SHIMADZU

Differential Analysis in Polysulfide Silane Coupling Agents by High Mass Accuracy MS^n and Multivariate Statistical Technique

ASMS 2011 TP343

Hiroki Nakajima[1], Takahiro Goda[1], Satoshi Yamaki[1], Ichiro Hirano[1], Tsutomu Nishine[1], Yuko Sekine[2], Fumito Yatsuyanagi[2]

[1] SHIMADZU CORPORATION, Kyoto, Japan

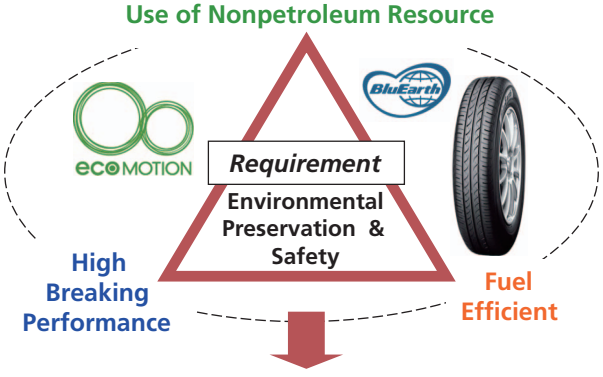
[2] THE YOKOHAMA RUBBER CO.,LTD., Kanagawa, JAPAN

Differential Analysis in Polysulfide Silane Coupling Agents by High Mass Accuracy MS^n and Multivariate Statistical Technique

Introduction

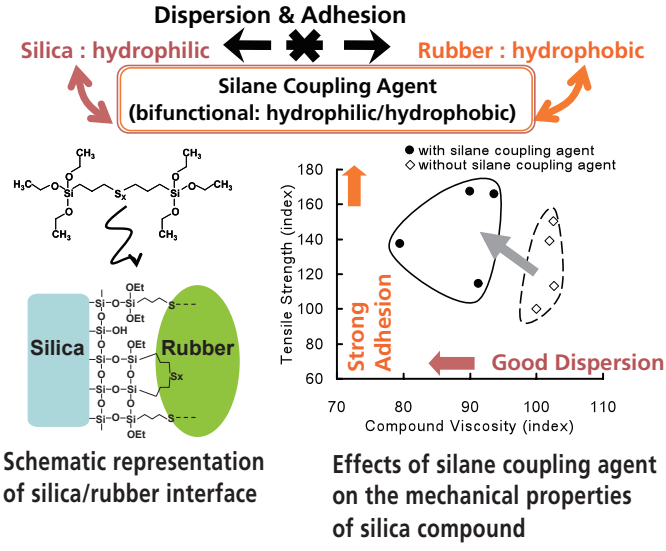
Silane coupling agents are organosilicone compounds having two functional groups with different reactivity. One of the two functional groups reacts with organic materials and the other reacts with inorganic materials. Therefore, they are effective for the improved adhesion at the interface between the organic and inorganic materials. Recently, they have been used in the manufacture of tires. Usually, fillers are added to rubber compound to enhance the strength and improve the performance of tires. Siliceous fillers that are nonpetroleum resources have recently been frequently utilized in the manufacture of tires (Fig. 1). Silane coupling agents can combine the siliceous fillers with the rubber molecules here (Fig. 2). Generally, polysulfide silane coupling agents are widely used in the Silica-containing rubber compounds. Analysis of silane coupling agents in tires is therefore important for the evaluation or improvement in developing of tires. However, it is very difficult to distinguish the same structured silane coupling agents produced by different manufacturers. Here, we present an example demonstrating the differential analysis of four same structured polysulfide silane coupling agents produced by different manufacturers using high mass accuracy MS^n and multivariate statistical technique (Fig. 3).

Background of this work



Utilization of Silica with Silane Coupling Agent is key technology for tire tread compound to contribute for environmental preservation & safety.

