

# Study on Modified Phenolic Resin. III. Modification with *p*-Hydroxyphenylmaleimide/Acrylic Ester Copolymer

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## SYNOPSIS

The improvement of toughness and heat resistance of phenolic resin was examined by blend of novolac and copolymers prepared from *p*-hydroxyphenylmaleimide (HPMI) and acrylic ester. Copolymers of HPMI and acrylic esters, such as methyl acrylate, ethylacrylate, *n*-butylacrylate, or 2-ethylhexyl acrylate, were synthesized. Average molecular weights, glass transition temperatures ( $T_g$ ) and thermal decomposition temperatures were measured. The miscibility of the copolymers with novolac was evaluated. It was found that these copolymers had higher average molecular weight and higher thermal decomposition temperature than those of novolac; they also had good miscibility with novolac. Molding compounds were prepared by hot roll-kneading of mixtures, which involved novolac, the copolymer, hexamethylenetetramine (hexamine), and glass fiber. Test pieces of the modified phenolic resins were prepared by transfer molding from the molding compounds. It was found that phenolic resin, modified with HPMI/ethylacrylate copolymer or HPMI/*n*-butylacrylate copolymer, which consisted of numerous units of acrylic ester, showed both good toughness and good heat resistance.

## INTRODUCTION

Phenolic resin is used widely as an industrial material because of its good heat resistance, electrical insulation, dimensional stability, and chemical resistance. Recently, improvement in properties, especially toughness and heat resistance, have been required particularly for the industrial field. However, the improvement of mechanical properties, especially toughness, is usually incompatible with the improvement of heat resistance.

Many approaches have been tried attempting to improve the heat resistance of phenolic resin. Fukuda et al.<sup>1</sup> have improved the heat resistance of the phenolic resins by means of the after-cure or an increase in hardening agent content. It was reported<sup>2</sup> that high temperature phenolic resins were produced by the addition of a modifier that has good heat re-

sistance. But in these approaches, mechanical properties of phenolic resin, for example, flexural strength or impact resistance, were reduced. While there were a few articles<sup>3,4</sup> related to the modified phenolic resins of which both heat resistance and mechanical properties were superior to unmodified phenolic resin, Shu et al.<sup>3</sup> have developed phenolic resin modified with alkyl titanate in which some phenolic hydroxyl group was reacted with alkyl titanate and the modified phenolic resin was cured by hexamine. Culbertson et al.<sup>4</sup> have developed phenolic resin cured by phenylene-bisoxazoline.

In the previous article<sup>5</sup> it was found that the modification of phenolic resin with HPMI/styrene copolymer improved both flexural strength and heat resistance, but didn't much improve the toughness. It is expected that phenolic resin modified with HPMI/acrylic ester copolymer has higher toughness than the phenolic resin modified with HPMI/styrene copolymer, because HPMI/acrylic ester copolymer is more flexible than HPMI/styrene copolymer. Therefore, we studied the heat resistance

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and mechanical properties, especially toughness, of phenolic resin modified with copolymer prepared from HPMI and acrylic ester.

In this study, copolymers of HPMI and acrylic ester, such as methylacrylate (MA), ethylacrylate (EA), *n*-butylacrylate (*n*-BuA), or 2-ethylhexylacrylate (EHA), were synthesized and identified by <sup>1</sup>H-NMR. Average molecular weight,  $T_g$ , and thermal decomposition temperature of the copolymers were measured by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetry (TG), respectively. Composition of the monomer unit in the copolymers was calculated from nuclear magnetic resonance (NMR) and elemental analysis of the copolymers. The miscibility of the copolymers with novolac was then evaluated from the DSC results, reactivity of the copolymers with hexamine was examined, and thermal and mechanical properties, especially toughness, of the test pieces from compounds prepared from novolac, the copolymer, hexamine, and glass fiber were investigated.

## EXPERIMENTAL

### Reagents and Materials

HPMI was supplied from Daihachi Chemical Industry Co., Ltd, and was recrystallized from methanol (mp. 189°C). Styrene (St), Methylacrylate, ethylacrylate, *n*-butylacrylate, and 2-ethylhexylacrylate were refined in the usual way before use. 2,2'-Azobis-isobutyronitrile (AIBN) was recrystallized from methanol. Dimethylformamide (DMF) was dried and distilled before use in a routine manner. Hexamine was used after pulverizing the chem-

ical grade reagent. Novolac (general purpose novolac) and glass fiber (chopped strand, 10.5 μmφ, 4 mm) were purchased from Asahi Yukizai Kogyo Co., Ltd. and Nippon Electric Glass Co., Ltd., respectively. Methanol and acetone, supplied as extra pure reagents, were used without further purification.

### Synthesis of HPMI/Acrylic Ester Copolymers

HPMI/acrylic ester copolymers were synthesized under condition shown in Table I. For example, HPMI/*n*-BuA copolymer (mol ratio, 1/1.2) was synthesized as follows: HPMI 306.72 g (1.62 mol), *n*-BuA 207.63 g (1.62 mol), AIBN 8.856 g (0.054 mol), and DMF 2700 mL were charged in a 3-L, four-necked flask, fitted with stirrer, thermometer, N<sub>2</sub> inlet, and reflux condenser under N<sub>2</sub>. The monomers were polymerized at 70°C for 6 h. The reaction mixture was then poured into a large amount of excess distilled water to precipitate the polymer. The reaction was identified by <sup>1</sup>H-NMR: δ 0.7–1.0 (broad, 3H, CH<sub>3</sub>), δ 1.1–1.8 (broad, 6H, CH<sub>2</sub>), δ 2.9 (s, 1H, CH), δ 3.9 (broad, 2H, CH), δ 3.9–4.3 (broad, 2H, CH<sub>2</sub>), δ 6.6–7.2 (m, 4H, ArH), δ 8.5 (s, 1H, OH). Composition of monomer unit in the copolymer was calculated from area ratio between the CH<sub>3</sub> group of *n*-BuA (0.7–1.0 ppm) and Ph-H group of HPMI (6.6–7.2 ppm). As a result, the composition of HPMI/*n*-BuA was 1/1.12. The composition was also calculated from elemental analysis: H, 6.2%, C, 64.4%, N, 4.1%. As a result, the composition was 1/1.20.

