

Compositional Analysis of NBR by pyrolysis GC/MS

Part 2: Analysis of constituents and monomer compositions by pyrolysis GC/MS

[Background] In the previous note (PYA3-048E), evolved gas analysis (EGA)-MS was conducted on two acrylonitrile-butadiene rubber (NBR) samples. From the EGA curves, the pyrolysis temperature was determined to be 600 °C. In this note, identification of polymer and additives was conducted by Py-GC/MS on the same NBR samples as the ones used in the previous note. Further, determination of the compositional ratios of monomers (acrylonitrile-butadiene ratio) was also made.

[Experimental] As described in the previous note, a GC/MS system was used in combination with a Multi-Shot Pyrolyzer (EGA/PY-3030D) directly interfaced to the GC injector. A separation column (UA5-30M-0.25F) was installed in place of an EGA tube (UADTM-2.5N) between the GC injector and a Vent-free GC/MS adapter directly connected to the mass detector. NBR standards with varied compositional ratios of acrylonitrile (AN) to 1,3-butadiene (BD) were used for constructing a calibration curve. The NBR samples were scraped off using a cutting knife, and then the scraped pieces were put into an Eco-Cup, precisely weighed, and introduced into the pyrolyzer furnace preheated at 600 °C.

[Results] Figure 1 shows pyrograms of the NBR samples and extracted ion chromatograms (EICs) of AN (m/z 53) and BD (m/z 54). In Fig. 1, pyrolyzates of NBR (BD and AN) were detected from both samples. Additives including *N*-phenyl-1,4-phenylenediamine (IPPD), 4,4'-bis(α,α -dimethylbenzyl)-diphenylamine (DCD), both of which are antidegradants, and bis(2-ethylhexyl)phthalate (DEHP; plasticizer) were detected in Sample 1. Trimethylolpropane trimethacrylate (TMPTM; co-crosslinking agent) and IPPD were mainly detected in Sample 2. A calibration curve used to determine the AN to BD compositional ratio is shown in Fig. 2, in which area values of the EIC peaks characteristics to AN (m/z 53) and BD (m/z 54) are plotted against the AN content (see equation given in Fig. 2). The determined AN:BD ratios for two samples are summarized in Table 1. As seen in Table 1, reproducibility is fairly good for both samples. From these results, polymer and additives in NBR samples were able to be identified by Py-GC/MS, and compositional ratios of monomers were determined with excellent reproducibilities.

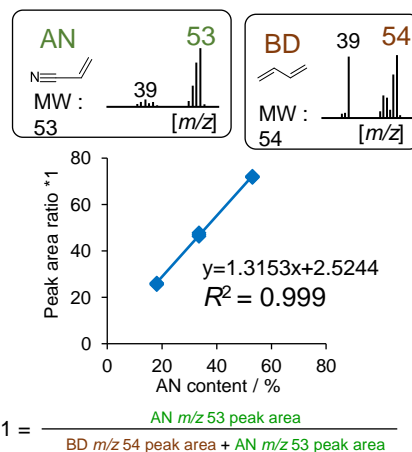
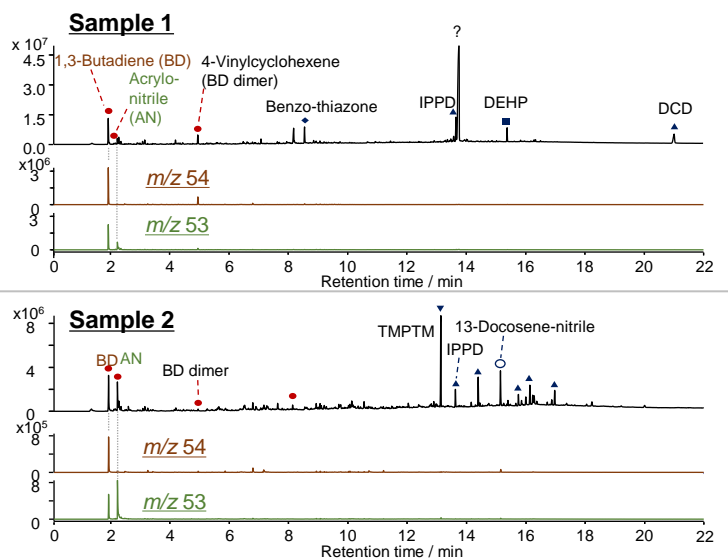


Fig. 2 Calibration curve.

Table 1 Results of AN:BD compositional ratios.

Sample	AN : BD	RSD (n=3)
1	20.0 : 80.0	2.8 %
2	48.5 : 51.5	0.2 %

Fig. 1 Pyrograms of the samples and EICs of AN and BD.

Furnace temp.: 600 °C, GC injector temp.: 300 °C, GC oven temp.: 40 °C(2 min) - 320 °C (20 °C/min, 14 min hold), Separation column: UA⁺-5 (5 % diphenyl-95 % dimethylpolysiloxane, L=30 m, i.d.=0.25 mm, df=0.25 μm), Column flow rate: 1.0 mL/min, Split ratio: 1/20, MS scan range: m/z 29 - 600, Sample amount: ca. 0.1 mg.

Keywords : NBR, Compounded rubber, Compositional analysis, Flash pyrolysis, Pyrolysis-GC/MS

Products used : Multi-Shot Pyrolyzer, Auto-Shot Sampler, MicroJet Cryo-Trap, UA⁺-5, Eco-Cup LF, Quartz wool, F-Search, Vent-free GC/MS adapter

Applications : General polymer analysis, Additives analysis, Quality control, Material analysis, Defect analysis

Related technical notes : [PYA3-048E \(Part1\)](#), [PYA1-047E](#)

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