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COMPOSITIONAL ANALYSIS OF ACRYLIC THEMOSETTING COATINGS BY PYROLYSIS-GAS CHROMATOGRAPHY

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ABSTRACT

A method for compositional analysis of acrylic coatings by pyrolysis-gas chromatography (Py-GC) is described. 2-Hydroxyethyl methacrylate (HEMA)-butyl acrylate (BA)-ethyl methacrylate (EMA) terpolymers cross-linked with butoxy melamine resin, containing either TiO_2, Fe_2O_3 or Carbon black pigment were used as model coating compounds. Pyrolysis was performed at 590°C using a Curie-point pyrolyzer. When the ratio of acrylic resin / melamine resin in the coating sample varied, the HEMA/EMA ratio in the pyrolytic products varied. This ratio was also affected by the kind and the amount of the pigment. Therefore, tile HEMA / EMA ratio in the sample could not be determined directly. On the other hand, the BA content could be directly determined from the BA monomer/diner ratio in the pyrolytic products. The composition of the acrylic resins in the coating samples could be calculated from the BA content and the BA/EMA ratio, directly by Py-GC.

Coatings; gas chromatography; polymers; pyrolysis; resins.

INTRODUCTION

Acrylic resins are widely used as coating materials. Most of the coatings are cross-linked with, for example, melamine resins by thermosetting and contain various pigments [1]. Such coatings have been characterized using IR or NMR after removal of the pigments. However, there is a need to establish a direct and simple method of characterization for very small samples of material, e.g. sub-milligram quantities.

Pyrolysis-gas chromatography (Py-GC) has been used for the characterization of very small samples of polymers regardless of their form [2-5] and has been successfully applied to the compositional analysis of acrylic polymer by using the characteristic peak area ratios on the pyrogram [6-8].

In this paper, the 2-hydroxyethyl methacrylate (HEMA)-butyl acrylate (BA)-ethyl methacrylate (EMA) terpolymers cross-linked with a butoxy

malamine resin, containing TiO_2, Fe_2O_3 or carbon black pigment were prepared as model compounds for acrylic coating polymers, and their compositional analysis was studied.

EXPERIMENTAL

Samples

The HEMA-BA-EMA terpolymers listed in Table 1 were synthesized as described in a previous paper [6], These acrylic resins were mixed with a butoxy melamine (Melane 22, Hitachi Chemical Co.) in different ratios, coated on a glass plate with or without pigments such as TiO2 (JR-602, Teikoku KaKo Co.), Fe2O3 (Bayferrox Iron Oxide Red 160M, Bayer) or carbon black (Neospectramark II, Columbian Chemical Co.) and were then thermoset at 170°C for 30 min. As summarized in Table 2, the prepared coating samples were classified into three series: A, B and C.

Pyrolysis -gas chromatographic conditions

An induction heating Curie-point pyrolyzer (Japan Analytical Industry, Model JHP-2) was used. A sample by less than 0.1 mg wrapped with a piece of foil, whose Curie temperature was 590°C, was subjected to pyrolysis under a flow of nitrogen carrier gas. A glass column (2 m x 3 mm I.D.) packed with 10% Thermon 3000 on Chromosorb W (60-80 mesh) was used for the gas chromatographic separation. The column temperature was programmed from 50°C to 220°C at a rate of 5 °C /min.

TABLE1
Composition of terpolymer samples

sample No.	composition (mole%)		
	HEMA	BA	EMA
1	10.0	20.0	70.0
2	10.0	45.0	45.0
3	20.0	70.0	20.0
4	20.0	20.0	60.0
5	20.0	40.0	40.0
6	40.0	60.0	20.0
7	40.0	20.0	40.0
8	40.0	30.0	30.0
9	40.0	40.0	20.0

