Oligomer pyrolyzates of multicomponent acrylate ester copolymers and monomer composition ratios

Part 2: Determination of monomer composition ratio using relative intensity of trimer peak

[Background] In the previous note (PYA1-179E), the trimer peaks observed in the pyrograms of a ternary acrylic copolymer were identified using time-of-flight mass spectrometry (TOFMS) and a structural analysis software program (msFineAnalysis AI). In this note, the determination of the monomer composition ratios of ternary acrylic copolymers is described based on the relative intensities of the identified trimer peaks.

[Experimental] Measurements were conducted on a Py-GC/MS system equipped with a Multi-Shot Pyrolyzer (EGA/PY-3030D) directly interfaced to the GC injector. Five ternary acrylic copolymers with known acrylic monomer compositions (butyl acrylate (BA) / 2-ethylhexyl acrylate (2-EHA) / 2-hydroxyethyl acrylate (HEA)) and varied mass ratios were used as samples. The monomer formulations for the five ternary copolymers are given in the upper left of Fig. 1. Each acrylic copolymer was put in a sample cup and introduced into the furnace heated at 600 ºC. The pyrolyzates were measured by GC/MS.

[Results] Figure 1 shows a trimer peak region of pyrograms of acrylic copolymers with known mass compositions. Peak **a** originates from a trimer composed of BA, BA, and HEA; Peak **b**, from BA, BA, and 2-EHA; and Peak **c**, from BA, 2-EHA, and HEA (PYA1-179E). The areas of these trimer peaks (**a**, **b**, and **c**) reflect the monomer composition ratio of each sample. For instance, in sample #5 where composition ratio BA/2-EHA is 20/60, the area ratio of Peak **a** (BA/BA/HEA) to peak **c** (BA/2-EHA/HEA) was approximately 1:3. Similarly, for sample #5 where composition ratio of BA/HEA is 20/20, the area ratio of Peak **b** (BA/BA/2-EHA) to Peak **c** (BA/2-EHA/HEA) was approximately 1:1. Figure 2 illustrates the correlation between the monomer composition ratio in the sample and the area ratio of each trimer peak. In both cases, a linear relationship was observed with an excellent coefficient of determination ($R^2 > 0.995$), indicating that the peak area ratio can correlate with the monomer composition ratio. This demonstrates that the relationship can be used to determine the monomer composition ratio of tertiary acrylic copolymers.

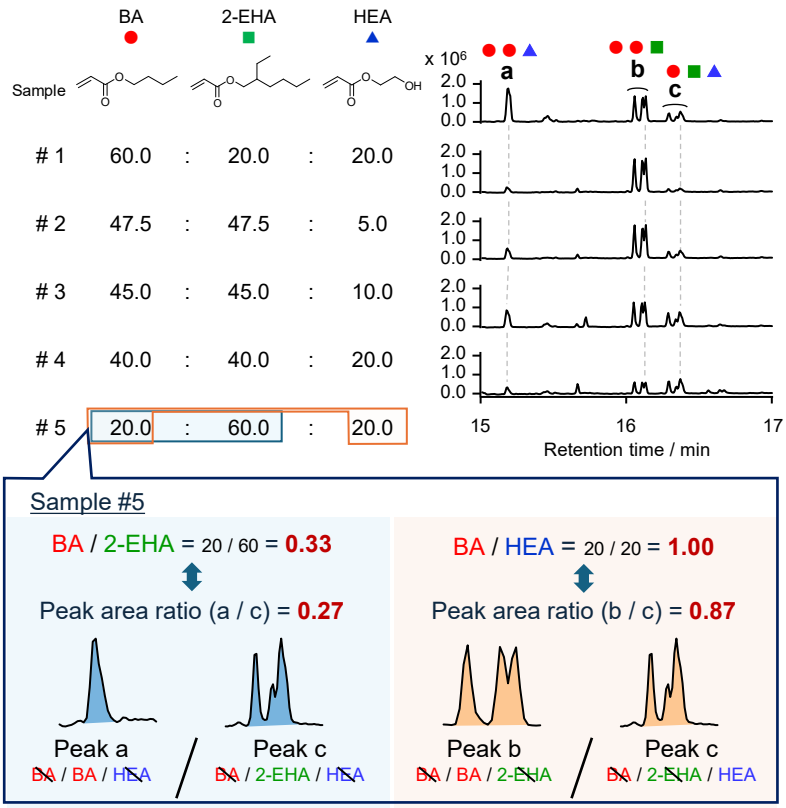

Fig. 1 Pyrograms of five ternary acrylic copolymers

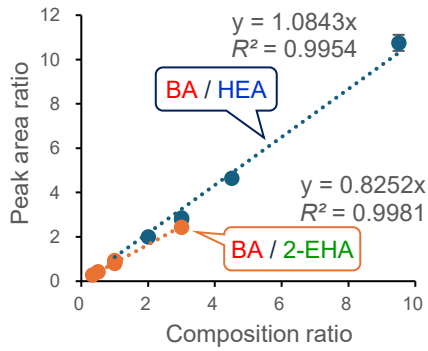

Fig. 2 Correlation between mass composition ratio and peak area ratio of each trimer

Furnace temp.: 600 ºC, Separation column: UA⁺-5 (5 % diphenyl 95 % dimethylpolysiloxane, *L*=30 m, i.d.=0.25 mm, df=0.25 µm), GC injector temp.: 300 ºC, Column flow rate: 1.0 mL/min, Split ratio: 1/100, GC oven temp.: 40 ºC (2 min hold) - 320 ºC(20 ºC/min, 14 min hold), Detector: quadrupole MS, Sample amount: 0.1 mg

Keywords : Adhesive, Time-of-flight mass spectrometry, Compositional analysis

Products used : Multi-Shot Pyrolyzer, Auto-Shot Sampler, UA⁺-5, Vent-free GC/MS adapter, F-Search

Applications : Material analysis, Quality assurance

Related technical notes : PYA1-179E

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