### Properties of HPMI/Acrylic Ester Copolymers

Average molecular weight,  $T_g$ , and thermal decomposition temperature of these copolymers were

**Table I** Properties of HPMI-Vinyl Compound Copolymers

Feed			Copolymer					
M1	M2	M1/M2 (mol/L) (mol/L)	Yield (%)	Mole Ratio M1/M2	$\overline{M}_n$	$\overline{M}_w$	$T_g$ (°C)	Temp. at Loss of 10 wt % (°C)
HPMI	St	0.37/0.37	95	1/1	$1.6 \times 10^4$	$9.1 \times 10^4$	196	397
HPMI	MA	0.60/0.60	92	1/1.1	$1.4 \times 10^4$	$2.4 \times 10^4$	180	329
HPMI	EA	0.60/0.60	88	1/0.8	$1.7 \times 10^4$	$2.9 \times 10^4$	157	364
HPMI	<i>n</i> -BuA	0.60/0.60	91	1/1.2	$1.2 \times 10^4$	$2.8 \times 10^4$	135	371
HPMI	2-EHA	0.60/0.60	94	1/0.9	$1.8 \times 10^4$	$3.1 \times 10^4$	110	354
HPMI	EA	0.24/0.96	83	1/3.8	$7.8 \times 10^3$	$2.6 \times 10^4$	30	369
HPMI	<i>n</i> -BuA	0.24/0.96	81	1/3.6	$1.1 \times 10^4$	$2.9 \times 10^4$	-2	376
HPMI	2-EHA	0.24/0.96	81	1/3.8	$1.6 \times 10^4$	$3.8 \times 10^4$	-23	372

Condition of polymerization: 70°C, 6 h in DMF.

Initiator: (AIBN) = 0.020 mol/L, except 0.144 mol/L in the case of HPMI/St copolymer.

measured by GPC, DSC, and TG, respectively. Composition of the monomer units in the copolymers were calculated from  $^1\text{H-NMR}$  and elemental analysis of the copolymers. Composition of the monomer units in the HPMI/St copolymer and HPMI/MA copolymer were only calculated from elemental analysis of the copolymers, because the absorption band of  $^1\text{H-NMR}$  from HPMI overlapped with that of the comonomer. The composition of the each copolymers is as follows: HPMI/St (1/1), HPMI/MA (1/1.1), HPMI/EA (1/0.8), HPMI/*n*-BuA (1/1.2), HPMI/EHA (1/0.9), HPMI/EA (1/3.8), HPMI/*n*-BuA (1/3.6), and HPMI/EHA (1/3.8) copolymer.

### Miscibility of Novolac with HPMI/Acrylic Ester Copolymer

Novolac and HPMI/acrylic ester copolymer were dissolved in tetrahydrofuran (THF). The blends of novolac and the copolymer were prepared from the polymer solution by evaporating THF. The miscibility of the blends was examined by DSC and optical microscope observation, equipped with hot plate.

### Molding and Test Pieces

The molding compounds were prepared by hot roll-kneading the mixture of novolac and HPMI/acrylic ester copolymer, hexamine (12 phr), zinc stearate (2 phr) as lubricant, and glass fiber (100 phr) at 100–110°C for a time that required moldability for transfer molding.

Three kinds of test pieces were prepared by transfer molding from the molding compounds preheated by high frequency dielectric heating. Molding conditions, such as temperature, pressure, and time, were 170°C, 100 kg/cm<sup>2</sup>, and 10 min, respectively.

Rectangular test pieces, 110 × 12 × 6 mm, were used for the measurements of deflection temperature under load and flexural properties. Notched rectangular test pieces, 88 × 15 × 15 mm, were used for measurement of impact strength. Disk test pieces, 50 mm  $\phi$  × 3 mm, were used for the measurement of electrical properties and water absorption.

### Testing Methods

#### Flexural Properties

The flexural properties were measured on the rectangular samples according to JIS K 6911. The span between the two supports was 100 mm, and the crosshead speed was 3 mm/min.

#### Impact Strength

Toughness was estimated by impact strength. The impact strength was measured on the rectangular notched sample by Charpy impact tester according to JIS K 6911. The weight of the hammer was 0.862 kg, and the distance between the axis of rotation and the center of gravity of the hammer was 21 cm.

#### Thermal Properties

Deflection temperature under load was measured on the rectangular sample according to JIS K 6911. The span between the two supports was 100 mm. Thermal decomposition behavior of samples was measured by TG in N<sub>2</sub> atmosphere. The heating rate was 10°C/min. The  $T_g$  was measured by DSC. The heating rate was 10°C/min.

#### Curing Behavior

The curing behavior was measured by DSC thermogram referred to JIS K 7122. The initial temperature ( $T_i$ ), the maximum temperature ( $T_p$ ), and the end temperature ( $T_e$ ) of exotherm curve were read and the exotherm energy of curing ( $\Delta H$ ) was calculated from the exotherm curve.

The gelation time at 150°C was measured by the stroke cure method, according to JIS K 6910.

The reactivity of HPMI/acrylic ester copolymer and hexamine was examined by Curelastometer V (Japan Synthetic Rubber Co.). The sample was charged in the molds in which the temperature was already adjusted to the preset level at 170°C. The molds were closed and the lower mold was oscillated 100 cpm at  $\pm\frac{1}{4}^\circ$ . When the viscosity of the sample in the molds increased to a certain value during cure, the value was detected as torque by a load cell that was attached to the upper mold. Curing behavior of the sample, namely the mode of increasing viscosity of the sample, was then obtained as a torque–cure time curve.

