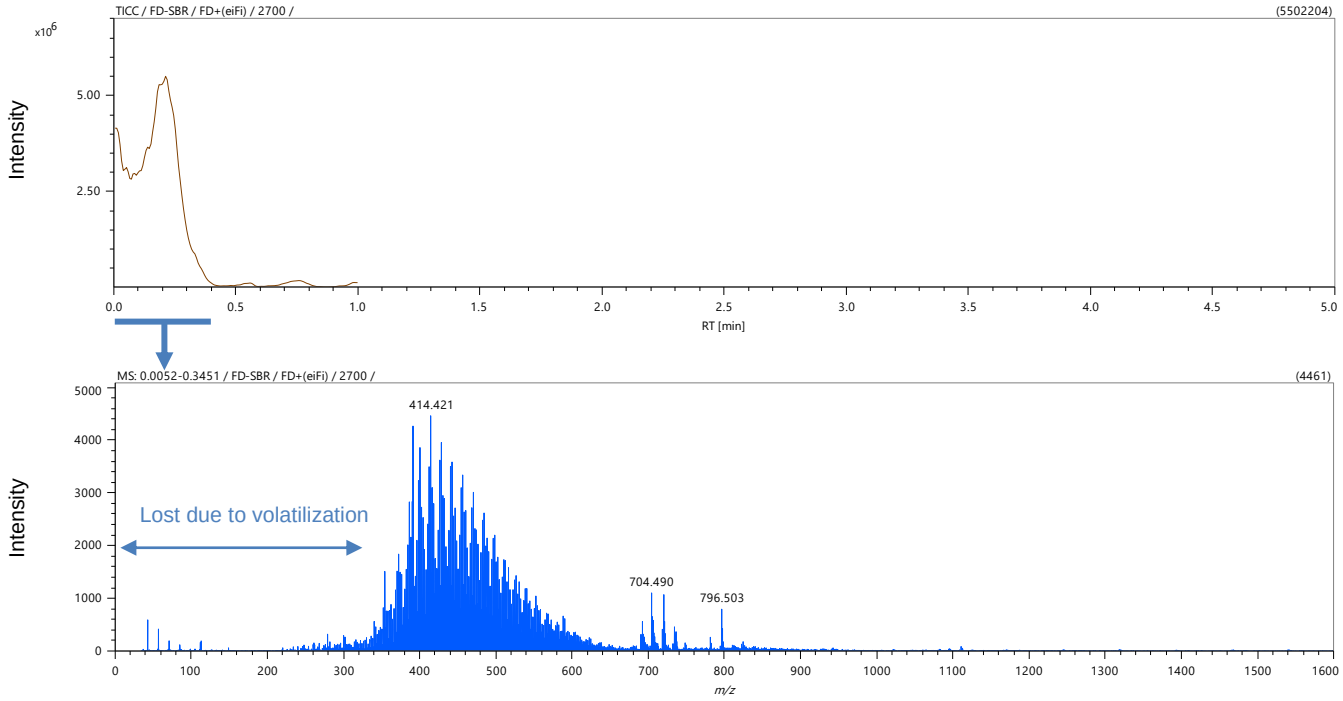

Figure 2 TIC chromatogram and mass spectrum

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Figure 3 shows a KMD plot created from the above mass spectrum. In the KMD plot, ion peaks from compounds with a common repeating structure are arranged in a straight line. In the case of copolymers such as SBR, they form a lattice pattern. The groups surrounded by yellow and green dashed lines were all SBR, but the polymerization tendency of styrene and butadiene was different. This suggests that two types of SBR with different properties were blended. The red peaks were additives such as plasticizers and antioxidants extracted using the target list. The peak at *m/z* 704.49 was the oxide (+O) of Tris (nonylphenyl) phosphite, an antioxidant. It was a high-boiling point compound and could only be detected by the FD method.

