Convenient Determination of Methoxy Groups of Methylated Melamine-Formaldehyde Resins by IR Spectroscopy

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Synopsis

The content of methoxy groups of methylated melamine-formaldehyde resins was determined by infrared spectroscopy. The correlation between the area ratio (S) of 815 cm^{-1} band to 913 cm^{-1} band, which are the characteristic absorption bands of triazine and methoxy residue, respectively, and methoxy groups values (OMe) determined by gas liquid chromatography analysis was expressed as $S = 1.08 \times OMe + 0.24$. The correlation coefficient was found to be 0.997.

INTRODUCTION

The content of methoxy groups in methylated melamine-formaldehyde (MF) resins can be calculated by elemental analysis together with the content of methanol by gas liquid chromatography (GLC) after phosphoric acid decomposition of MF resins. This method, however, requires a long time and cannot be applied for methoxy group analysis of cured film.

In the case of analytical characterization of alkylated amino resins, which was reviewed by Christensen,[1] we may use three methods for the qualitative identification and the quantitative determination of the usually encountered alkoxy group of amino resins: nuclear magnetic resonance (NMR) spectroscopy, alcohol exchange reaction followed by GLC, and Zeisel cleavage followed by GLC. The methoxy group content of one mole of melamine residue cannot be obtained by means of ^1H NMR spectroscopy without the combined use of GLC.[2] Both alcohol exchange reaction and Zeisel cleavage take a long time to perform. Moreover, the samples must be soluble in some solvent. On the other hand, infrared (IR) spectroscopy can be used to investigate the change of each characteristic absorption of the functional groups during reaction.[3-7]

In the present study, we describe the correlation between the methoxy group content and one parameter of the IR spectrum: the area ratio of the methoxy group absorption at 913 cm^{-1} to the triazine characteristic absorption at 815 cm^{-1}. This convenient method allows a determination of the methoxy group of MF resins not only in a solution but in cured film.

Journal of Applied Polymer Science, Vol. 34, 2601-2607 (1987)
 CCC 0021-8995/87/072601-07$04.00

EXPERIMENTAL

Materials

MF resins and methylolmelamine (MM) were supplied by Sanwa Chemical Co. Super special-grade methanol and 2-ethoxyethanol were used for the calibration curve.

The molecular weight of fundamental structure unit, that is melamine residue (T.) was obtained from the nitrogen content by micro-Kjeldahl method using following equation.

$$T. = 14.01 \times 6 \times 100/[\mathrm{N}] \quad (1)$$

Gas-Liquid Chromatography (GLC)

GLC was carried out using Yanaco G80-F equipped with flame ionization detector and 2.25 m × 3 m (i.d.) glass column packed with 15% PEG-1000 on 60–80 mesh Chromosorb W. The nitrogen (99.999%) flow rate was 30 mL/min and chart speed was 20 mm/min. Injection port and detector temperature were 150°C and column temperature was held at 120°C.

IR SPECTROSCOPY

The IR spectra were recorded over the range 1000–750 cm^{-1} using JASCO A-3 infrared spectrometer. The absorbance of KBr or NaCl crystal was compensated by using a blank KBr pellet or NaCl crystal in the reference

