

Analysis of Residual Solvent in Polymers by GC/MS Double-shot Pyrolyzer (PY-2020D)

Pyrolysis gas chromatograph mass spectrometers (Py-GC/MS) are commonly used for polymer analyses. The combination of a temperature controllable double-shot pyrolyzer (PY-2020D:Frontier Lab Ltd.) and a gas chromatograph mass spectrometer (GCMS-QP5050A) enables simple analyses of polymers, as well as residual solvents and additives in polymers by various methods including the EGA (evolved gas analysis) method and double-shot

analysis (multiple-stage pyrolysis) method.

This article demonstrates two analyses of residual solvents in polymers. Part 1 is an example of quantification of residual solvents in a polymer sample using a liquid sample injection unit (an accessory of the main unit). Part 2 is an example of EGA analysis to grasp the changes in residual solvents due to thermal processing on the polymer sample.

■ Part 1 Quantification of residual solvents in polymer

Residual solvent (benzyl alcohol) in a epoxy polymer film was quantified using pyrolysis GC/MS. The liquid sample injection unit allows the injection of solvents into the PY-2020D to analyze. Commercially available syringes with 50mm-length needles are used for injection.

Table 1 shows the analysis conditions. Benzyl alcohol was diluted with acetone to 1, 2 and 10mg/mL, and 1 μ L solutions of each concentration were introduced into the PY-2020D liquid sample injection unit as standard samples. (The solvent flash method was used for injection.) Fig. 1 shows the mass chromatograms for each concentration and Fig. 2 shows the calibration curve obtained by these results.

Table 1 Analytical conditions of Double-shot method

Model	: GCMS-QP5050A
	: PY-2020D (FRONTIER LAB)
-GC-	
Column	: Ultra ALLOY+5 (30m \times 0.25mm I.D. df=0.25 μ m)
Column Temp.	: 40°C (1min)-15°C/min-120°C -25°C/min-300°C (7min)
Carrier Gas	: 100kPa (1min)-9kPa/min-150kPa -13kPa/min-240kPa (7min)
Injector Temp.	: 280°C
Injection Method	: Split 1 : 100
-MS-	
Interface Temp.	: 300°C
Ionization Method	: EI
Scan Range	: m/z 35-300
Scan Interval	: 0.3sec

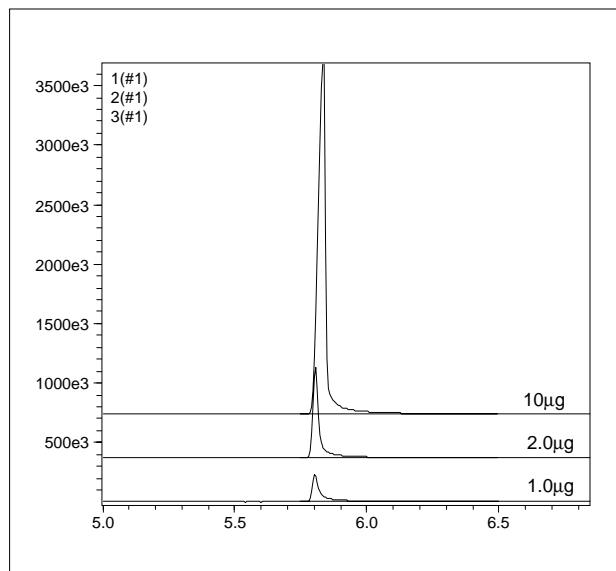


Fig.1 Mass chromatograms of benzyl alcohol (m/z: 108)

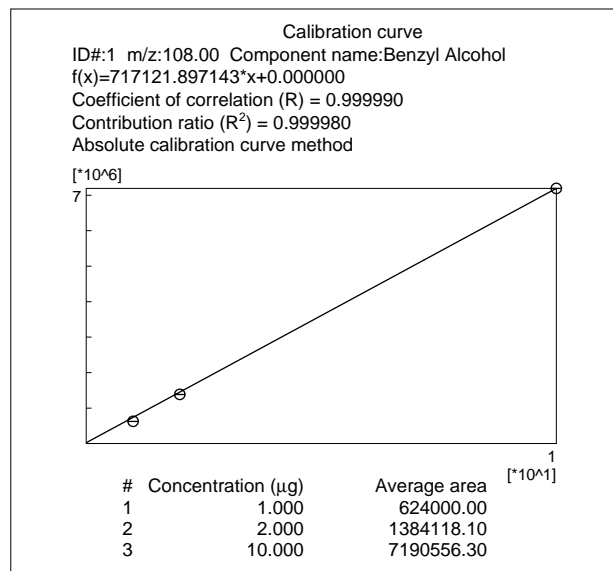


Fig.2 Calibration curve of benzyl alcohol

Fig.3 shows the mass chromatograms obtained by heating the polymer sample at 230°C. Tailing of the benzyl alcohol peaks is more apparent than for standard samples. This is thought to be due to the time required for the substance to evolve from the polymer.

