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Differential Analysis in sulfenamide-based vulcanizing accelerators for rubber products by High mass Accuracy MS and Multivariate Statistical Technique

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Takahiro Goda, Hiroki Nakajima, Satoshi Yamaki,
Tsutomu Nishine, Masaru Furuta, Naoki Hamada
Shimadzu Corporation, Kyoto, JAPAN

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Introduction

Vulcanization is a cross-linking reaction for forming bridges between individual polymer chains via addition of sulfur (Fig. 1). The purpose of vulcanization is to convert the rubber into a more durable material. In general, a reaction rate of vulcanization is increased by adding vulcanizing accelerator to mixture of rubber and sulfur.
Each tire manufacturer employs one particular accelerator from among many commercially available reagents in order to meet set standards .Therefore, analyzing vulcanizing accelerator compounds is a key stage in the tire manufacturing process, however, it is difficult to detect differences in similar structures when produced by different manufacturers.
In this study we show differential analysis of similar structured sulfenamide-based vulcanizing accelerators (Fig. 2) produced by different manufacturers using high mass accuracy MS^n and multivariate statistical technique.

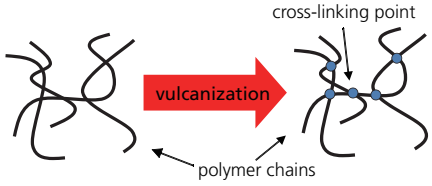

Fig. 1 Schematic drawing of vulcanization.

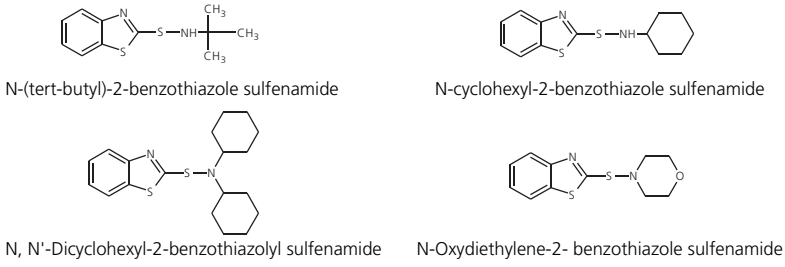

Fig. 2 Typical sulfenamide-based vulcanizing accelerators.

Methods

Five N-(tert-butyl)-2-benzothiazole sulfenamide (NS; NS-1, NS-2, NS-3, NS-4, NS-5) and five N-cyclohexyl-2-benzothiazole sulfenamide (CZ; CZ-1, CZ-2, CZ-3, CZ-4, CZ-5) were used in this study. Each NS and each CZ were produced by different manufacturers. Sample solutions were prepared at 100 mg/L dissolved in tetrahydrofuran and acetonitrile. Equal amount of NS solutions were mixed and used as a quality control (QC) sample for NS analysis to identify robust and reproducible ion signals. The QC sample for CZ analysis also was prepared by the same method. LCMS measurement was performed by LCMS-IT-TOF (Shimadzu Corporation, Kyoto, Japan). SIMCA-P+ (Umetrics) and MetID Solution (Shimadzu Corporation) were used for multivariate statistical analysis and for searching structural analogues using MS^n data acquired by LCMS-IT-TOF measurement, respectively. Formula Predictor (Shimadzu Corporation) was used for predicting the formulae of characteristic compounds (Fig. 3).