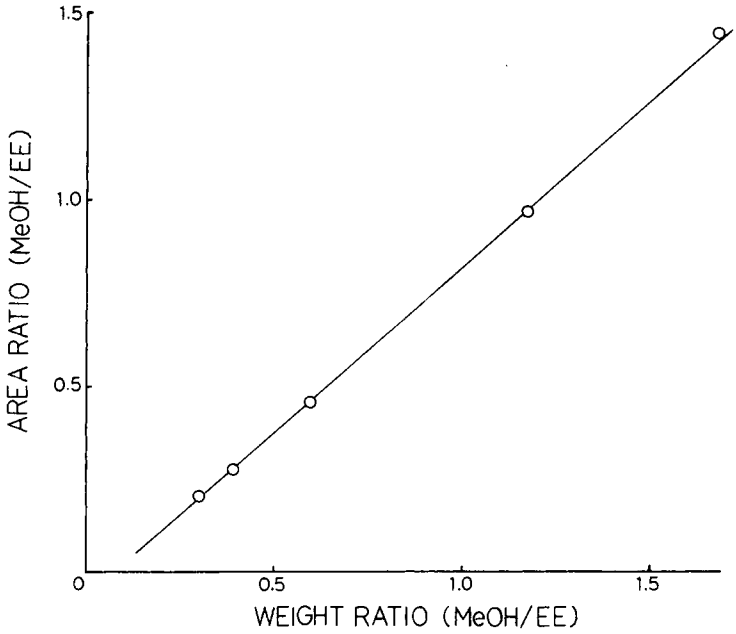

Fig. 1. GLC calibration curve for determining methanol using 2-ethoxyethanol (EE).

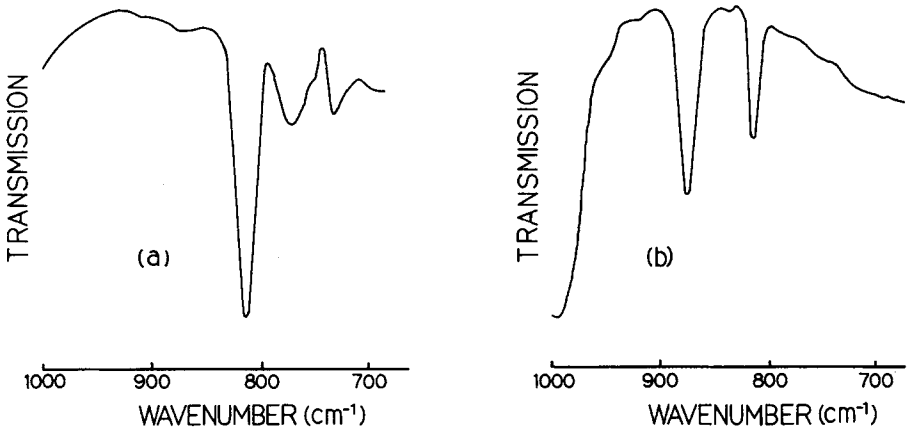

Fig. 2. IR spectra of melamine (a) and MM (b).

beam. The intensity of the band at 913 cm^{-1} was adjusted so that the peak was located between 20 and 40% transmission.

RESULTS AND DISCUSSION

The determination of methoxy group of MF resins was carried out by GLC analysis of methanol after phosphoric acid decomposition of MF resins. The calibration used was obtained from the peak area ratio (Y) of chromatograms with different weight ratio (X) of methanol to 2-ethoxyethanol as internal standard. The calibration curve is shown in Figure 1. The equation was obtained by the least-squares method as follows:

$$Y = 0.876X - 0.061 \tag{2}$$

The methoxy group content of one mole of melamine residue, OMe (mol/*T.*), was calculated by nitrogen analysis using the equation as follows:

$$\text{OMe (mol/}T.\text{)} = (T. \times [\text{MeOH}])/(100 \times 32.0) \tag{3}$$

IR spectra of melamine, MM, and MF resins are shown in Figures 2 and 3. The triazine band at 815 cm^{-1} is common in three spectra, and the characteristic absorption bands at 870 cm^{-1} in MM and at 913 cm^{-1} in MF resin are assigned to methylol group and methoxy group, respectively.[9,10] In order to obtain correlation between the absorbance ratio at 913 cm^{-1} band to 815 cm^{-1} band as internal standard and OMe values determined by GLC, several different base line configurations were evaluated, and the one shown in Figure 3 gave best correlation. Base line tangents are drawn between the tops of the peaks in question; A: between 940 cm^{-1} and about 840 cm^{-1}, B: between 890 cm^{-1} and about 840 cm^{-1}, C: between 830 cm^{-1} and 790 cm^{-1}. S is the ratio of S_{913}, which is obtained by subtracting the area under B (S_B, the shadowed portion) from the area under A (S_A), to S_{815} (the area under C). The areas were measured using a planimeter. S was plotted against OMe by GLC.