TABLE 2

Prepared coatjng samples

Sample	Acrylic resin No	Acrylic resin/ melamine resin	Pigment/resin		
			TiO2,	Fe2O3	Carbon
A-1	2	9/1	-	-	-
A-2	2	8/2	-	-	-
A-3	2	7/3	-	-	-
A-4	2	6/4	-	-	-
A-5	8	9/1	-	-	-
A-6	8	8/2	-	-	-
A-7	8	7/3	-	-	-
A-8	8	6/4	-	-	-
B-l	2	7/3	1/1	-	-
B-2	2	7/3	2/1	-	-
B-3	2	7/3	-	1/2	
B-4	2	7/3	-	1/1	
B-5	2	7/3	-	-	1/10
B-6	2	7/3	-	-	1/5
B-7	8	7/3	1/1	-	-
B-8	8	7/3	2/1	-	-
B-9	8	7/3	-	1/2	
B-10	8	7/3	-	1/1	
B-11	8	7/3	-	-	1/10
B-12	8	7/3	-	-	1/5
C-1	1	7/3	2/1	-	-
C-2	2	7/3	2/1	-	-
C-3	3	7/3	2/1	-	-
C-4	4	7/3	2/1	-	-
C-5	5	7/3	2/1	-	-
C-6	6	7/3	2/1	-	-
C-7	7	7/3	2/1	-	-
C-8	8	7/3	2/1	-	-
C-9	9	7/3	2/1	-	-

Identification of the peaks was carried out by a pyrolysis-gas chromaiography-mass spectrometer system (JEOL, JMS-DX 303, electron impact, 70 eV) .

RESULTS AND DISCUSSION

Effect of cross-linked melamine resin

The pyrograms of HEMA-BA-EMA terpolymer with or without cross-linking with the butoxy melamine resin and that of butoxy melamine resin are shown in Fig. 1 .The main pyrolytic products of the butoxy melamine

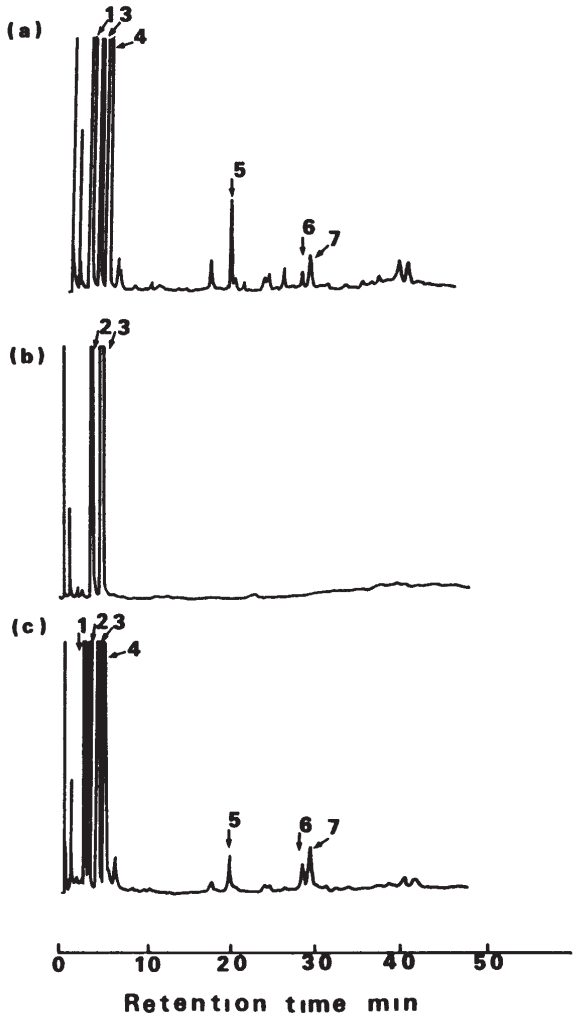

Fig 1 Typical pyrogram of acrylic resin cross linked with butoxy melamine resin (a) HEMA–BA–EMA terpolymer (b) butoxy melamine resin (c) cross linked acrylic resin (sample A 3 in Table 2) Peaks 1 = EMA 2 = isobutanol 3 = *n* butanol 4 = BA 5 = HEMA 6 = BA dimer (1) $CH_2-CH_2-CH_2$ ($COOC_4H_9$, $COOC_4H_9$) 7 = BA dimer (2) $CH_2=C-CH_2-CH_2$ ($COOC_4H_9$, $COOC_4H_9$)

resin are isobutanol and n-butanol, and those of the cross-linked polymer consist of the products of HEMA-BA-EMA terpolymer in addition to the characteristic ones of the melamine resin.