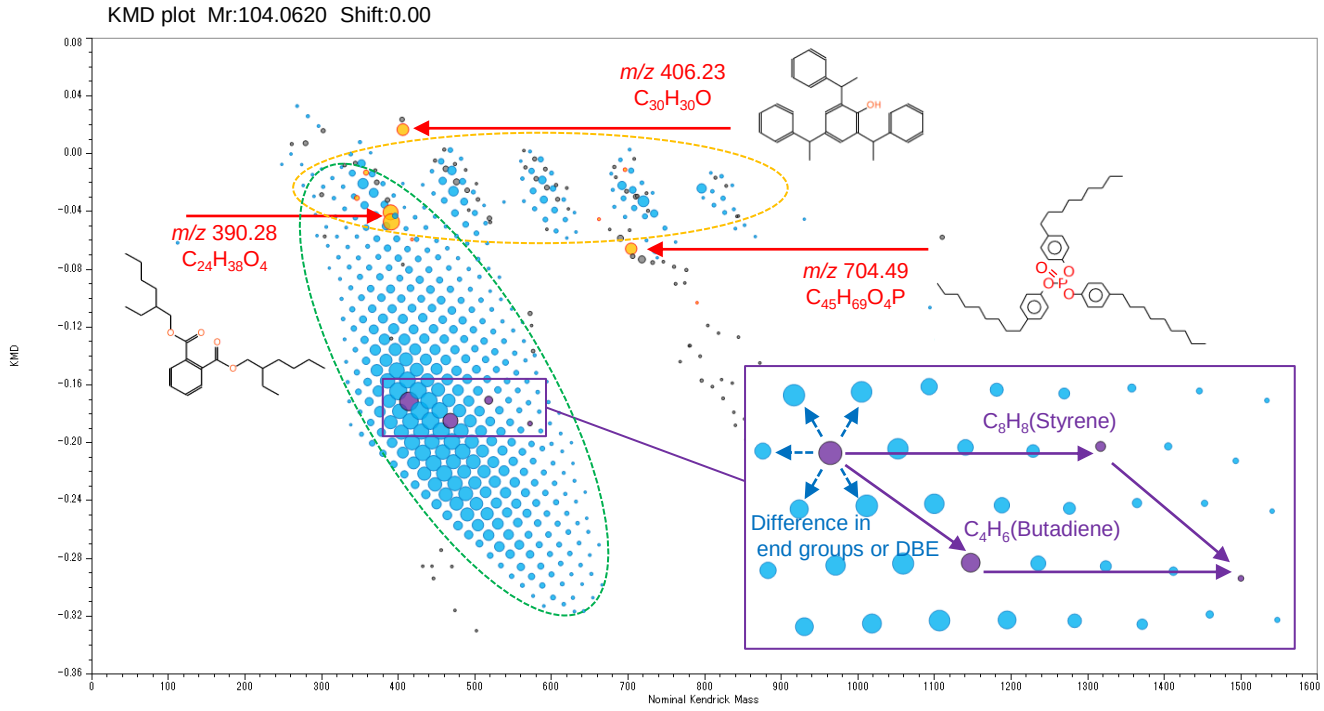

Figure 3 KMD plot

Results ② - Pyrolysis-GC-MS method

Figure 4 shows the results window of msFineAnalysis AI, and Table 2 shows the peak list. ID027 2,2,4-trimethyl-1H-quinoline was a low-boiling point compound and could only be detected by the pyrolysis-GC-MS method. In addition, it is not registered in the NIST library, so AI structural analysis was required to obtain the structural formula.