Fig. 1 Utilization of silica with silane coupling agent for tire tread compounding



Schematic representation of silica/rubber interface

Effects of silane coupling agent on the mechanical properties of silica compound

Fig. 2 Roles of silane coupling agent for silica tread compound

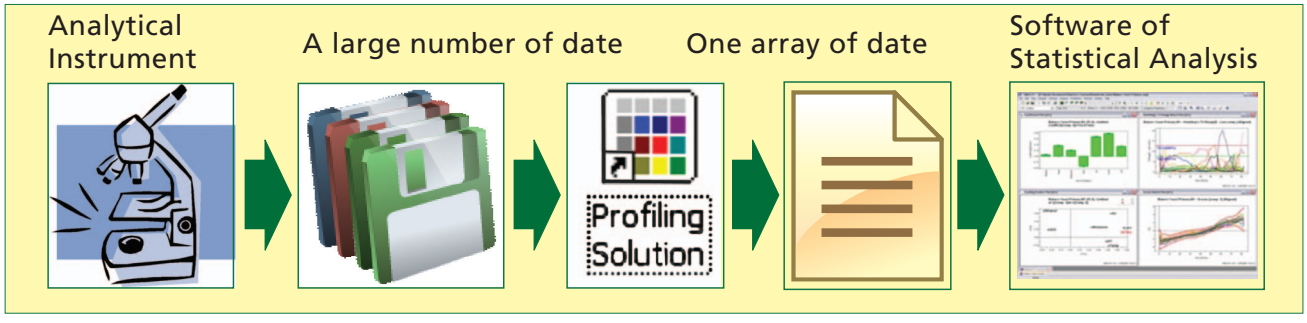
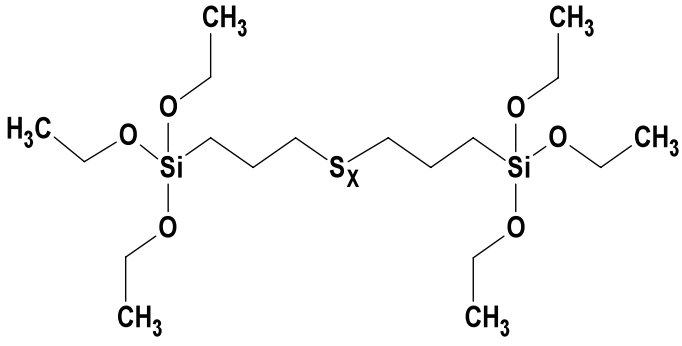


Fig. 3 Procedure of multivariate statistical analysis

Differential Analysis in Polysulfide Silane Coupling Agents by High Mass Accuracy MS^n and Multivariate Statistical Technique

Experiment

Four Bis (triethoxysilylpropyl) polysulfide (TESPP; sample A, B, C, D) produced by different manufacturers were used in this study (Fig. 4). Sample solutions were prepared at 1/10,000 dilution with methanol. Equal amount of all sample solutions were mixed and it was used as a quality control (QC) sample to identify robust and reproducible ion signals. LC-MS measurement was performed using Prominence UFLC and LCMS-IT-TOF (SHIMADZU CORPORATION). SIMCA-P (Umetrics) was used for multivariate statistical analysis.



$C_{18}H_{42}O_6Si_2Sx$ (x=2 -10)

Fig. 4 Structure of TESPP

Table 1 LC-MS analytical conditions

Column	: Shim-pack XR-ODS (2.0 mmI.D.x75 mm, 2.2 μm)
Flow rate	: 0.45 mL/min
Column temp.	: 40 °C
Mobile phaseA	: water containing 5 mmol ammonium formate
Mobile phaseB	: acetonitrile
Time prog.	: 70%B(0 – 0.11 min) – 100%B(6.67 – 12 min) –70%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 discussions

The main compound peaks of 4 polysulfide silane coupling agents were able to detect in Total Ion Current Chromatograms (TICCs) (Fig. 5). It was suggested that they had a distribution of the number of sulphur element. TICCs of sample A and B were very similar. And, on the score plot, the plots of them were located at the same site (Fig. 6a). From the above result, it was showed that they had almost common components.