Fig. 2 shows the HEMA/EMA and BA/EMA peak area ratios on the pyrogram for the A-series samples in Table 2 as a function of the mixed melamine content. The dashed line in Fig.2 indicates the values for the HEMA-BA-EMA terpolymer without butoxy melamine resin. These data show that as the melamine resin content increases the HEMA/EMA ratio decreases but the BA/EMA ratio is almost constant regardless of the

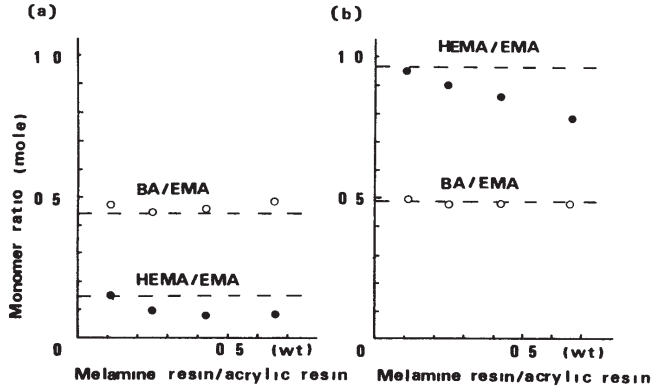

Fig 2 Variation of HEMA/EMA and BA/EMA ratios in the pyrolytic products with the melamine resin/acrylic resin ratio in the cross linked polymer (a) A 1–A 4 samples in Table 2 (b) A 5–A 8 samples in Table 2 The dashed line indicates the values without butoxy melamine resin

coexisting melamine resin. The variation of the HEMA/EMA ratio in Fig. 2 is a consequence of the fact that the -OH functional group of HEMA monomer reacts with the $N\text{-}CH_2OR$ functional group of melamine resin by thermosetting.

Effect of pigment

The effect of typical pigments such as TiO2, Fe_2O_3 and carbon black is shown for the B-series samples in Table 2.

Table 3 shows the variations of HEMA/EMA and BA /EMA ratios in the pyrolytic products with the pigment content in the samples. It is noted that the HEMA/EMA ratio changes depending on the kind and the amount

TABLE 3

Variation of HEMA/EMA and BA/EMA mole ratios in the pyrolytic products with the kinds and the amounts of the pigments

Pigment		Sample	HEMA/ EMA	BA/ EMA	Sample	HEMA/ EMA	BA/ EMA
Kind	P/R *						
TiO_2	1 0	B 1	0 07	0 45	B 7	0 57	0 47
TiO_2	2 0	B 2	0 04	0 45	B 8	0 41	0 47
Fe_2O_3	0 5	B 3	0 10	0 44	B 9	0 75	0 48
Fe_2O_3	1 0	B 4	0 10	0 44	B 10	0 71	0 49
Carbon black	0 1	B 5	0 14	0 46	B 11	0 91	0 49
Carbon black	0 2	B 6	0 13	0 45	B 12	0 94	0 50
–	–	No 2	0 15	0 44	No 8	0 96	0 49

* P/R = pigment/resin (w/w)

of the pigments. In the case of carbon black pigment, this ratio is almost constant, but in the case of the TiO_2 and Fe_2O_3 pigments, this ratio decreases as the pigment content increases. The rate of decrease in TiO_2 is larger than that in Fe_2O_3.

The BA/EMA ratio is constant regardless of the kind and the amount of the pigments. These data suggest that the effect of the pigments is more significant for the degradation of the HEMA unit than for that of the BA and EMA units.

