Determination of fatty acids in vulcanized SBR using reactive pyrolysis GC/MS

[Background] Various additive packages are added to SBR to vary the chemical and physical properties of the polymer. The qualitative and quantitative analysis of these additives generally requires sample pretreatment, such as solvent extraction, to isolate or concentrate the additives of interest. For example, when analyzing SBR for the total amount of fatty acids, the sample is first extracted using ethanol/toluene followed by titration (ISO-7781 and JIS-K6237); however, this method requires large amounts of solvent, requires excessive analyst time and is prone to contamination. The result of this additional 'sample handling' reduces laboratory productivity and results often exhibit poor precision and accuracy. Analyzing rubber directly, using either thermal desorption-GC or pyrolysis-GC, results in low recovery and poor reproducibility. Fatty acids are reactive; the GC peak tails which degrades the accuracy and precision of the peak integration. For this reason, fatty acids are analyzed as methyl esters. Methyl esters are inert and the GC peaks are symmetrical. The most efficient method to determine fatty acids in a complex mixture like rubber is reactive-pyrolysis using an organic alkali like tetramethylammonium hydroxide (TMAH). TMAH hydrolyses the acid and forms the ester at temperatures beyond 250ºC. In this report, reactive pyrolysis-GC/MS using TMAH to determine the fatty acids (stearic acid, and palmitic acid) in vulcanized SBR is described.

[Experimental] The analysis of the rubber was done using a Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Labs) directly interfaced to the injector of a GC/MS. The analysis was automated using an Auto-Shot Sampler (AS-1020E, Frontier Labs). The separation column was an Ultra ALLOY-5 metal capillary column (Frontier Labs). A Micro Puncher (2 mm, Frontier Labs) was used to cut a plug of sample (200 µg) which was placed in a sample cup. Next, 2 µL of 25 wt% TMAH was added to the cup and the cup was placed in the Auto-Shot carousel. The sample cup was subsequently dropped into the hot zone (350ºC) of the quartz liner. The derivatized fatty acids were swept though the GC splitter and focused at the separation column inlet.

[Results] The total ion chromatogram of the products formed using reactive pyrolysis have peaks for the methyl esters of palmitic (C16:0) and stearic acid (C18:0) - Fig. 1a. No peak tailing is observed in the extracted ion chromatograms of the M+ ions - Fig.1b and Fig.1c. The concentration of each acid was determined to be 0.16 wt% (C16:0) and 0.46 wt% (C18:0) using the peak area of the M+ ions and a single point external standard calibration. Total fatty acid concentration is 0.62 wt% which is in good agreement with the original formulation concentration of 0.6 wt%. The precision (n=5) of the individual fatty acids determinations is 2.1 and 3.8 %RSD.

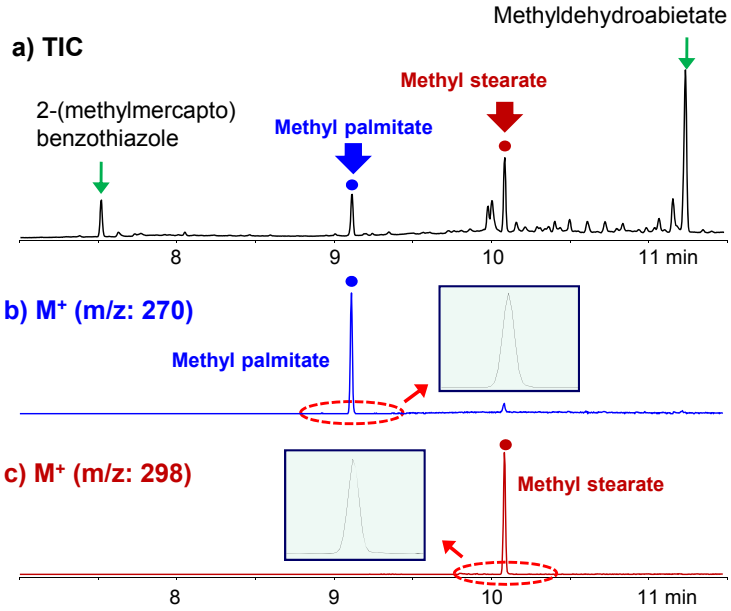

Fig. 1 Chromatogram of vulcanized SBR obtained by reactive pyrolysis-GC/MS

	Quantitated values (wt%) of fatty acids in vulcanized SBR < formulation concentration 0.6 wt% >		
Sample wt. (µg)	**Palmitic acid**	**Stearic acid**	**Total fatty acid contents**
197	0.160	0.456	0.616
194	0.155	0.441	0.596
203	0.152	0.449	0.601
202	0.156	0.479	0.635
204	0.159	0.479	0.639
Average	0.156	0.461	0.617
RSD (%)	2.12	3.84	3.16

Table 1 Quantitation of total amount of fatty acids in vulcanized SBR and reproducibility (n=5)

Pyrolysis temp.: 350ºC, GC oven temp.: 70 – 280ºC (20 ºC/min, 2 min hold), GC inj temp.: 300ºC
Separation column: Ultra ALLOY+-5 (5% diphenyl 95% dimethylpolysiloxane), L=30 m, i.d.=0.25 mm, df=0.25 µm
Column flow rate: 1 ml/min (He), split ratio: 1/100, sample weight: approx. 200 µg

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Keyword : Vulcanized SBR, additives, fatty acids, stearic acid, palmitic acid, reactive pyrolysis GC/MS, TMAH

Applications : General polymer analysis

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