Table 2 shows the reproducibility obtained by repeated analyses of the polymer. Stable reproducibility was obtained.

Table 2 Reproducibility

	1	2	3	4	5	CV value (%)
Measured value (µg)	8.3	7.8	8.3	8.1	8.8	
Sample amount (mg)	2.1	2.2	2.1	2.0	2.1	
Concentration (µg/mg)	4.0	3.5	4.0	4.1	4.2	6.10

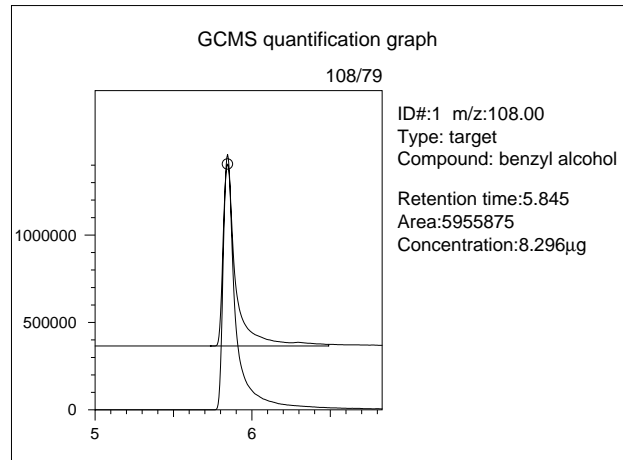


Fig.3 Quantification result of benzyl alcohol

■ Part 2 Analysis of changes in residual solvents during heat treatment by EGA method

In the EGA method, a temperature-programmable pyrolysis unit is used to introduce volatile components and substances created by the decomposition of the polymer generated during the heating process directly into the MS unit.

Polyimide was analyzed in this example. Samples treated at high and low temperatures were analyzed using the EGA method. Fig.4 shows the total ion chromatograms (TIC) for these samples. Two peaks were obtained for the polymer treated at a low temperature. The peak at 200 to 400°C mainly consists of the residual solvent, while the peak at 600 to 700°C represents the decomposed polymer. No peak appeared at 200°C to 300°C for the polymer treated at a high temperature. These results suggest heat processing at a high temperature eliminated the residual solvent.

Table 3 Analytical conditions of EGA method

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

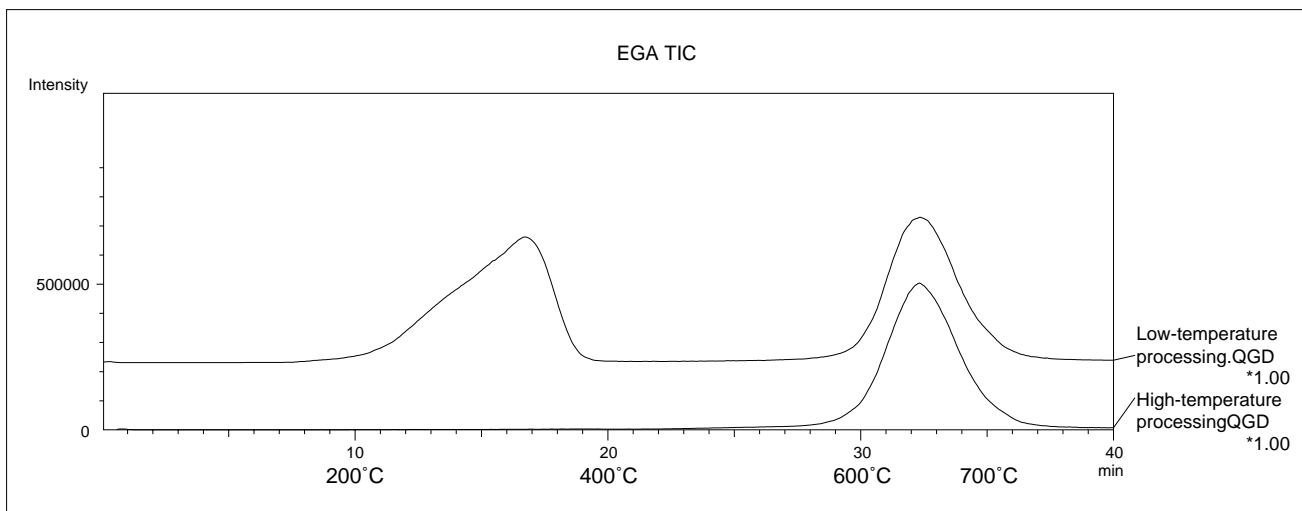


Fig. 4 EGA curve of polyimide



SHIMADZU CORPORATION. International Marketing Division

3. Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan Phone: 81(3)3219-5641 Fax: 81(3)3219-5710
Cable Add.: SHIMADZU TOKYO

Printed in Japan 3100-03308-10A-1K