#### Electrical Properties

Surface and volume resistivities were measured by a High Resistance Meter (Yokogawa–Hewlett–Packard Co.).

#### Boiling Tests

Test pieces (disks) were treated in boiled, distilled water for 2 or 4 h, and the water absorption and electrical properties of the treated disks were measured at room temperature.

### Molecular Weight

Molecular weight was measured by GPC. (eluent: THF; standard: polystyrene  $\overline{M}_n = 1800 \times 10^3$ ,  $670 \times 10^3$ ,  $200 \times 10^3$ ,  $110 \times 10^3$ ,  $37 \times 10^3$ ,  $20.4 \times 10^3$ ,  $10 \times 10^3$ ,  $4 \times 10^3$ ,  $2 \times 10^3$ , and  $0.8 \times 10^3$ ; equipment: Waters ALC/GPC 150C)

## RESULTS AND DISCUSSION

### Properties of HPMI/Acrylic Ester Copolymers

Properties of HPMI-vinyl compound copolymers are shown in Table I. The average molecular weight of these copolymers was much higher than that of novolac ( $\overline{M}_n = 500\text{--}600$ ). The order of the thermal decomposition temperature was as follows: HPMI/St copolymer > HPMI/acrylic ester copolymers > novolac (298°C). The  $T_g$  of HPMI/acrylic ester copolymers decreased with an increase in the length of the alkyl group of acrylic ester.

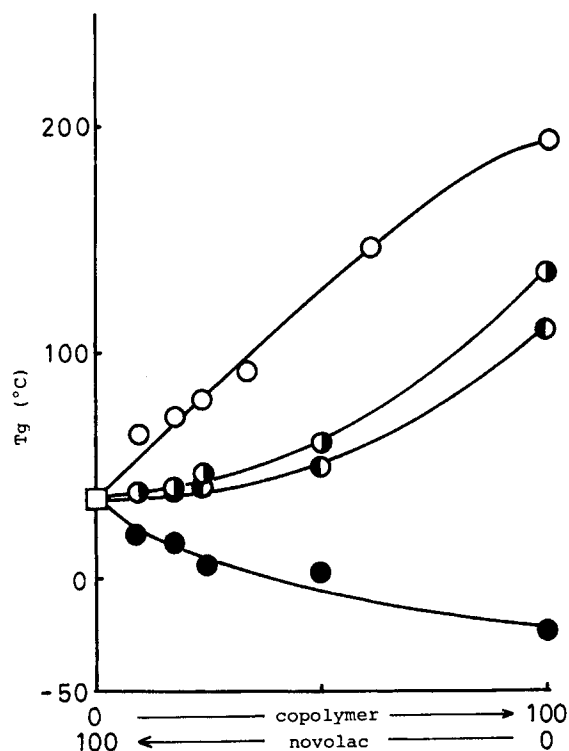
The results of the experiment suggest that these copolymers will be effective for the improvement of the heat resistance of phenolic resin, and especially that the copolymers, which have low  $T_g$  and high average molecular weight, will be effective for the improvement of the toughness of phenolic resin, because they have considerable flexibility.

### Modification of Two-Stage Phenolic Resin with HPMI/Acrylic Ester Copolymer

#### Miscibility of Novolac and HPMI/Acrylic Ester Copolymer

It is expected that HPMI/acrylic ester copolymers react with an hardening agent and change into a crosslinked structure, because the copolymers have a phenolic group. It is also expected that the copolymers are miscible with novolac. In addition, it is conceivable that the copolymer was more flexible than the HPMI/St copolymer or the HPMI homopolymer. We tried to improve the properties of the two-stage phenolic resin by the addition of the copolymer.

First of all, the miscibility of the copolymers and novolac was examined by DSC. Figure 1 shows the relationship between  $T_g$  of the blends and wt % of the copolymer in the mixture. The  $T_g$  of the mixture increased with increasing the fraction of the copolymer. The results suggest that these copolymers are miscible with novolac. The observation in the optical microscope was also recognized; when the temperature of the mixture was raised slowly, the samples



**Figure 1**  $T_g$  of mixture of novolac and HPMI-vinyl compound copolymer. ○: HPMI/St (1/1) copolymer ( $\overline{M}_n = 16000$ ,  $\overline{M}_w = 91000$ ) ○●: HPMI/*n*-BuA (1/1.2) copolymer ( $\overline{M}_n = 12000$ ,  $\overline{M}_w = 28000$ ) ●●: HPMI/EHA (1/0.9) copolymer ( $\overline{M}_n = 18000$ ,  $\overline{M}_w = 31000$ ) ●●: HPMI/EHA (1/3.8) copolymer ( $\overline{M}_n = 16000$ ,  $\overline{M}_w = 38000$ ).

flowed at a specific, precise temperature. These results were supported by a solubility parameter value (SP value), which was calculated from eq. (1), proposed by Fedors.<sup>6</sup>

$$\delta = (\sum \Delta e_i / \sum \Delta v_i)^{1/2} \quad (1)$$

where  $\delta$ : solubility parameter value (SP value),  $\Delta e_i$ : energy of vaporization of atom or group, and  $\Delta v_i$ : molar volume of atom or group.