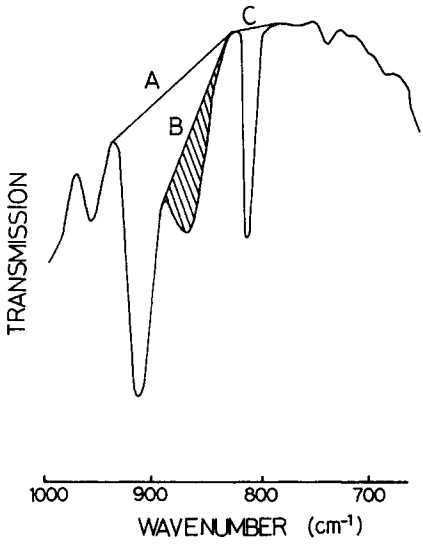

Fig. 3. IR spectrum of MF resin.

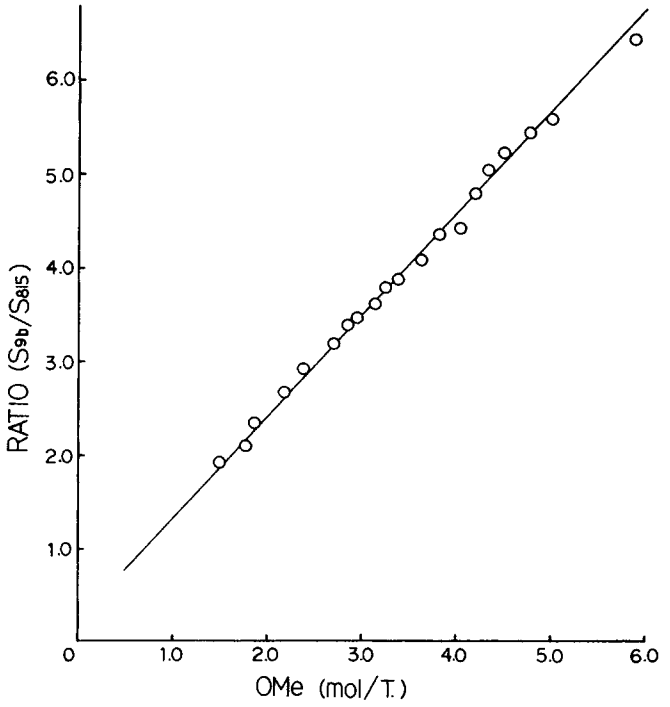

Fig. 4. IR calibration curve for determining methoxy group content.

TABLE I
Methoxy Group Content in MF Resin by GLC and IR

Sample no.	Composition (%)		OMe content (mol/*T*.)			Deviation (%)[a]
	[N]	[MeOH]	GLC	Area ratio	IR	
HM	0	0	0	0	−0.21	
1	32.6	18.9	1.52	1.90	1.54	1.3
2	35.9	24.3	1.78	2.13	1.75	−1.7
3	32.9	23.5	1.87	2.36	1.96	4.8
4	35.0	29.5	2.21	2.68	2.26	2.3
5	31.3	28.5	2.39	2.92	2.48	3.8
6	29.6	30.4	2.70	3.21	2.75	1.8
7	29.9	32.9	2.89	3.40	2.92	1.0
8	27.8	31.4	2.96	3.48	3.00	1.3
9	24.5	29.5	3.16	3.63	3.14	−0.6
10	23.5	29.4	3.28	3.78	3.28	0
11	23.7	30.8	3.41	3.87	3.36	−1.5
12	24.3	33.7	3.64	4.09	3.56	−2.2
13	23.3	34.2	3.85	4.35	3.81	−1.0
14	24.3	37.6	4.06	4.65	4.08	0.5
15	25.4	40.7	4.21	4.78	4.20	−0.2
16	24.2	40.1	4.35	5.05	4.45	2.3
17	25.3	43.7	4.53	5.25	4.64	2.4
18	24.1	44.0	4.79	5.44	4.81	0.4
19	23.3	44.7	5.03	5.58	4.94	−1.8
20	21.9	49.5	5.93	6.44	5.74	−3.2

