

Study on Modified Phenolic Resin. I. Modification with Homopolymer Prepared from *p*-Hydroxyphenylmaleimide

A. MATSUMOTO,*¹ K. HASEGAWA,¹ A. FUKUDA,¹ and K. OTSUKI²

¹Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536, Japan;

²Daihachi Chemical Industry Co., Ltd., Osaka, Japan

SYNOPSIS

We studied the improvement of heat resistance and mechanical properties of phenolic resin modified with polymers prepared from *p*-hydroxyphenylmaleimide (HPMI). Homopolymers of HPMI and copolymers of HPMI with some vinyl monomers were synthesized and \bar{M}_n , T_g , and thermal decomposition temperature of them were measured by GPC, DSC, and TG, respectively. The miscibility of homopolymer with novolac was examined by DSC. It was found that the homopolymer had good heat resistance and good miscibility with novolac. Molding compounds were prepared by hot roll-kneading the mixtures of novolac, the homopolymer, hexamethylenetetramine, and glass fiber. It was found that molded test pieces had 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 heat resistance, is required particularly for the industrial field. Many approaches have been tried to improve the heat resistance of phenolic resin, most of them consisting of an increase in cross-linking density, for example, by means of after cure,¹ an increase of hardening agent content,¹ or addition of a modifier that has good heat resistance.² In the approaches mentioned above, occasionally, mechanical properties, for example, flexural strength or impact resistance, were reduced. Phenolic resins modified with boron,³ silicon,⁴ phosphorus,⁵ or heavy metals⁶ have been reported as high-temperature plastics, but are not used much because these resins are expensive or they have poor moldability.

In the polymerization of HPMI, Yamada et al.^{7,8} reported monomer reactivity ratios for HPMI with styrene and thermal properties of homopolymer prepared from HPMI. They reported that the homopolymer prepared from HPMI had relatively high

molecular weight and good heat resistance. Aida et al.⁹ reported the intrinsic viscosity and glass transition temperature of a copolymer of HPMI with methylacrylate.

However, there is no report concerning phenolic resin modified with polymers prepared from HPMI. As the homopolymer has phenolic nuclei, it was expected that it could react with hexamethylenetetramine (hexamine) to form a cross-linked structure. Therefore, we studied phenolic resin modified with homopolymer prepared from *p*-hydroxyphenylmaleimide (HPMI homopolymer) to improve its heat resistance without reduction of the mechanical properties. In this paper, molecular weight, glass transition temperature, and thermal decomposition temperature of both HPMI homopolymer and copolymers of HPMI with some vinyl monomers are reported. Then, the miscibility of the HPMI homopolymer with novolac and the mechanical and thermal properties of test pieces molded with compounds prepared from novolac, the homopolymer, hexamine, and glass fiber are described.

EXPERIMENTAL

Reagents and Materials

HPMI was supplied from Daihachi Chemical Industry Co., Ltd. It was recrystallized from methanol

* To whom correspondence should be addressed.

(mp 189°C). Monomers such as styrene (St), methyl methacrylate (MMA), methyl acrylate (MA), acrylonitrile (AN), and vinyl acetate (VAc) were refined in the usual way before use. Maleic anhydride (MAh) was recrystallized from chloroform. 2,2'-Azobis-butyronitrile (AIBN) was recrystallized from methanol. Dimethylformamide (DMF) was dried and distilled before use in a routine manner. Hexamethylenetetramine (hexamine) was used after pulverizing the chemical-grade reagent. Novolac (general purpose novolac) and glass fiber (chopped strand, 10.5 $\mu\text{m}\phi$, 4 mm) were purchased from Asahi Yukizai Kogyo Co., Ltd., and Nippon Electric Glass Co., Ltd., respectively. Ethyl ether, methanol, and acetone supplied as extra-pure reagents were used without further purification.

Synthesis of Homopolymer and Copolymers of HPMI

A glass tube was charged with given amounts of DMF, AIBN, and either HPMI or HPMI with comonomer such as St, MMA, MA, AN, VAc, and MAh and was sealed after replacement of air inside the tube with N_2 and evacuation with freeze-thawing. The tube was then kept at 70°C in a shaking water bath for 6 h. After polymerization, the reaction mixture was diluted by acetone and poured into an excess amount of ethyl ether to precipitate the products.

HPMI homopolymer-1, which was used for modified phenolic resin, was synthesized on a large scale as follows: HPMI 606.6 g (3.21 mol), AIBN 88.67 g (0.54 mol), and DMF 2700 mL were charged under N_2 atmosphere in a 3 L four-necked flask fitted with stirrer, thermometer, and reflux condenser. The mixture was kept at 70°C for 6 h. After polymerization, the reaction mixture was diluted by acetone and poured into an excess amount of distilled water to precipitate the polymer. HPMI homopolymer-2 was also synthesized in the same manner as was HPMI homopolymer-1, except that the amount of AIBN used was 8.867 g (0.054 mol).

