SHIMADZU APPLICATION NEWS

LA146-E021

● GASCHROMATOGRAPHY MASS SPECTROMETRY

No.M201

Polymer Analysis by Pyrolysis GCMS with Evolved Gas Analysis (EGA) and Double-Shot Methods

Pyrolysis analysis using the evolved gas analysis (EGA) or double-shot (multi-step pyrolysis) analysis method can be performed by combining a double-shot pyrolyzer with heating features and a gas chromatograph mass spectrometer. In this example, the PY-2020D double-shot pyrolyzer from Frontier Laboratories Ltd. and Shimadzu GCMS-QP5050A gas chromatograph mass spectrometer were used.

With the EGA method, the pyrolyzer outlet is connected directly to the MS with a metal inert capillary tube and the substances evolved from the heated sample are analyzed online. This method provides EGA curve similar to thermogravimetric analysis (TG). From information on the constituent substances of the sample gained from that data, the temperature fraction corresponding to the target substance can be clearly determined.

The double-shot method first analyzes volatile substances, such as additives and residual solvents, in the polymer by thermal desorption at a low temperature (100 - 300˚C), and then pyrolyzes the remaining polymer substrate. By this stepped heating process, polymers containing solvents and the mixed polymers with different decomposition temperatures can be separated for analyzing individual substances.

In this Application News, the sample analyzed using PYR4A in Application News M174 (a vinyl acetate based adhesive) was analyzed in more detail using the EGA and double-shot methods.

The vinyl acetate adhesive was analyzed using the EGA method. Table 1 shows the analytical conditions, Fig. 1 the obtained chromatogram, and Fig. 2 mass spectra for major peaks.

The results show that the main constituent of Peak 1, is methyl acetate, and the main constituent of Peak 2, thought to be a polymer decomposition product, is acetic acid. Peak 3 contains many constituents and cannot be identified by the mass spectrum alone. Peak 3 must be further separated by using a chromatograph.

Table 1 Analytical Conditions for the EGA Method

Model	: GCMS-QP5050A		
	: PY-2020D (FRONTIER LAB)		
-Pyrolyzer-			
Pyrolysis Temp.	: 40˚C (2min) -20˚C/min-700˚C		
-GC-		-MS-	
Column	: Ultra ALLOY UADTM-2.5N (2.5m×0.15mm i.d.)	Interface Temp.	: 300˚C
		Ionization Method	: EI
Column Temp.	: 300˚C	Scan Range	: m/z 35-500
Carrier Gas	: 20kPa	Scan Interval	: 3sec
Injection Temp.	: 300˚C		
Injection Method	: Split 1:50		