Figure 4 Result window of msFineAnalysis AI

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Table 2 Peak list

General				Total Result											
ID	RT [min]	Meas. RI [iu]	IM m/z	Compound Name	CAS# / PubChem CID	Lib.	Match Factor / AI Score	ΔRI [iu]	Formula	DBE	Adduct/Loss	Calculated m/z	Mass Error [mDa]	Isotope Matching	EI Fragment Coverage
001	1.30	522	33.98736	Hydrogen sulfide	7783-06-4	mainlib	580	183	H2 S	0.0	none	33.98717	0.19	0.91	50
002	1.36	530	54.04678	1,3-Butadiene	106-99-0	mainlib	904	141	C4 H6	2.0	none	54.04640	0.38	0.97	100
003	1.61	561	66.04670	1,3-Cyclopentadiene	542-92-7	mainlib	889	38	C5 H6	3.0	none	66.04640	0.30	0.83	100
004	1.67	569	68.06255	Cyclopentene	142-29-0	mainlib	825	17	C5 H8	2.0	none	68.06205	0.50	0.96	100
005	2.32	653	78.04691	Benzene	71-43-2	mainlib	907	1	C6 H6	4.0	none	78.04640	0.51	0.98	100
006	2.40	663	80.06232	1,3-Cyclohexadiene	592-57-4	mainlib	894	8	C6 H8	3.0	none	80.06205	0.27	0.73	100
007	3.64	765	92.06242	Toluene	108-88-3	mainlib	907	1	C7 H8	4.0	none	92.06205	0.37	0.68	100
008	3.96	787	112.12499	Heptane, 3-methylene-	1632-16-2	mainlib	840	8	C8 H16	1.0	none	112.12465	0.34	0.70	100
009	4.78	834	108.09371	Cyclohexene, 4-ethenyl-	100-40-3	mainlib	923	5	C8 H12	3.0	none	108.09335	0.36	0.71	100
010	5.24	860	106.07794	Ethylbenzene	100-41-4	mainlib	939	5	C8 H10	4.0	none	106.07770	0.24	0.92	100
011	5.42	870	108.09348	1,5-Dimethyl-1,4-cyclohexadiene	4190-06-1	mainlib	828	0	C8 H12	3.0	none	108.09335	0.13	0.78	100
012	5.80	892	104.06231	Styrene	100-42-5	mainlib	980	1	C8 H8	5.0	none	104.06205	0.26	0.75	100
013	5.82	893	106.07736	o-Xylene	95-47-6	mainlib	894	5	C8 H10	4.0	none	106.07770	-0.34	0.93	88
014	6.78	946	118.07774	Tetracyclo[3.3.1.0(2,8).0(4,6)]-non-2-ene	-	mainlib	872	0	C9 H10	5.0	none	118.07770	0.04	0.66	100
015	6.91	953	120.09357	Benzene, propyl-	103-65-1	mainlib	932	0	C9 H12	4.0	none	120.09335	0.22	0.73	100
016	7.41	981	118.07793	α-Methylstyrene	98-83-9	mainlib	917	5	C9 H10	5.0	none	118.07770	0.23	0.90	100
017	7.65	995	118.07800	Bicyclo[4.2.0]octa-1,3,5-triene, 7-methyl-	55337-80-9	mainlib	926	0	C9 H10	5.0	none	118.07770	0.30	0.63	100
018	8.20	1028	118.07791	1,3-Methanopentalene, 1,2,3,5-tetrahydro-	128600-88-4	mainlib	672	0	C9 H10	5.0	none	118.07770	0.21	0.87	89
019	8.50	1045	116.06227	1-Propyne, 3-phenyl-	10147-11-2	mainlib	932	0	C9 H8	6.0	none	116.06205	0.22	0.93	100
020	10.20	1151	130.07789	Benzene, (1-methyl-2-cyclopropen-1-yl)-	65051-83-4	mainlib	803	0	C10 H10	6.0	none	130.07770	0.19	0.35	100
021	10.28	1156	146.10945	Benzene, 3-pentenyl-	1745-16-0	mainlib	829	0	C11 H14	5.0	none	146.10900	0.45	0.42	100
022	10.41	1164	146.10908	Benzene, 4-pentenyl-	1075-74-7	mainlib	727	24	C11 H14	5.0	none	146.10900	0.08	0.94	100
023	10.70	1183	162.14019	Cyclooctene, 5,6-diethenyl-, trans-	53264-71-4	mainlib	821	0	C12 H18	4.0	none	162.14030	-0.12	0.71	100
024	10.81	1190	144.09355	Benzene, (2-cyclopropylethenyl)-	-	mainlib	824	0	C11 H12	6.0	none	144.09335	0.20	0.55	100
025	12.43	1302	144.09348	Benzene, 1-cyclopenten-1-yl-	825-54-7	mainlib	869	0	C11 H12	6.0	none	144.09335	0.12	0.93	100
026	12.92	1337	158.10902	Benzene, 3-cyclohexen-1-yl-	4994-16-5	mainlib	892	8	C12 H14	6.0	none	158.10900	0.02	0.83	100
027	14.34	1444	173.11934	2,2,4-trimethyl-1H-quinoline	8981	AI	890	0	C12 H15 N	6.0	none	173.11990	-0.56	0.94	100
028	14.37	1447	157.08880	Quinoline, 2,7-dimethyl-	93-37-8	mainlib	830	24	C11 H11 N	7.0	none	157.08860	0.20	0.74	100
029	16.61	1630	212.15574	Cyclohexane, 1-phenyl-3,4-divinyl-, (1R,3trans,4trans)-	-	mainlib	887	0	C16 H20	7.0	none	212.15595	-0.22	0.81	100
030	20.13	1957	256.23981	n-Hexadecanoic acid	57-10-3	mainlib	854	11	C16 H32 O2	1.0	none	256.23968	0.12	0.78	100
031	21.87	2140	282.25602	Oleic Acid	112-80-1	mainlib	774	1	C18 H34 O2	2.0	none	282.25533	0.69	0.77	100
032	22.05	2159	284.27042	Octadecanoic acid	57-11-4	mainlib	905	13	C18 H36 O2	1.0	none	284.27098	-0.57	0.77	100
033	24.49	2445	300.20820	Dehydroabietic acid	1740-19-8	mainlib	843	12	C20 H28 O2	7.0	none	300.20838	-0.18	0.72	100
034	24.78	2480	302.16625	Phenol, 2,4-bis(1-phenylethyl)-	2769-94-0	mainlib	839	54	C22 H22 O	12.0	none	302.16652	-0.27	0.71	92
035	25.17	2530	390.27654	Bis(2-ethylhexyl) phthalate	117-81-7	mainlib	978	5	C24 H38 O4	6.0	none	390.27646	0.08	0.84	100
036	26.77	2742	330.20802	10,10,13,14,14-pentamethyl-1,3-diazapentacyclo[11.7.0.03,11.04,9.015,20]icosa-4,6,8,11,15,17,19-heptaene	343568	AI	899	0	C23 H26 N2	12.0	none	330.20905	-1.03	0.79	88
037	28.70	3017	406.22783	Phenol, 2,4,6-tris(1-phenylethyl)-	18254-13-2	mainlib	782	11	C30 H30 O	16.0	none	406.22912	-1.28	0.67	100
038	28.81	3035	406.22831	Phenol, 2,4,6-tris(1-phenylethyl)-	18254-13-2	mainlib	785	7	C30 H30 O	16.0	none	406.22912	-0.81	0.72	100

mainlib = The compound name and structural formula obtained by NIST library, AI = AI predicted library

Conclusion

SBR product was analyzed using FD and Pyrolysis-GC-MS method of JMS-T2000GC. FD method was able to obtain rough qualitative information about the blended polymers and additives in a short measurement. Pyrolysis-GC-MS method was able to obtain detailed qualitative information such as structural formulas. By using these two methods in combination, it was possible to obtain qualitative information efficiently.

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