The SP values of novolac, HPMI/MA (1/1.1) copolymer, HPMI/EA (1/0.8) copolymer, HPMI/*n*-BuA (1/1.2) copolymer, and HPMI/EHA (1/0.9) copolymer, which were calculated from eq. (1), were 14.1, 13.6, 13.7, 12.5, and 12.0 (cal/cm<sup>3</sup>)<sup>1/2</sup>, respectively. The differences between the SP value of novolac and that of the HPMI/acrylic ester copolymer were 0.5, 0.4, 1.6, and 2.1 (cal/cm<sup>3</sup>)<sup>1/2</sup> respectively (Table II). For comparison, SP values polyphenyleneether (PPE) and polystyrene (PS), which are well known as miscible polymers, were 11.3 (cal/cm<sup>3</sup>)<sup>1/2</sup> and 9.8 (cal/cm<sup>3</sup>)<sup>1/2</sup>, respectively, according to eq. (1). The difference of both SP val-

**Table II SP Value of Polymers**

	$\delta$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	$\Delta\delta^a$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>
Novolac	14.1	
HPMI/1.1 MA	13.6	0.5
HPMI/0.8 EA	13.7	0.4
HPMI/1.2 <i>n</i> -BuA	12.5	1.6
HPMI/0.9 EHA	12.0	2.1
<i>cf.</i> PPE	11.3	
PS	9.8	1.5

<sup>a</sup>  $\Delta\delta = \delta(\text{Novolac}) - \delta(\text{copolymer})$ , or  $\delta(\text{PPE}) - \delta(\text{PS})$ .

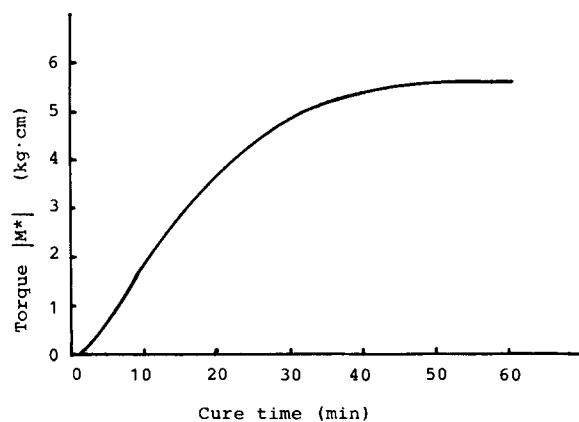
ues were 1.5 (cal/cm<sup>3</sup>)<sup>1/2</sup>. Thus, it was concluded that HPMI/acrylic ester copolymer should have good miscibility with novolac.

### The Reactivity of HPMI/Acrylic Ester Copolymer and Hexamine

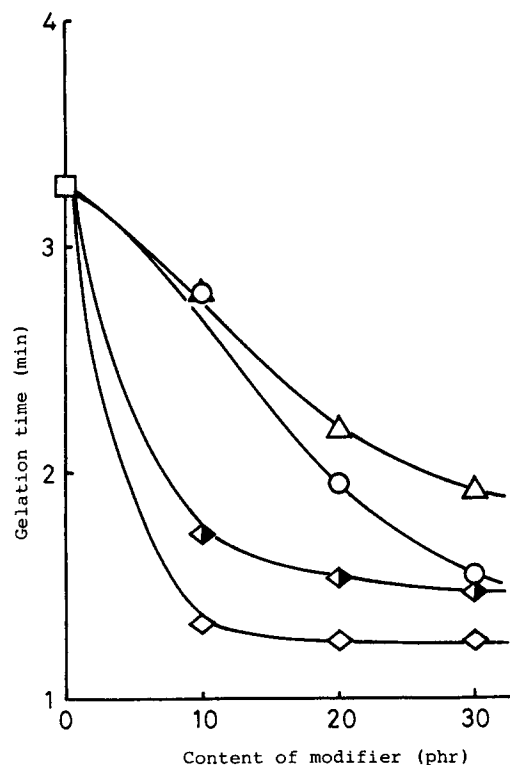
The reactivity of HPMI/*n*-BuA (1/3.6) copolymer and hexamine was examined. HPMI/*n*-BuA (1/3.6) copolymer ( $\overline{M}_n = 1.1 \times 10^4$ ) 15 g and hexamine 2.7 g were dissolved in acetone. The mixture of the copolymer and hexamine was prepared from the polymer solution by evaporating THF. The reactivity of the mixture was measured by Curelasmeter. As a result, the mixture cured, although the curing time was long (Fig. 2).

It was concluded that the copolymer was miscible with novolac before the curing reaction, and that it reacted with the hardening agent changing into a crosslinked structure.

In Figure 3 and Table III, the gelation time by the stroke cure method and the curing behavior of



**Figure 2** Torque-cure time curve of the mixture of HPMI/*n*-BuA (1/3.6) and hexamine obtained by Curelasmeter at 170°C.



**Figure 3** Gelation time of modified phenolic resin ○: modified with HPMI/St (1/1) copolymer ( $\overline{M}_n = 1.6 \times 10^4$ ,  $\overline{M}_w = 9.1 \times 10^4$ ) △: modified with HPMI/*n*-BuA (1/1.2) copolymer ( $\overline{M}_n = 1.2 \times 10^4$ ,  $\overline{M}_w = 2.8 \times 10^4$ ) ◇: modified with HPMI/EHA (1/0.9) copolymer ( $\overline{M}_n = 1.8 \times 10^4$ ,  $\overline{M}_w = 3.1 \times 10^4$ ) ◻: modified with HPMI/EHA (1/3.8) copolymer ( $\overline{M}_n = 1.6 \times 10^4$ ,  $\overline{M}_w = 3.8 \times 10^4$ ).

**Table III Curing Behavior of Modified Phenolic Resin**

Content of Modifier (phr) <sup>a</sup>	Ti <sup>b</sup> (°C)	Tp <sup>c</sup> (°C)	Te <sup>d</sup> (°C)	$\Delta H^e$ (kJ/kg)
0	124	145	168	57.5
HPMI/St <sup>f</sup>				
10	121	141	176	74.1
20	118	141	180	72.6
30	122	141	188	71.1
HPMI/1.2 <i>n</i> -BuA <sup>g</sup>				
10	121	150	196	72.1
20	123	150	198	76.4
30	117	150	196	70.2

<sup>a</sup> Part of modifier per hundred part of phenolic resin hexamine content: 12 phr of modified phenolic resin.

<sup>b</sup> Initial temperature at exotherm curve.

<sup>c</sup> Peak temperature at exotherm curve.