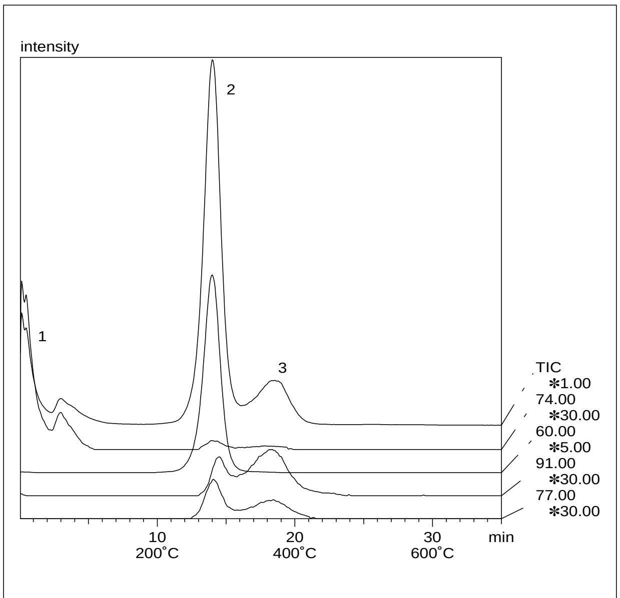

Fig.1 EGA Curves of Adhesive

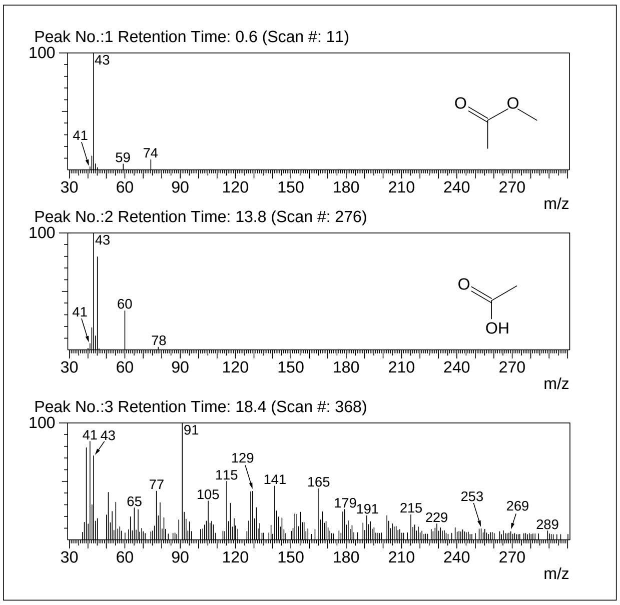

Fig.2 EGA Mass Spectra of Adhesive

Based on the EGA results, multi-stepped pyrolysis was performed. From the EGA chromatogram, decomposition temperatures were set at 200˚C, 330˚C and 550˚C. As shown here, if EGA measurements are made in advance, the optimum temperatures for pyrolysis can be easily determined. Table 2 shows the analytical conditions the single-shot and double-shot methods.

Fig. 3 shows the TIC for single-shot pyrolysis at 550˚C. In this chromatogram, peaks deriving from the solvents and polymers are both detected. Figs. 4 ~ 6 show TICs obtained by double-shot pyrolysis, where substances deriving from solvents and polymers are separately detected.

As shown in Fig. 7, the origin of each substance can be clearly identified by comparing the TICs obtained by the single-shot and double-shot pyrolysis methods. Thus the composition of polymer materials can be clearly identified by combining the EGA and double-shot pyrolysis methods.

Table 2 Analytical Conditions for the Single-Shot and Double-Shot Methods

Model	: GCMS-QP5050A
	: PY-2020D (FRONTIER LAB)
-GC-	
Column	: Ultra ALLOY+5
	(30m×0.25mm I.D. df=0.25μm)
Column Temp.	: 50˚C (2min) -10˚C/min-300˚C (13min)
Carrier Gas	: 100kPa
Injection Temp.	: 300˚C
Injection Method	: Split 1:50
-MS-	
Interface Temp.	: 300˚C
Ionization Method	: EI
Scan Range	: m/z 35-500
Scan Interval	: 0.5sec

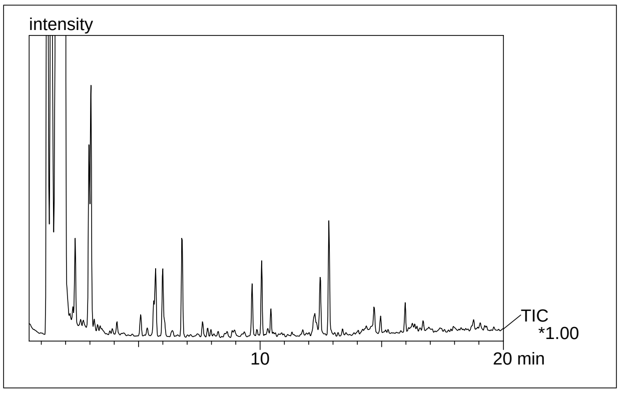

Fig.3 TIC of Adhesive (Single Shot : Pyrolysis Temp. 550˚C)