The unique peaks of each sample C and D were observed on the loading plot (Fig. 6b).

The formula of compound 1 was predicted as $C_{18}H_{42}O_6Si_2S$ (Bis(triethoxysilylpropyl)monosulfide (TESPM)) by high mass accuracy MS^n data and formula prediction software "Formula Predictor 4.3" (SHIMADZU CORPORATION). The formula of compound 2 and 3 were predicted as $C_{17}H_{40}O_6Si_2S_3$ and $C_{17}H_{40}O_6Si_2S_4$, respectively. Considering MS^n spectra and neutral loss ions, it was determined that compound 2 had the structure of Bis (triethoxysilylpropyl)trisulfide (TESPT) substituted $-OCH_3$ for $-OCH_2CH_3$ (Fig. 8).

Compound 2 and 3 were regarded as impurities or by-product in the process of synthesis. We also could determine the structure of other characteristic compounds by the same method (Table 2). It was showed that those compounds, as well as main compound, had a distribution of the number of sulphur element.

Differential Analysis in Polysulfide Silane Coupling Agents by High Mass Accuracy MS^n and Multivariate Statistical Technique

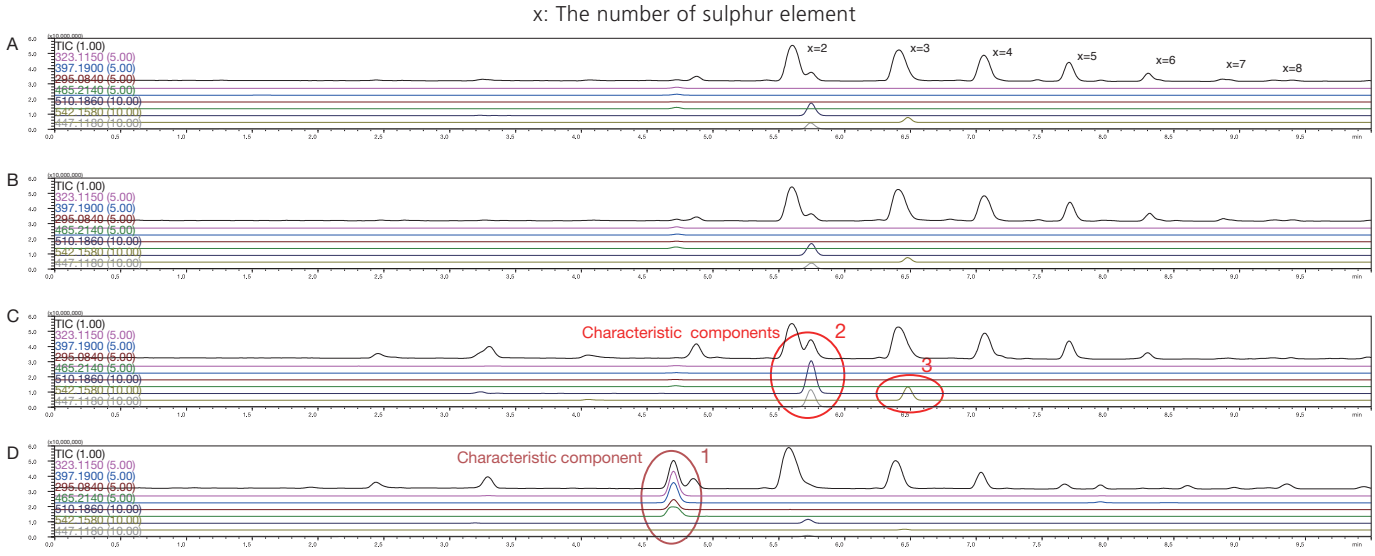


Fig. 5 TICCs and Extracted Ion Chromatograms (XICs) of Sample A, B, C and D

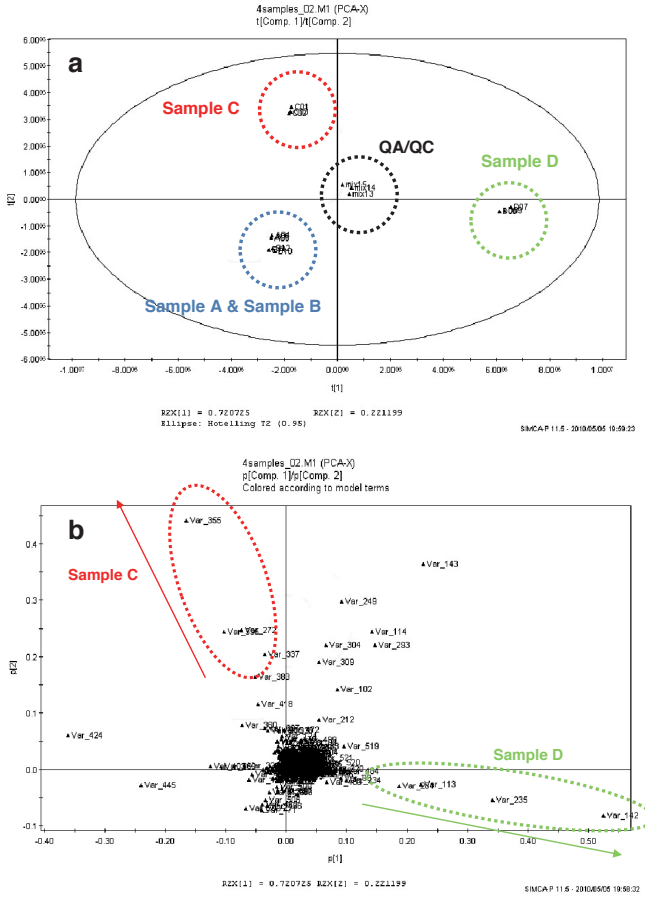


Fig. 6 Result of principal component analysis (PCA) for sample A,B,C and D (a: score plot , b: loading plot)

