Analysis of Pressure Sensitive Adhesives by GC/MS and GC/AED with Temperature Programmable Pyrolyzer

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Gas chromatograph/mass spectrometer (GC/MS) and gas chromatograph/atomic emission detector (GC/AED) with temperature programmable pyrolyzer were used for analysis of pressure sensitive adhesives in adhesive tapes. Evolved gas analysis (EGA) profile of the adhesives was obtained by this temperature-programmed pyrolyzer directly coupled with MS via a deactivated metal capillary tube. The EGA profile suggested the optimal thermal desorption condition for additives and the subsequent optimal pyrolysis temperature for the remaining polymeric material. Rubbers were identified from pyrograms with the assistance of a new polymer library. The additives were selectively detected by monitoring hetero elements and these screening results of GC/AED enabled one to easily find additive peaks in complex chromatograms of GC/MS with interference of tackifier. The additives were able to be identified by the corresponding GC/MS data. Furthermore, the EGA profile gave significant data for crosslinking agents by using specific ion monitoring.

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A pressure sensitive adhesive generally consists of rubber as a main component and additives such as tackifier, filler, crosslinking agent, and antioxidant. It is important to analyze each component without interference of the other components. In the conventional analytical methods for adhesives, a variety of analytical instruments are used after cumbersome pretreatment such as fractionation. Hence, we need to develop a rapid and convenient method for their analysis. On the other hand, evolved gas analysis (EGA), which is a kind of thermal analysis, is an analytical method which tracks chemical species produced during temperature-programmed heating of the sample. Especially, by using the mass spectrometer (MS) as a detector, it becomes possible to directly obtain chemical information on the thermal desorption and/or thermal decomposition products. The EGA-MS system which directly connected thermogravimetry (TG) with MS has been applied to the analysis of the polymeric materials.¹ However, this generally needs a sample amount of as much as 10 mg. Additionally, organic substances with strong polarity and/or high boiling-point caused serious problems; they were adsorbed at active and/or cooler spots in the interface which combined TG with MS. Recently, a micro-furnace pyrolyzer which has temperature programming capability was developed,² and a new EGA-MS system, where the pyrolyzer is directly connected with MS through a deactivated metal capillary tube, was also developed.³ The serious adsorption problems were substantially improved and the necessary sample size was reduced down to several hundred µg with the new EGA-MS system. Thus, obtained EGA profile suggested the optimal thermal desorption temperature for volatile components such as residual solvents and additives and the subsequent optimal pyrolysis temperature. This system enabled us to analyze volatile components separately, and subsequently analyze the remaining polymer without

interference of the volatile components.^{4,5} In addition, a new library for polymer identification was included in this system. The original polymeric material can often be identified using the new polymer library of mass spectra for standard polymers based on average spectra over a selected region of EGA profile. On the other hand, an atomic emission detector (AED) which can measure 23 different elements is a very useful detector for monitoring elements selectively in complex samples.⁶⁻⁸ In the analysis of polymeric materials, an AED is considered effective for screening of additives which generally contain hetero elements.⁹

In this study, rubbers in the adhesives were identified from pyrograms with the assistance of the new polymer library. Based on the result of EGA profile which was obtained by the new EGA-MS system, a temperature was set below pyrolysis starting temperature of rubber for studying thermal desorption of additives. However, vaporized components derived from tackifier produced a lot of peaks and they overlapped the peaks from the other additives. Then, AED was used for screening of additives that contained hetero elements. In addition, EGA profile provided further significant data for crosslinking agents by using specific ion monitoring.

Experimental

Sample preparation

Two different kinds of adhesive tapes were commercially available. One of them was a craft adhesive (CA) tape, and the other was an aluminum adhesive (AA) tape. Pressure sensitive adhesives were scraped away from the base materials. About 0.3 mg of the adhesive was directly analyzed by EGA-MS as well as pyrolyzer-GC/MS and GC/AED.

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Instrumentation

(1) EGA

A double-shot pyrolyzer (Frontier Laboratories, Fukushima, Japan) attached to a HP6890 GC equipped with a HP5973 MS (Hewlett-Packard, Palo Alto, USA) was used for EGA. This pyrolyzer is a vertical micro-furnace type and has temperature programming capability. Figure 1 shows a schematic diagram of the EGA-MS system, where a deactivated metal capillary

Fig. 1 Schematic diagram of EGA-MS system. A, pyrolyzer; B, GC; C, MS; D, deactivated metal capillary tube.