Compositional analysis of acrylic resin

The results from Fig. 2 and Table 4 indicate that the HEMA/EMA ratio among the pyrolytic products is affected by the ratio of acrylic resin/melamine resin, and the kinds and the amount of the pigments. Therefore, the sample composition could not be directly obtained using the associated peak ratios in the pyrolytic products. On the other hand, the BA/EMA ratio in the sample might be determined directly from the corresponding pyrolytic products, because the associated peak ratios are almost constant regardless of the coexisting reagents. The BA/EMA ratio of the acrylic resin in the coating is determined by the method reported in a previous paper for the HEMA-acrylate-methacrylate terpolymers [6]. Fig. 3 shows the analytical results for the C-series coating samples. The results are in good agreement with those of the original terpolymer samples.

Then, the determination of BA content in the coating samples was studied. In the usual radical reaction, the distribution is controlled by the ratio of monomer feed in the reaction system. Furthermore, the acrylic monomer/dimer ratio in the pyrolytic products changes depending on the distribution of acrylate monomer units in the acrylate-metacrylate copolymer [8]. Fig. 4 shows the relationship between the BA content in the terpolymer in Table 1 and the observed BA monomer/dimer ratio in the pyrolytic products. As the observed monomer/dimer ratio changes as a

TABLE 4

Results from the Py-GC analysis

Sample	Composition (mole %)			Result (mole %)		
	HEMA	BA	EMA	HEMA	BA	EMA
C 2	10 0	45 0	45 0	15 6	42 0	42 4
C 3	10 0	70 0	20 0	7 3	70 0	22 7
C 5	20 0	40 0	40 0	26 5	35 0	38 5
C 6	20 0	60 0	20 0	16 2	62 0	21 8
C 8	40 0	30 0	30 0	36 6	32 0	31 4
C 9	40 0	40 0	20 0	30 1	47 0	22 9

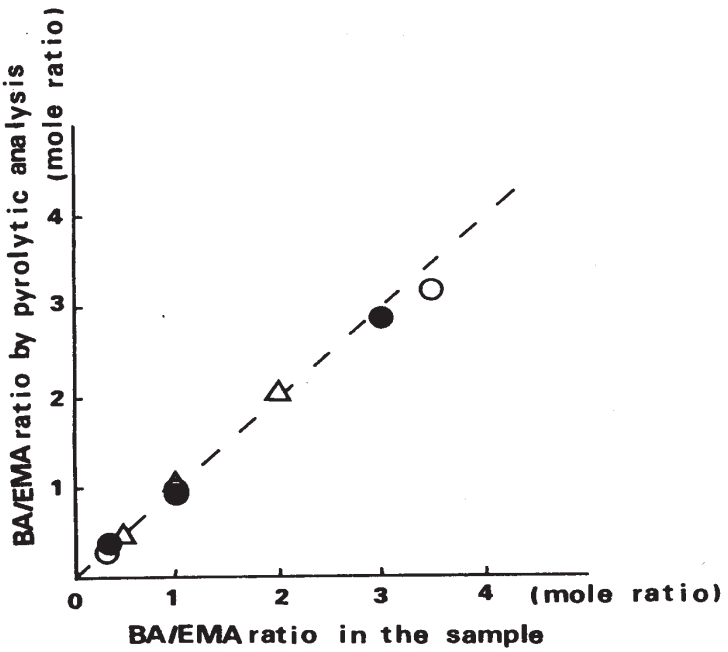

Fig. 3. Correlation of the BA/EMA ratio in the sample and that obtained by pyrolytic analysis. Samples: C-series samples in Table 2 containing 10 mole % (○), 20 mole % (●) and 40 mole % (△) of HEMA unit. Dotted line indicates 1 : 1 relationship between the two ratios.

function of the BA content, the composition of a given sample can be determined using these relationships directly. Fig. 5 shows the relationships between the BA content in the coating samples and the observed results using the BA monomer/dimer ratio. These show good agreement.