Properties of Polymers Prepared from HPMI

Molecular weight, glass transition temperature, and thermal decomposition temperature of the polymers were measured by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetry (TG), respectively.

Miscibility of Novolac with HPMI Homopolymer

Novolac and the homopolymer were mixed with tetrahydrofuran (THF). After THF was evaporated,

the miscibility of novolac with the homopolymer was examined by DSC and also observed by a hot-plate microscope.

Molding

The molding compounds were prepared by hot roll-kneading the mixture (100 phr) of the novolac and HPMI homopolymer, hexamine (12 phr), zinc stearate (2 phr), and glass fiber (100 phr) at 100–110°C until they had the required moldability for transfer molding.

Test Pieces

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/cm², and 10 min, respectively.

Rectangular test pieces, 110, 12, and 6 mm, were used for the measurement of the heat-distortion temperature (HDT) and flexural properties. Notched rectangular test pieces, 88, 15, and 15 mm, were used for measurement of impact strength. Disk test pieces, 50 mm ϕ \times 3 mm, were used for the measurement of electrical properties and water absorption after boiling.

Testing Methods

1. Flexural properties: The flexural properties were measured on the rectangular samples according to JIS K 6911. The span between supports was 100 mm, and the crosshead speed was 3 mm/min.
2. Impact strength: The impact strength was measured on the rectangular notched sample by Charpy impact tester according to JIS K 6911. The weight of hammer was 0.862 kg, and the distance between the axis of rotation and the center of gravity of the hammer was 21 cm.
3. Thermal properties: HDT was measured on the rectangular sample according to JIS K 6911. The span between supports was 100 mm. Thermal decomposition behavior of samples was measured by TG. The heating rate was 10°C/min. Glass transition temperature (T_g) was measured by DSC. The heating rate was 10°C/min.
4. Curing behavior: The curing behavior was measured by a DSC thermogram according to JIS K 7122. The initial temperature (T_i), the maximum temperature (T_p), and the end

Table I Properties of Polymers Prepared from Either HPMI or HPMI with Vinyl Monomers

Monomers Used in Polymerization			Convsn. (%)	\bar{M}_n	\bar{M}_w	T_g (°C)	Temp. at Loss of 10 wt % (°C)
M1	M2	M1/M2 (mol/l) (mol/l)					
HPMI	—	1.2/0	82	3.0×10^3	7.3×10^3	257	383
HPMI	St	0.6/0.6	92	6.6×10^4	1.8×10^5	220	396
HPMI	MMA	0.6/0.6	86	3.9×10^3	2.7×10^4	184	336
HPMI	MA	0.6/0.6	76	4.0×10^3	9.7×10^4	127	332
HPMI	AN	0.6/0.6	23	3.4×10^3	5.4×10^3	191	279
HPMI	VAc	0.6/0.6	66	4.4×10^3	7.9×10^3	172	243
HPMI	MAnh	0.6/0.6	0	—	—	—	—

Condition of polymerization: 70 °C, 6 hr in DMF; Initiator: AIBN 20 mmol/l.

temperature (T_g) of the exotherm curve were read, and the exotherm energy of curing (ΔH) was calculated from the exotherm curve. The gelation time at 150°C was measured by the stroke cure method according to JIS K 6910.

- Electrical properties: Surface and volume resistivities were measured on a high-resistance meter (Yokogawa-Hewlett-Packard Co.).
- Boiling tests: Test pieces (disk) were boiled in distilled water for 2 or 4 h, and the water absorption and electrical properties of the boiled disks were measured.
- Molecular weight: Molecular weight was measured by GPC (eluent: THF; standard: polystyrene $\bar{M}_n = 1800 \times 10^3, 670 \times 10^3, 200 \times 10^3, 110 \times 10^3, 37 \times 10^3, 20.4 \times 10^3, 10 \times 10^3, 4 \times 10^3, 2 \times 10^3, \text{ and } 0.8 \times 10^3$; equipment: Waters ALC/GPC 150C).

Measured values of the properties were treated statistically: Number of repeats was 3–6, and region marks in Figures 4–11 represent the regions of 95% confidence limit.