[a] $\frac{\text{OMe(IR)} - \text{OMe(GLC)}}{\text{OMe(GLC)}} \times 100.$

The result is shown in Figure 4. The regression line shown in the figure was expressed as follows:

$$S = 1.08 \times \text{OMe} + 0.24 \tag{4}$$

The correlation coefficient was 0.997. In order to compare both methods, the values of S and OMe determined by GLC and IR are shown in Table I. The values of OMe obtained from Eq. (4) by IR spectra were in fair agreement with those by GLC.

The MF resin solution was applied on NaCl crystal directly and allowed to dry at 30°C under reduced pressure (below 5 mmHg) for 1 h. Figure 5 shows the comparison of OMe values obtained by GLC of analytical samples and those by IR of MF resin solutions. As seen in the figure, it can be considered that the method by casting MF resin solution approximately satisfies Eq. (4). This method can be applied to determine OMe of cured resin which is not soluble in any solvent, allowing the behavior of OMe in the curing process of MF resin to be studied. OMe values of films casting varnish on NaCl crystal before curing were carried out. Table II shows the results that OMe contents of MF resin blended in acrylic copolymers consisting of methyl methacrylate, ethyl acrylate, and 2-hydroxypropyl acrylate also agreed with those obtained from MF resin itself by GLC.

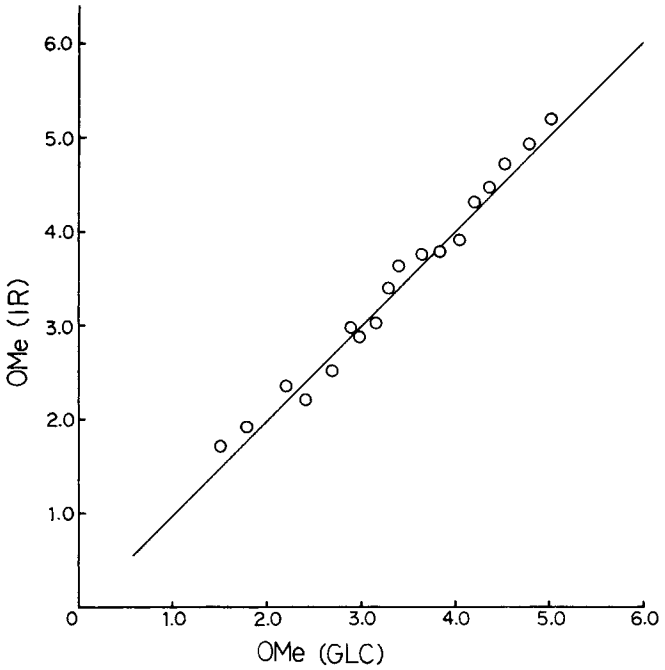

Fig. 5. OMe values obtained by GLC of analytical samples and by IR spectrum of MF resin solutions.

TABLE II
Determination of Methoxy Groups in Varnish

Sample no.	Area ratio	OMe (mol/*T.*)	
		IR	GLC[a]
21	1.25	0.94	1.04
22	3.31	2.84	2.83
23	3.61	3.12	3.02
24	4.29	3.75	3.61
25	4.96	4.37	4.50
26	5.67	5.03	5.10

[a]Values for MF resins before mixing acrylic copolymers.

In conclusion, the characteristic of OMe group determination of MF resin by IR spectroscopy is in application to OMe group of cured film, which cannot be determined by any other method, and this method is useful to follow the behavior of OMe in the curing process of MF resin.

The authors wish to thank Sanwa Chemical Co. for presentation of samples. They are also grateful to Dr. M. Nakashima for many valuable discussions.

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Received August 20, 1986
Accepted March 30, 1987