Fig. 2 EGA total ion profile obtained (a) from the adhesive in the CA tape and (b) from that in the AA tape by EGA-MS.

tube (2.5 m $\times$ 0.15 mm i.d., Frontier Laboratories) kept at 300°C was used to connect the pyrolyzer directly with MS. During heating the sample from 60 to 700°C at 20°C/min, the resulting evolved gas was directly detected by MS. The temperature of GC injection port was 300°C. Helium was used as carrier gas for the capillary tube with a flow rate of 0.8 ml/min, and the split ratio was set at 50:1. The MS was operated in the electron ionization mode at 70 eV electron energy and with a scan range of m/z 10 to 700. The EGA-MS Polymer Library (Frontier Laboratories, mass spectra of 136 kinds of polymers), which works with library search for an average mass spectrum of any range of the EGA profile, was used for the assistance of polymer identification.

(2) Thermal desorption and pyrolysis

The apparatus used for thermal desorption and pyrolysis was basically the same as for EGA shown in Fig. 1 except for the tube. The deactivated capillary tube was replaced with a separation column. The thermal desorption temperature was 300°C and the pyrolysis temperature was 580°C. An Ultra Alloy-5 metal capillary column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness, Frontier Laboratories) was used for the separation of thermally desorbed components and/or pyrolysis products. The pyrolyzer-GC equipped with a HP G2350A AED (Hewlett-Packard, Palo Alto, USA) was used for screening of additives. The temperature of the column was maintained at 35°C for 3 min, raised to 320°C at 10°C/min, and held for 5 min. GC injection port temperature was 300°C. Helium was used as carrier gas with column flow rate of 1 ml/min in constant flow mode and the split ratio was set at 50:1. The MS was operated in the electron ionization mode at 70 eV electron energy and with scan range of m/z 10 to 700. The AED was operated by monitoring five emission lines for carbon (193 nm), nitrogen (174 nm), phosphorus (178 nm), sulfur (181 nm), and oxygen (171 nm) elements.

Results and Discussion

EGA profile

EGA profiles indicate thermal characteristics of the adhesive similar to those obtained by thermal analysis. Figure 2 shows EGA profiles detected by MS. In the case of the CA tape (a),

Fig. 3 Comparison of average mass spectra corresponding to the specific EGA profile for the CA tape and reference mass spectra. A1, average mass spectrum from 300 to 390°C; R1, reference mass spectrum of NR; A2, average mass spectrum from 390 to 450°C; R2, reference mass spectrum of IIR.

Fig. 4 Pyrograms of (A) the rubber components in the CA tape and (B) those in the AA tape. a, propylene; b, isobutene; c, isoprene; d, toluene; e, *m*-xylene; f, limonene; g, 1-butene; h, 1-butanol; i, butyl acrylate; j, dimer; k, trimer.

Fig. 5 Comparison of (B) average mass spectrum corresponding to the specific EGA profile for the AA tape from 320 to 440°C and (R) reference mass spectrum of PBA.

three peaks with their peak tops at 250, 370 and 410°C were observed. The first peak might be related to volatile compounds such as additives eluted below 300°C and the second and the third peaks might be related to rubber decomposition at higher temperatures. In the case of the AA tape (b), three peaks with their peak tops at 170, 260, and 390°C were observed. The first two peaks may be related to volatile compounds and the last peak may be related to rubber decomposition.

Using these EGA profile data, thermal desorption temperature for the both samples was empirically determined as 300°C to prevent interference of main polymer decomposition. The subsequent pyrolysis temperature was fixed at 580°C, about 50°C higher than the ending temperature of thermal decomposition for the rubber component.