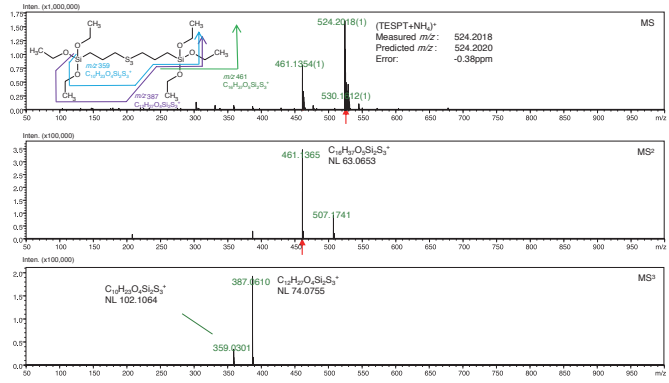


Fig. 7 MS^n spectra of TESPT

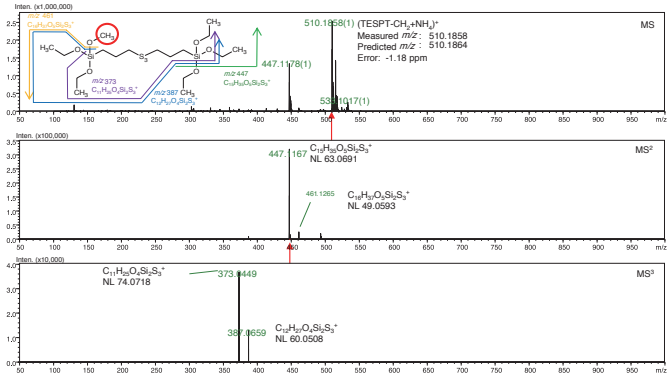
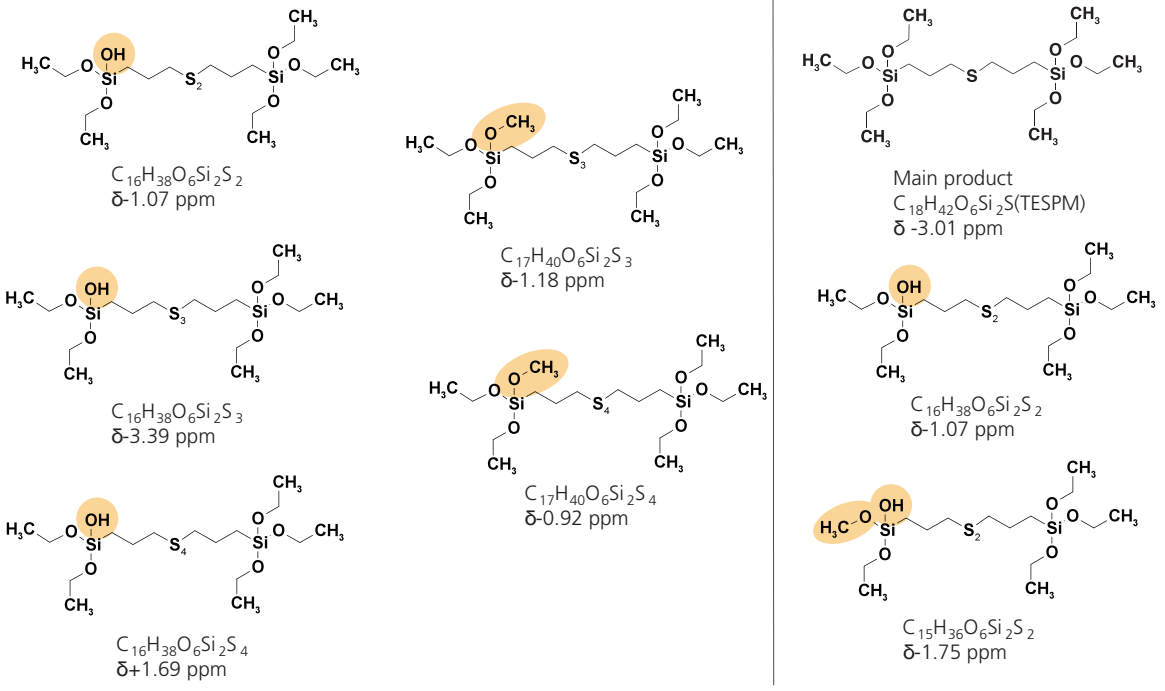


Fig. 8 MS^n spectra of compound 2

Table 2 Result of structure analysis for characteristic compounds

Characteristic Compounds	
Sample C	Sample D



Conclusion

We could demonstrate that the combination of high mass accuracy MS^n and multivariate statistical technique could be a remarkably-helpful analytical method to distinguish the same structured polysulfide silane coupling agents produced by different manufacturers. The summaries are as follows.

- It was showed that sample A and B consisted of almost common components.
- Characteristic compounds of each sample C and D were detected, and we could determine the structure of those compounds.
- It was confirmed that the level of impurity incorporation in each of 4 polysulfide silane coupling agents differed from manufacturer to manufacturer.

Founded in 1875, Shimadzu Corporation, a leader in the development of advanced technologies, has a distinguished history of innovation built on the foundation of contributing to society through science and technology. We maintain a global network of sales, service, technical support and applications centers on six continents, and have established long-term relationships with a host of highly trained distributors located in over 100 countries. For information about Shimadzu, and to contact your local office, please visit our Web site at **www.shimadzu.com**

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
URL http://www.shimadzu.com

For Research Use Only. Not for use in diagnostic procedures. Shimadzu Corporation ("Shimadzu") reserves all rights including copyright in this publication. The content of this publication shall not be reproduced, altered or sold for any commercial purpose without the written approval of Shimadzu. The information contained herein is provided to you "as is" without warranty of any kind including without limitation warranties as to its accuracy or completeness. Shimadzu does not assume any responsibility or liability for any damage, whether direct or indirect, relating to, or arising out of the use of this publication. This publication is based upon the information available to Shimadzu on or before the date of publication, and subject to change without notice.