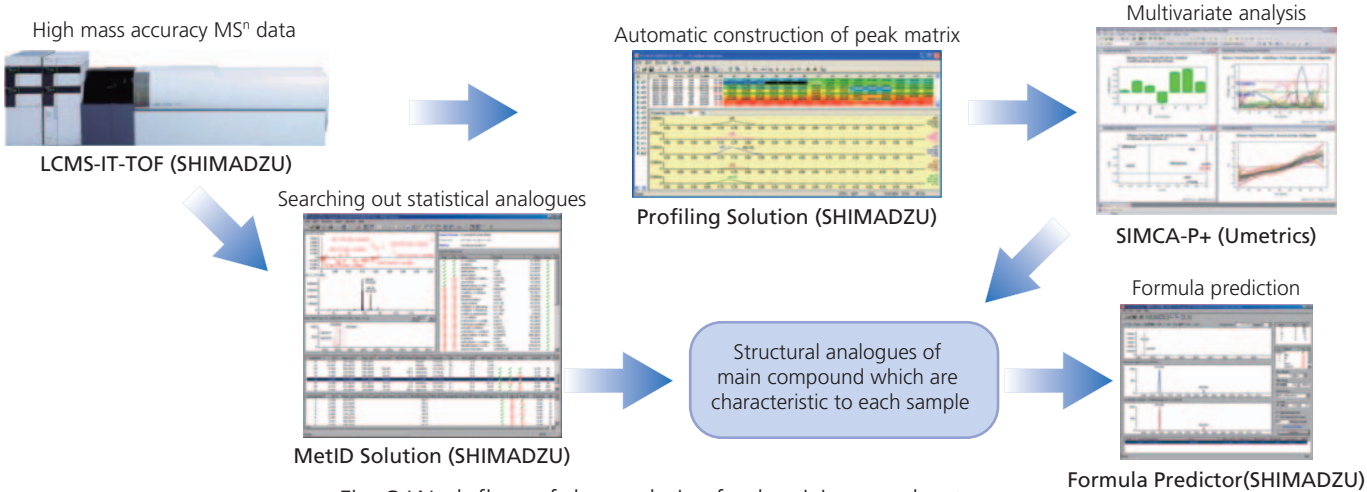

Fig. 3 Work flow of the analysis of vulcanizing accelerators.

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Table 1 LCMS analytical conditions.

Column	: Shim-pack XR-ODS (2.0 mmI.D.x75 mmL、2.2 μm)
Flow rate	: 0.45 mL/min
Column temperature	: 40°C
Mobile phaseA	: water containing 5 mmol ammonium acetate
Mobile phaseB	: acetonitrile
Time program	: 0%B(0 min) – 100%B(9 – 12 min) – 0%B(12.01 – 15 min)
Injection volume	:1 μL
Ionization mode	: ESI(+)
Probe voltage	: 4.5kV
CDL temperature	: 200°C
BH temperature	: 200°C
Nebulizing gas flow	: 1.5 L/min
Drying gas pressure	: 0.1 MPa
Scan range	: *m/z* 100 - 1000

Results and discussion

As a result of principal component analysis (PCA) for NS, the groups of each sample type were located at the different sites on the score plot (Fig. 4a) showing that they were comprised of different components. The unique peaks of each sample were observed on the loading plot (Fig. 4b). Candidates of the structural analogues of NS were identified using unique peaks based on fragment ions and neutral losses (Fig. 5).

The extracted ion chromatograms (EICs) suggested that these were characteristic components of each sample (Fig. 6). By the same method, each sample of CZ was identified as containing characteristic components.

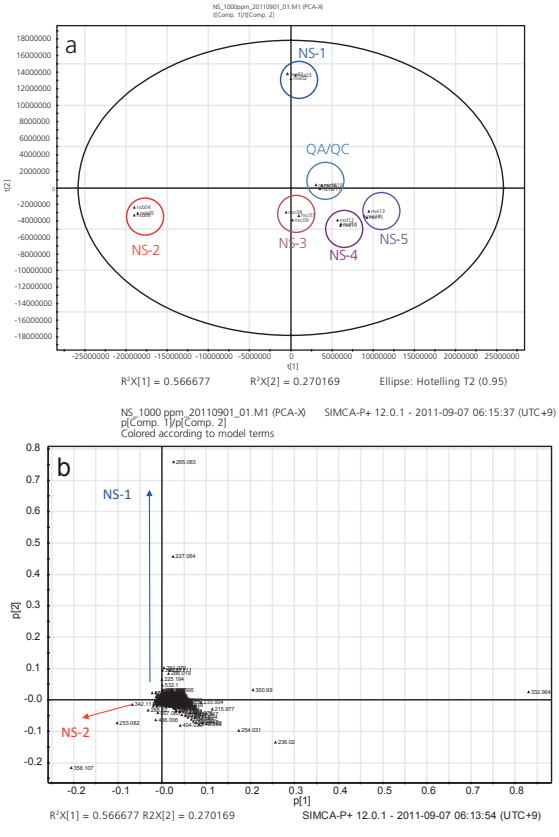

Fig. 4 Result of PCA for NS (a: score plot, b: loading plot).

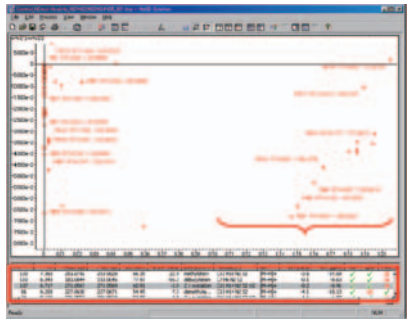

Fig. 5 Analysis window of MetID Solution.

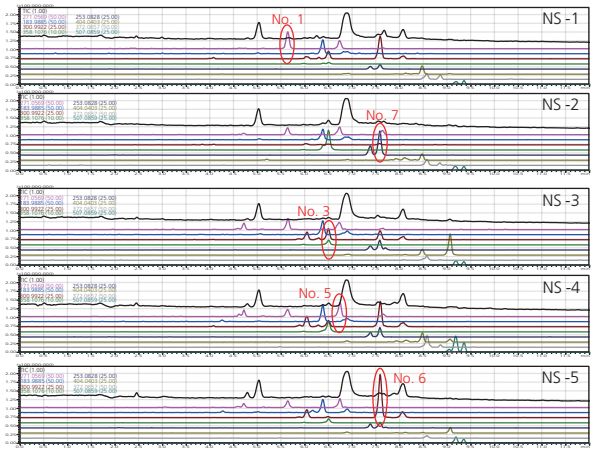

Fig. 6 EICs of characteristic peaks of each samples.

