Effects of Separation Conditions to Analysis Accuracy in Composition Analysis of A Blend Rubber by Py-GC Technique

Background] The Py-GC technique is a useful analytical tool which offers facile and prompt compositional analysis of various blend polymers.1) With this technique, however, not only peaks due to constituent monomers, but peaks due to various by-products are also observed on the pyrograms and those peaks often overlap, causing the analytical accuracy to be deteriorated. For example, in analysis of a three-dimensional blend rubber such as polybutadiene(PB) - polyisoprene(PI) - polystyrene(PS), depending on the analytical conditions, peaks for butadiene, the monomer of PB, and isobutene, a pyrolysis by-product may not be well resolved on the pyrogram. Here, in this report such effects to the analytical accuracy were studied.

[Experimental] In the Py-GC system, a Double-Shot Pyrolyzer® directly attached to the split/splitless injection port of a GC was connected to an FID via a capillary separation column. The GC separation conditions used were conditions recommended by ISO7270 (Condition A) and those used to separate isobutene and butadiene in this study (Condition B). Composition ratios of unknowns are determined using a calibration curve generated from three standard samples of varied composition ratios.

[Results] Fig. 1 shows a pyrogram of the PB-PI-PS blend rubber obtained using Condition A, while Fig. 2 shows a pyrogram obtained using Condition B. On both pyrograms, peaks due to the constituent monomers of butadiene (BD), isoprene (IP), and styrene (ST) are observed as major peaks, however, in the pyrogram obtained with Condition A, peaks for IB and BD were not resolved, so it is difficult to obtain the peak area of each peak by integration using a vertical drop line. Therefore, in calculation of composition ratio, peak area was obtained from two peak areas combined and was used as peak area for BD. On the other hand, in the pyrogram obtained with Condition B, peaks for IB and BD are marginally resolved, thus the peak area of each was obtained by integration using a vertical drop line. Table 1 shows starting composition ratios and composition ratios obtained with both conditions. In the results obtained with Condition A, composition ratios were obtained with fairly good accuracy, but with regard to PB, relatively large error of -0.8wt% are shown. On the other hand, composition ratios obtained with Condition B gave a good accuracy and even the largest error made was mere +0.2wt% for PS.

Table 1. Composition ratios for unknowns and starting material (wt%)

	PB	PI	PS
Starting composition ratio	37.2	25.0	37.8
With Condition A	36.4	25.2	38.4
(error)	(-0.8)	(+0.2)	(+0.6)
With Condition B	37.1	24.9	38.0
(error)	(-0.1)	(-0.1)	(+0.2)

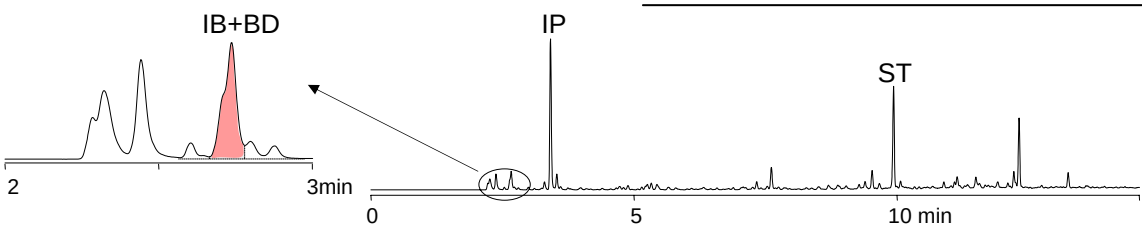

Figure 1. Pyrogram of a blend rubber obtained with conditions recommended by ISO7270 (Condition A)

Pyrolysis temp. : 550ºC, Detector : FID, Separation column : Ultra ALLOY+-5 (5%-diphenyl-95%-diphenyl-95%-dimethylpolysiloxane)
Length 30m, id 0.25mm, Film thickness 1.0µm
GC oven temp. : 50ºC (2min hold) – 280ºC (10ºC/min), Injection port pressure : 175kPa, Split ratio : 1/60, Sample size : ca.200µg

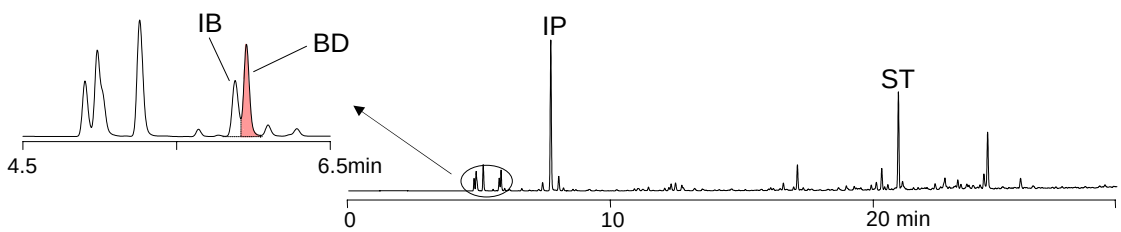

Figure 2. Pyrogram of a blend rubber obtained with conditions used in this study (Condition B)

Separation column : Ultra ALLOY+-5 (5%-diphenyl-95%-dimethylpolysiloxane), Length 60m, id 0.25mm, Film thickness 1.0µm
GC oven temp. : 50ºC (7min hold) – 280ºC (10ºC/min), Other conditions are the same as those in Fig. 1.

Keyword : Blend rubber, Composition analysis, Butadiene, Isoprene, Styrene

Applications : Rubber industry

Related technical notes : PYA1-047E

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