<sup>d</sup> End temperature at exotherm curve.

<sup>e</sup> Exotherm energy of curing.

<sup>f</sup>  $\overline{M}_n = 1.6 \times 10^4$ ,  $\overline{M}_w = 9.1 \times 10^4$ .

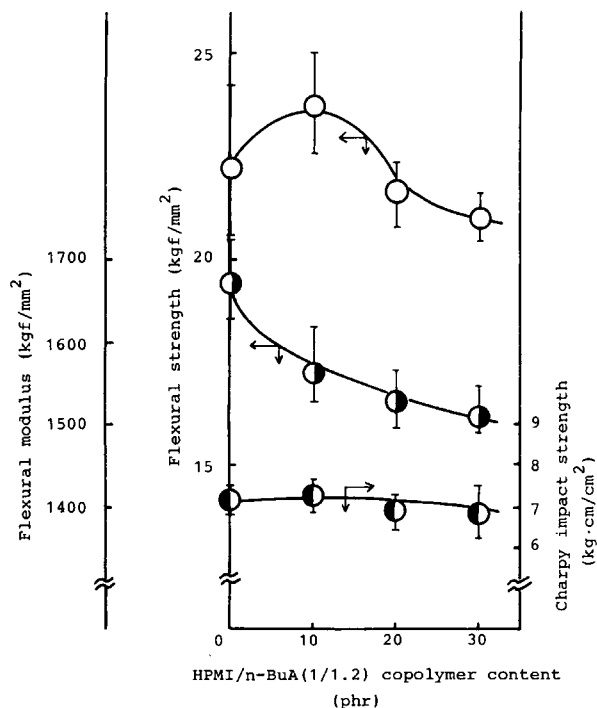
<sup>g</sup>  $\overline{M}_n = 1.2 \times 10^4$ ,  $\overline{M}_w = 2.8 \times 10^4$ .

modified phenolic resins are shown, respectively. The gelation time shortens with an increase in the content of the copolymers and with an increase in the length of the alkyl group in the copolymer. Probably at an early stage of the cure, the melting point of phenolic resin modified with HPMI/acrylic ester copolymer became above 150°C, due to the high molecular weight of the HPMI additives. There is not much difference in the initial and maximum temperatures of the phenolic resin and the modified phenolic resins, but their end temperatures on the exotherm curve increases and the exothermal energy of the cure increases by the modification with HPMI/acrylic ester copolymer.

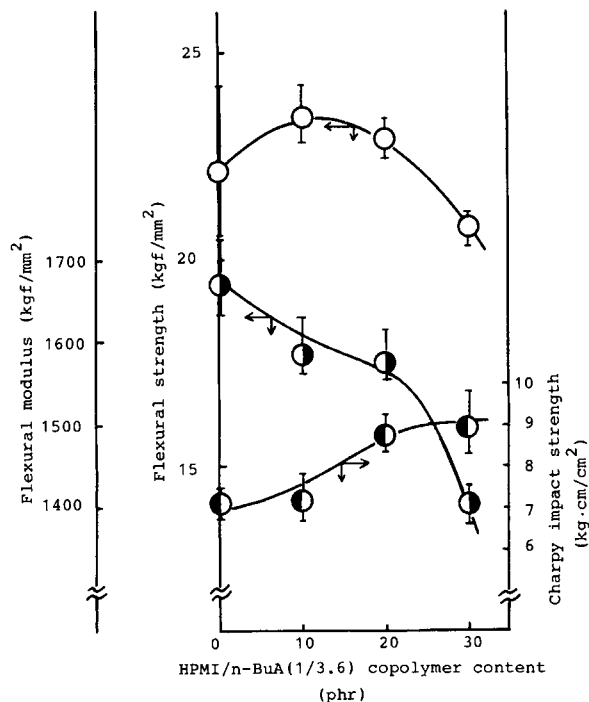
### Properties of Modified Phenolic Resin

#### Mechanical Properties of Modified Phenolic Resin

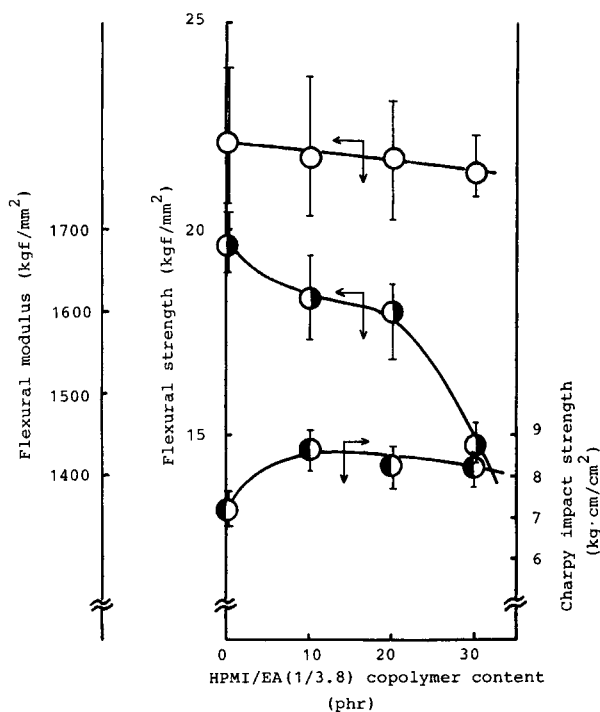
Mechanical properties of phenolic resin modified with HPMI/*n*-BuA (1/1.2) copolymer are shown in Figure 4. The flexural modulus decreased with an increase in the HPMI/*n*-BuA (1/1.2) copolymer because of the flexibility of the copolymer. In addition, the flexural strength increased by the addition of the copolymer when the content of the co-



**Figure 4** Mechanical properties of phenolic resin modified with HPMI/*n*-BuA (1/1.2) copolymer ( $\bar{M}_n = 6.2 \times 10^3$ ,  $\bar{M}_w = 1.4 \times 10^4$ ) ○: Flexural strength ●: Flexural modulus ●: Charpy impact strength.