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The formula of peak No. 7 (Fig.6) of NS-2 was predicted as $C_{12}H_{16}N_2S_2$. Considering MSn spectra and neutral loss ions, it was determined that peak No. 7 has the structure of NS with addition of $–CH_2$ to the phenyl group (Fig. 7). We also determined the structures of other characteristic compounds and thought to be either impurities or by-products in the process of synthesis.

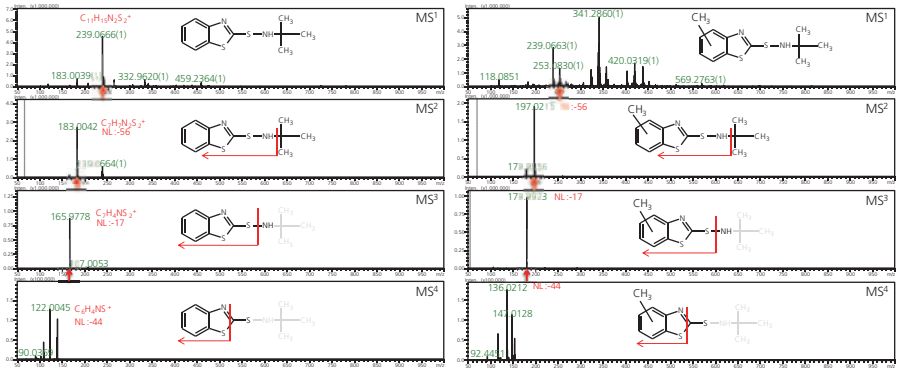

Fig. 7 MS^n spectra of NS (left) and peak No. 7 (right) detected from NS-2 sample (see Fig. 6).

Table 2 Predicted formulae and structures of characteristic components of NS (left) and CZ (right).

No.	R.T. (min)	Predicted formula and structure	ions: Measured value (m/z)	ions: Theoretical value (m/z)	ions: Error (ppm)	Sample
1	5.62	$C_{11}H_{14}N_2O_2S_2$	271.0567	271.0569	-0.74	1
2	6.35	$C_7H_5NOS_2$	183.9887	183.9885	1.09	4
3	6.48	$C_{14}H_8N_2S_3$	300.9923	300.9922	0.33	3
4	6.50	$C_{15}H_{23}N_3OS3$	358.1062	358.1076	-3.91	2
5	6.72	$C_{11}H_{14}N_2O_2S_2$	271.0582	271.0569	4.80	4
6	7.52	$C_{14}H_8N_2S_3$	300.9921	300.9922	-0.33	5
7	7.58	$C_{12}H_{16}N_2S_2$	253.0831	253.0828	1.24	2
8	8.48	$C_{14}H_{17}N_3O_5S_2$	404.0399	404.0403	-0.99	4
9	8.85	$C_{18}H_{17}N_3S_3$	372.0647	372.0657	-2.69	4
10	9.17	$C_{18}H_{26}N_4O_5S_4$	507.0850	507.0859	-1.77	4

No.	R.T. (min)	Predicted formula and structure	ions: Measured value (m/z)	ions: Theoretical value (m/z)	ions: Error (ppm)	Sample
1	3.62	$C_{10}H_{17}NO_3$	200.1280	200.1281	-0.50	4
2	4.78	$C_{11}H_{11}NO_2S_2$	254.0308	254.0304	1.57	4
3	5.07	$C_{11}H_{11}NO_4S_2$	286.0207	286.0202	1.75	4
4	6.25	$C_{13}H_{10}N_2S$	227.0628	227.0637	-3.96	4
5	6.83	$C_{11}H_{14}N_2S_2$(NS)	239.0671	239.0671	0.00	1
6	7.30	$C_{14}H_8N_2S_4$	332.9648	332.9643	1.50	4
7	8.25	$C_{30}H_{48}N_2O$	468.3956	468.3948	1.71	1
8	8.31	$C_{12}H_{12}N_2O_5S$	297.0533	297.0540	-2.36	4
9	8.36	$C_{14}H_{13}N_2S_2$	279.0985	279.0984	0.36	1
10	8.90	$C_{24}H_{25}N_3OS_4$	500.0950	500.0953	-0.3	4

Conclusion

- Differences in similar structured sulfenamide-based vulcanizing accelerators were identified from different manufacturers with characteristic components of each sample detected using high mass accuracy MS^n and multivariate statistical techniques.
- The structural analogues of main compounds were detected using MS^n data analysis software (MetID Solution).
- Formulae and structures of the analogues were assigned using Formula Predictor software.
- The impurities detected from each sulfenamide-based vulcanizing accelerator differed from manufacture to manufacture.

Acknowledgement

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