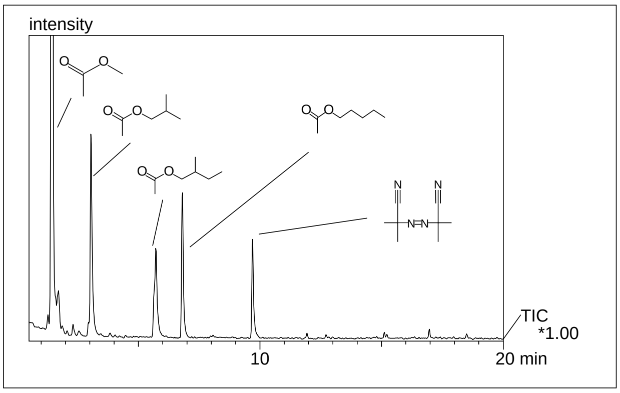

Fig.4 TIC of Adhesive (Double Shot : Pyrolysis Temp. 200˚C)

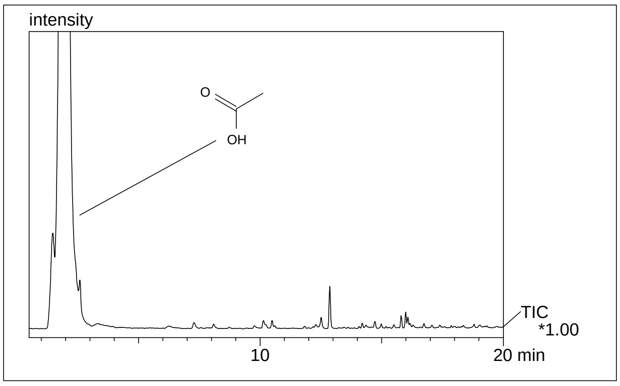

Fig.5 TIC of Adhesive (Double Shot : Pyrolysis Temp. 200→330˚C)

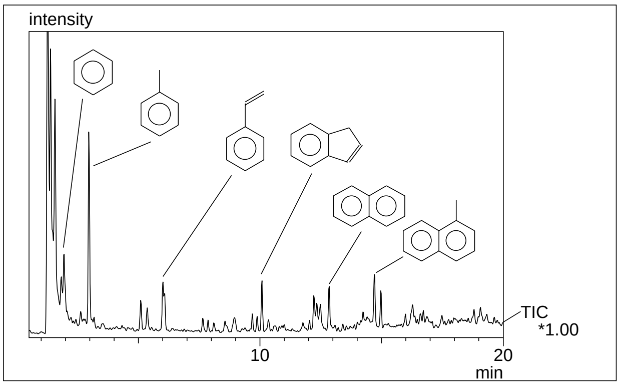

Fig.6 TIC of Adhesive (Double Shot : Pyrolysis Temp. 330→550˚C)

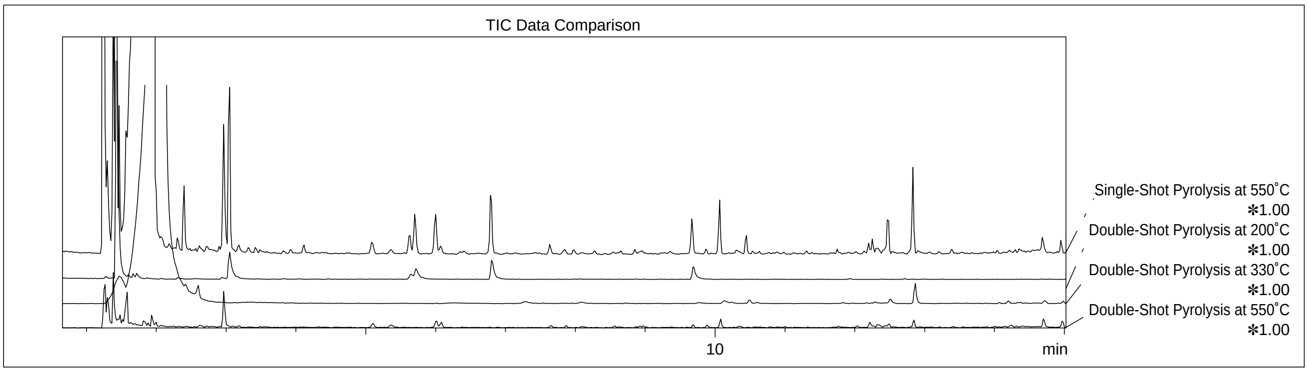

Fig.7 TIC of Adhesive (Comparison with Single-Shot and Double-Shot methods)

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