**Figure 5** Mechanical properties of phenolic resin modified with HPMI/*n*-BuA (1/3.6) copolymer ( $\bar{M}_n = 1.1 \times 10^4$ ,  $\bar{M}_w = 2.9 \times 10^4$ ) ○: Flexural strength ●: Flexural modulus ●: Charpy impact strength.

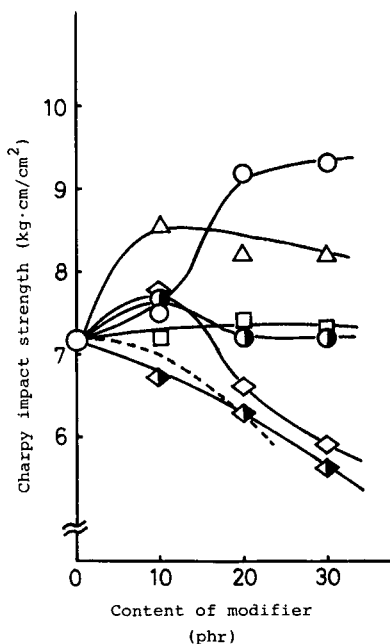


**Figure 6** Mechanical properties of phenolic resin modified with HPMI/EA (1/3.8) copolymer ( $\bar{M}_n = 7.8 \times 10^3$ ,  $\bar{M}_w = 2.6 \times 10^4$ ) ○: Flexural strength ●: Flexural modulus ●: Charpy impact strength.

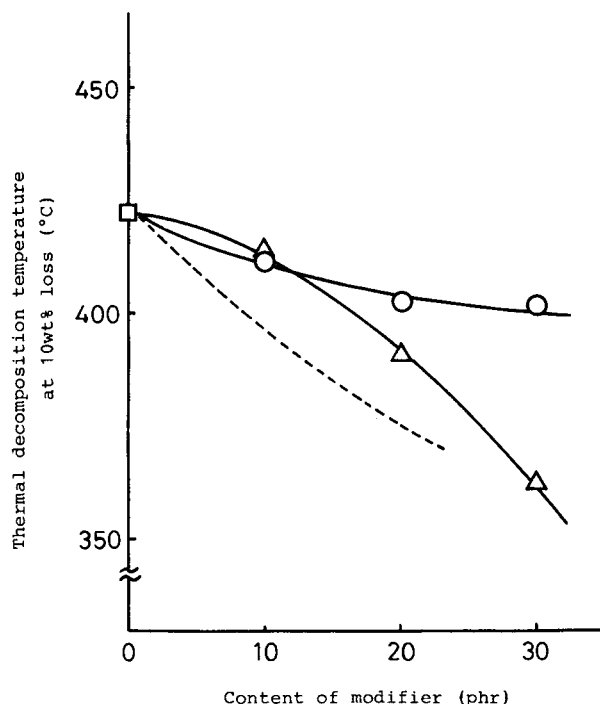
polymer was little, while in the case of phenolic resin modified with HPMI homopolymer, the flexural strength did not increase by the addition of the homopolymer.<sup>7</sup> The reason for this phenomenon could be as follows: Because the HPMI/*n*-BuA (1/1.2) copolymer is more flexible than HPMI homopolymer, the curing reaction of phenolic resin modified with the copolymer can progress smoothly in comparison to that of the phenolic resin modified with HPMI homopolymer. In other words, moldability of the former is better than that of the latter.

The flexural strength, however, decreased when the content of the copolymer was increased. The reason for this phenomenon could be as follows: At an early stage of the curing reaction,  $T_g$  of the mixture of novolac and the copolymer increased rapidly, and then the curing reaction doesn't progress smoothly. These phenomena were similar to those for phenolic resin modified with HPMI/St copolymer.<sup>5</sup>

The mechanical properties of phenolic resin, modified with HPMI/*n*-BuA (1/3.6) copolymer, are shown in Figure 5. Its flexural strength and flexural modulus were of the same tendency as those of the



**Figure 7** Charpy impact strength of modified phenolic resin  $\Delta$ : modified with HPMI/EA (1/3.8) copolymer  $\circ$ : modified with HPMI/*n*-BuA (1/3.6) copolymer  $\diamond$ : modified with HPMI/EHA (1/3.8) copolymer  $\bullet$ : modified with HPMI/*n*-BuA (1/1.2) copolymer  $\circ$ : modified with HPMI/EHA (1/0.9) copolymer  $\square$ : modified with HPMI/St (1/1) copolymer -----: modified with HPMI homopolymer ( $\overline{M}_n = 3.8 \times 10^3$ ,  $\overline{M}_w = 1.0 \times 10^4$ ).



**Figure 8** Thermal decomposition temperature of modified phenolic resin  $\circ$ : modified with HPMI/St (1/1) copolymer ( $\overline{M}_n = 1.6 \times 10^4$ ,  $\overline{M}_w = 9.1 \times 10^4$ )  $\Delta$ : modified with HPMI/*n*-BuA (1/3.6) copolymer ( $\overline{M}_n = 1.1 \times 10^3$ ,  $\overline{M}_w = 2.9 \times 10^4$ ) -----: modified with HPMI homopolymer ( $\overline{M}_n = 3.8 \times 10^3$ ,  $\overline{M}_w = 1.0 \times 10^4$ ).

phenolic resin modified with HPMI/*n*-BuA (1/1.2) copolymer. But the Charpy impact strength of phenolic resin modified with HPMI/*n*-BuA (1/3.6) copolymer was increased with an increase of the content of the copolymer. The reason for this phenomenon could be as follows: Because HPMI/*n*-BuA (1/3.6) copolymer is more flexible than HPMI/*n*-BuA (1/1.2) copolymer, the former can absorb more impact energy than the latter.