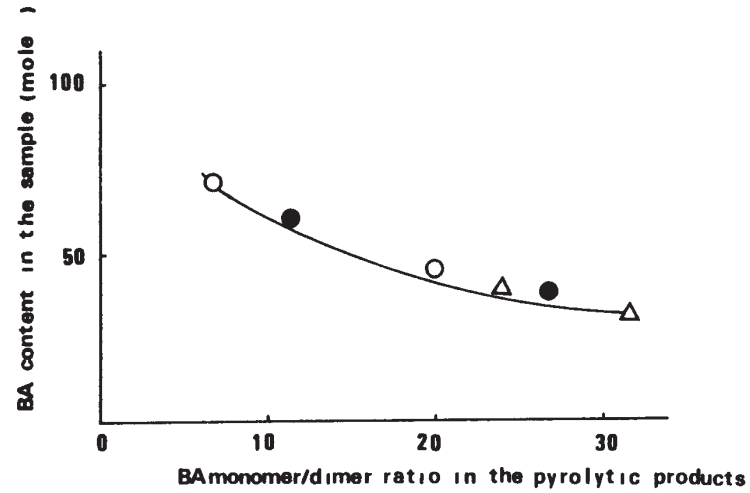

Fig 4 Relationships between the ratio of BA monomer/dimer in pyrolytic products and BA content in HEMA–BA–EMA terpolymers Samples terpolymer samples in Table 1 containing 10 mole % (○) 20 mole % (●) and 40 mole % (△) of HEMA unit In the case of samples No 1 4 and 7 the BA monomer/dimer ratio can not be obtained owing to the small amount of BA dimer product

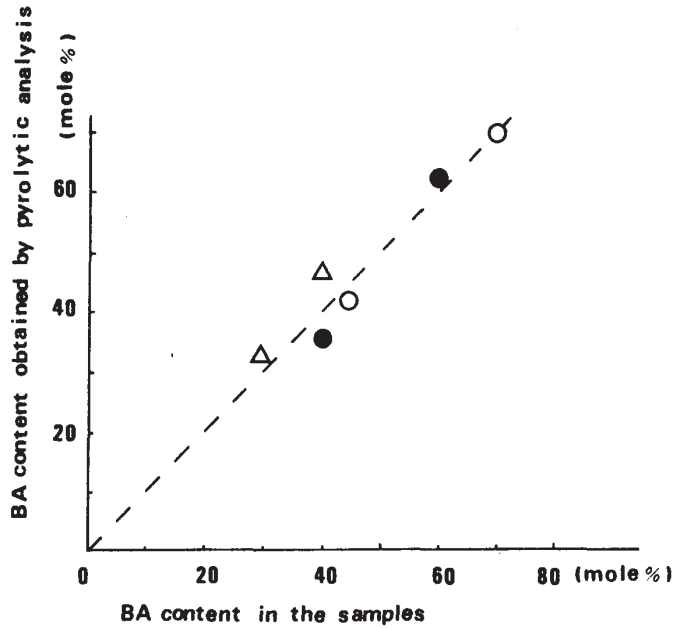

Fig. 5. Correlation of the BA content in the sample and that obtained by pyrolytic analysis. Samples: C-series samples in Table 2 containing 10 mole % (○), 20 mole % (●) and 40 mole % (△) of HEMA unit. In the case of samples C-1, C-4 and C-7, the BA content can not be obtained owing to the small amount of BA dimer product.

Finally by combining the observed data for the BA/EMA ratio and the BA content in the coating samples, the whole composition of the HEMA-BA-EMA terpolymers can be calculated. As shown in Table 5, there is good agreement between them. The relative error was within 9.1% by the method described.

Reproducibility of data was studied for sample No. C-5. In six repeated measurements of the monomer area ratio in the pyrogram, the standard deviation and the coefficients of variation of BA/EMA were 0.02 and 3.7%, those of HEMA/EMA were 0.01 and 6.9%, and those of BA monomer/dimer were 1.58 and 9.3%, respectively.

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