Identification of rubber

As for the CA tape, two average mass spectra corresponding

to the specific EGA profile from 300 to 390°C (A1) and that from 390 to 450°C (A2) shown in Fig. 2 (a) were used for the identification of polymeric materials. Using EGA-MS Polymer Library, these rubbers were identified as natural rubber (NR) and isobutylene-isoprene rubber (IIR), respectively. The observed mass spectra for A1 and A2 are shown in Fig. 3 together with the reference spectra in the library. Figures 4 (A) and (B) show the pyrograms obtained at 580°C for the rubber components in the CA tape and those in the AA tape, respectively. The pyrogram (A) fundamentally showed a typical pattern of a mixture of NR and IIR. The main decomposition products were identified as propylene, isoprene, toluene, *m*-xylene and limonene derived from NR and isobutene derived from IIR. In the same manner, the rubber component in the AA tape was identified as poly(butyl acrylate) (PBA) using the EGA-MS Polymer Library. An average mass spectrum corresponding to the specific EGA profile from 320 to 440°C (B) shown in Fig. 2 (b) was used for the identification. The observed mass spectrum for B is shown in Fig. 5 together with the reference spectrum in the library. The pyrogram (B) also showed a typical pattern of PBA. The main decomposition products were identified as 1-butene, 1-butanol, butyl acrylate, dimer of butyl acrylate and trimer of butyl acrylate derived from PBA.

Additives analysis

Figures 6 and 7 show total ion chromatograms (TIC) by MS and specific elemental chromatograms by AED for the thermally desorbed components from the CA tape, and for those from the AA tape, respectively. With results of screening by GC/AED, it was possible to easily find compounds which contained heteroatoms such as nitrogen, sulfur and oxygen in a complex GC/MS chromatogram with vaporized component peaks derived from tackifier. The heteroatom-containing compounds were also able to be identified by the corresponding GC/MS data. As regards the CA tape, it was found that tolylenediisocyanate, trimethylolpropane, and tolylenediamine were used as crosslinking agents, and 2,6-di-*t*-butyl-4-methylphenol and 2,2'-methylenebis-(4-methyl-6-*t*-butylphenol) were used as antioxidants. In

Fig. 6 Thermal desorption chromatograms obtained from the adhesive in the CA tape by pyrolyzer-GC/MS and GC/AED. a, 2,4-tolylenediisocyanate and 2,6-tolylenediisocyanate; b, tolylenediamine; c, 2-phenyl-benzothiazole; d, trimethylolpropane; e, 2,6-di-*t*-butyl-4-methylphenol; f, 2,2'-methylene-bis-(4-methyl-6-*t*-butylphenol).

Fig. 7 Thermal desorption chromatograms obtained from the adhesive in the AA tape by pyrolyzer-GC/MS and GC/AED. a, 2,4-tolylenediisocyanate and 2,6-tolylenediisocyanate; b, 2,4,6-triaminotriazine; c, trimethylolpropane.

addition, 2-phenyl-benzothiazole was found to be a compound related to vulcanization of the rubber. With regard to AA tape, it was found that tolylenediisocyanate, trimethylolpropane, and 2,4,6-triaminotriazine were used as crosslinking agents. Figures 8 (A) and (B) show specific ion monitoring in the EGA profile

for the additives in the CA tape and those in the AA tape, respectively. Specific ion monitoring as a function of temperature for each additive indicated the temperature profiles for the characteristic evolved gases. As for the adhesive of the CA tape, the maximum evolution temperatures for

Fig. 8 Specific ion monitoring in the EGA profile for (A) the additives in the CA tape and (B) those in the AA tape. a, tolylenediisocyanate (m/z 174); b, trimethylolpropane (m/z 86); c, tolylenediamine (m/z 122); d, 2,6-di-*t*-butyl-4-methylphenol (m/z 220); e, 2,2'-methylene-bis-(4-methyl-6-*t*-butylphenol) (m/z 340); f, 2-phenylbenzothiazole (m/z 211); g, 2,4,6-triaminotriazine (m/z 126).

tolylenediisocyanate, trimethylolpropane, tolylenediamine, 2,6-di-*t*-butyl-4-methylphenol, 2,2'-methylene-bis-(4-methyl-6-*t*-butylphenol), and 2-phenylbenzothiazole were estimated to be around 270, 280, 250, 140, 200, and 210°C respectively. As for the adhesive of the AA tape, the maximum evolution temperatures for tolylenediisocyanate, trimethylolpropane, and 2,4,6-triaminotriazine were estimated to be around 260, 270, and 270°C respectively. Thus, it was confirmed that the crosslinking agents of the rubber evolved at around 270°C, which was below the pyrolysis starting temperature of the rubber (*ca.* 300°C).

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