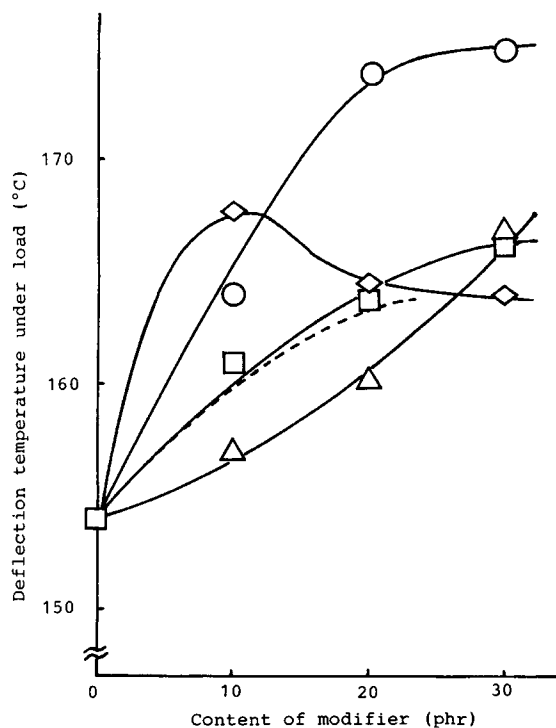
The Charpy impact strength of phenolic resin, modified with HPMI/EA (1/3.8) copolymer, was also increased with an increase of the content of the copolymer (Fig. 6). The reason for this phenomenon could be the same as in the case of phenolic resin modified with HPMI/*n*-BuA (1/3.6) copolymer, as described above.

The comparison of the Charpy impact strength of some kinds of phenolic resin modified with HPMI/vinyl compound copolymer is shown in Figure 7. The phenolic resin modified with HPMI/acrylic ester copolymer, in which the mol content of acrylic ester was about four times as much as it was in HPMI, had high impact strength. The reason for this phenomenon could be that these copolymers

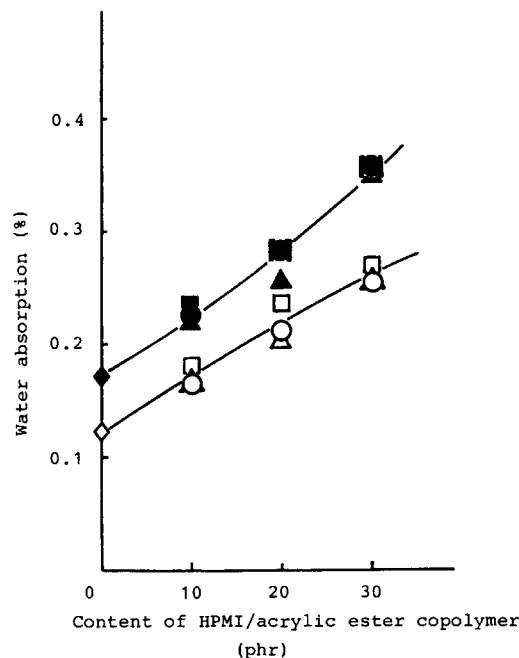
can absorb the impact energy because they have high flexibility. But phenolic resin modified with the HPMI/EHA (1/3.8) copolymer had the opposite tendency. The reason for the phenomenon may be as follows: the HPMI/EHA copolymer becomes immiscible with novolac during the early stages of the cure and the modified phenolic resin does not form the structure of micro phase separation, but of macro phase separation.

### Thermal Properties of Modified Phenolic Resin

Thermal decomposition temperature was defined as the temperature at which the sample showed 10 wt % loss on heating at 10°C/min in N<sub>2</sub> atmosphere (Fig. 8). The samples used for this measurement were the modified phenolic resins that did not contain glass fiber. It was found that thermal decomposition temperature became low with an increase in the content of the copolymer, similar to the case of phenolic resin modified with HPMI homopolymer.<sup>7</sup> The difference in thermal decomposition behavior between phenolic resin modified with HPMI/



**Figure 9** Heat resistance of modified phenolic resin  $\Delta$ : modified with HPMI/EA (1/3.8) copolymer  $\circ$ : modified with HPMI/n-BuA (1/3.6) copolymer  $\diamond$ : modified with HPMI/EHA (1/3.8) copolymer  $\square$ : modified with HPMI/St (1/1) copolymer ----: modified with HPMI homopolymer ( $\overline{M}_n = 3.8 \times 10^3$ ,  $\overline{M}_w = 1.0 \times 10^4$ ).



**Figure 10** Water absorption of phenolic resin modified with HPMI/acrylic ester copolymer after 2 h boiling ( $\circ$ ,  $\Delta$ ,  $\square$ ) and 4h boiling ( $\bullet$ ,  $\blacktriangle$ ,  $\blacksquare$ )  $\circ$ ,  $\bullet$ : modified with HPMI/EA (1/3.8) copolymer  $\Delta$ ,  $\blacktriangle$ : modified with HPMI/n-BuA (1/1.2) copolymer  $\square$ ,  $\blacksquare$ : modified with HPMI/n-BuA (1/3.6) copolymer.

St (1/1) copolymer and it of modified with HPMI/n-BuA (1/3.6) copolymer is a result of the difference of thermal decomposition temperature between HPMI/St (1/1) copolymer and HPMI/n-BuA (1/3.6) copolymer (Table I).

In Figure 9, deflection temperature under a load of modified phenolic resin is shown. It was found that heat resistance was increased by modification with HPMI polymers. Phenolic resin modified with HPMI/n-BuA (1/3.6) copolymer was most effective in HPMI polymers. The reason for this could be as follows: the crosslinking density of phenolic resin modified with HPMI/n-BuA (1/3.6) copolymer may be highest in the modified phenolic resins, probably because the phenolic resin, modified with HPMI/n-BuA (1/3.6) copolymer, has good moldability for the moderate flexibility of the copolymer and its curing reaction progress smoothly.

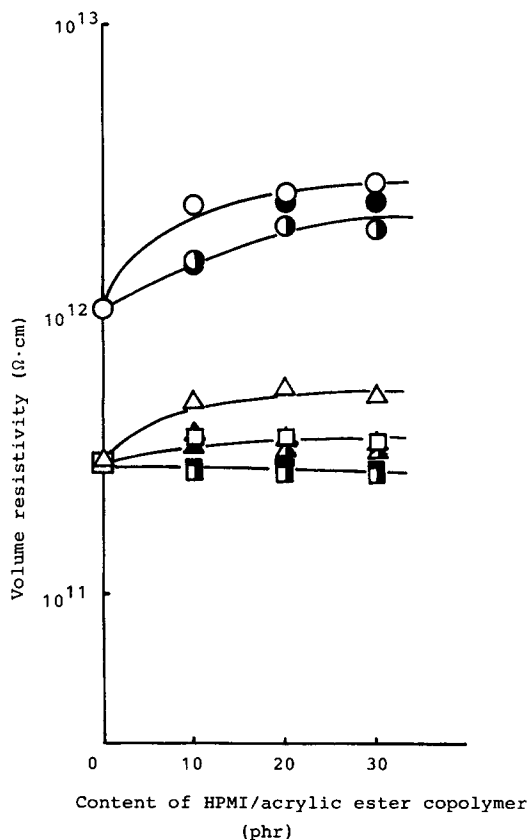
It was concluded from the results described above that phenolic resins modified with HPMI/EA (1/3.8) copolymer or with HPMI/n-BuA (1/3.6) copolymer have higher impact resistance and better physical heat resistance than unmodified phenolic resin.



**Water Absorption and Electrical Insulation**

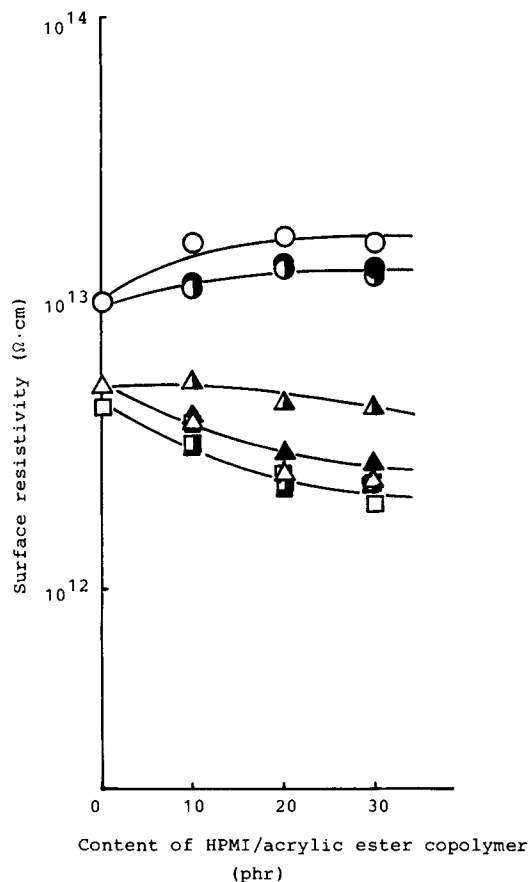
The water absorption of the test pieces was measured at room temperature for samples that were treated by boiling for 2 and 4 h. The results are shown in Figure 10. The amount of water absorption increases with an increase in the content of the HPMI/acrylic ester copolymer, due to its hydrophilic acrylate group and the maleimide group of the copolymer. There was little difference between modified phenolic resins.

The volume and surface resistivities of phenolic resin, modified with HPMI/acrylic ester copolymer, are shown in Figures 11 and 12. The properties of modified phenolic resin after 2 and 4 h of boiling are also shown in the Figures 11 and 12. After boil-



**Figure 11** Volume resistivity of phenolic resin modified with HPMI/acrylic ester copolymer.

modifier	before boiling	after 2h boiling	after 4h boiling
HPMI/EA (1/3.8)	○	△	□
HPMI/n-BuA (1/1.2)	●	▲	■
HPMI/n-BuA (1/3.6)	●	▲	■



**Figure 12** Surface resistivity of phenolic resin modified with HPMI/acrylic ester copolymer.

modifier	before boiling	after 2h boiling	after 4h boiling
HPMI/EA (1/3.8)	○	△	□
HPMI/n-BuA (1/1.2)	●	▲	■
HPMI/n-BuA (1/3.6)	●	▲	■

ing, the surface resistivity of a part of the modified phenolic resin was decreased a little with an increase in the content of the copolymer, but the volume resistivities of the modified phenolic resin were not decreased with an increase of the content of the copolymer. Before boiling, however, the volume and surface resistivities were increased a little by modification with HPMI/acrylic ester copolymer. The reasons for these phenomena could be as follows: (i) Although maleimide group and carbonyl group are polarity groups, the main chain of the modifier is hydrocarbon that was not slightly electrified, (ii) After boiling, electric resistivities decrease because of absorbed water.

## CONCLUSIONS

Copolymers of HPMI and acrylic esters such as MA, EA, *n*-BuA, and EHA were synthesized, and their average molecular weight,  $T_g$ , and thermal decomposition temperature were measured by GPC, DSC, and TG, respectively. It was found that these copolymers had a higher average molecular weight and a higher thermal decomposition temperature than those of novolac.

Molding compounds were prepared by hot roll-kneading of mixtures that involved novolac, the copolymer, hexamine, and glass fiber. Modified phenolic resins were prepared by transfer molding from the molding compounds. It was found that the phenolic resin, modified with HPMI/acrylic ester copolymer, had better heat resistance and better mechanical properties than unmodified phenolic resin. Phenolic resin modified with HPMI/EA (1/3.8) copolymer or HPMI/*n*-BuA (1/3.6) copolymer es-

pecially showed both good toughness and good heat resistance.

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