RESULTS AND DISCUSSION

Properties of Polymers Prepared from HPMI

Properties of polymers prepared from HPMI are shown in Table I. The number-average molecular weight of the homopolymer was 3000, and its T_g was 257°C, which was the highest in polymers prepared from HPMI. The thermal decomposition temperature of the homopolymer was higher than for these copolymers except for the HPMI–St copolymer. The HPMI–St copolymer had the highest number-average molecular weight, 66,000. Average molecular

weight of other copolymers was between 3400 and 4400. The results described above suggest that the homopolymer and these copolymers, especially, HPMI–St, HPMI–MMA, and HPMI–MA, will have good heat resistance.

Modification of Two-stage Phenolic Resin with the Homopolymer

Miscibility of Novolac and the Homopolymer

Because of the phenolic group, it was expected that the homopolymer would react with the hardening

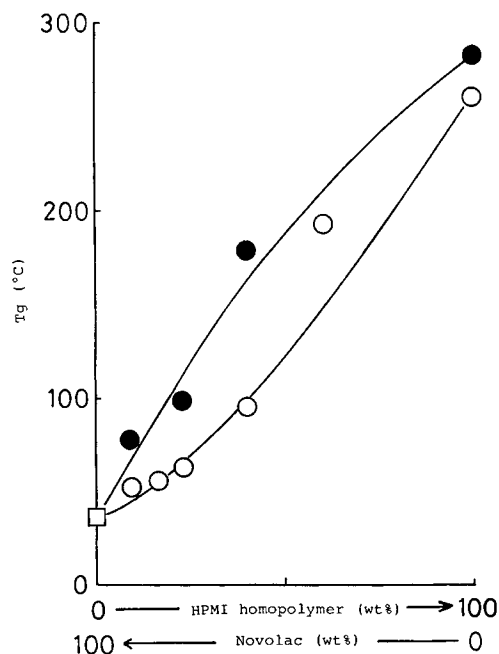


Figure 1 T_g of mixture of novolac and HPMI homopolymer: (○) homopolymer-1 $\bar{M}_n = 3800, \bar{M}_w = 10000$; (●) homopolymer-2 $\bar{M}_n = 4800, \bar{M}_w = 12000$.

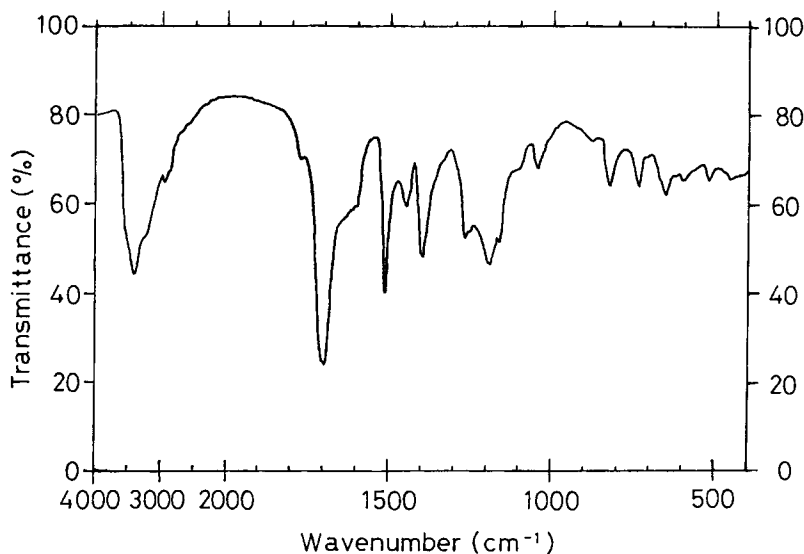


Figure 2 IR spectrum of THF insolubles.

agent and change into a cross-linked structure and also would be miscible with novolac. We tried to improve the properties of the two-stage phenolic resin by addition of the HPMI homopolymer. To get good results, the mixture of novolac and the homopolymer should be homogeneous. Therefore, the miscibility of homopolymer and novolac was examined.

When the homopolymer and novolac are not miscible, in other words, the mixture is not homogeneous, it shows two T_g s that depend on each component. On the other hand, when the mixture is homogeneous, it has one T_g that shifts with its composition. Figure 1 shows the relationship between T_g and the component of the mixture. As the T_g of the mixture shifted according to the composition of the mixture, it was found that these homopolymers were miscible with novolac. Also, the miscibility of novolac with the homopolymer was observed by the hot-stage microscope. When the temperature of the mixture was raised slowly, it melted sharply at a specific temperature. These results are supported by solubility parameter values (SP value) that were calculated from eq. (1) proposed by Fedors¹⁰:

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

where δ = solubility parameter value; Δe_i = energy of vaporization of atom or group; and Δv_i = molar volume of atom or group.

The SP values of novolac and that of the homopolymer that were calculated from eq. (1) were 14.1 (cal/cm³)^{1/2} and 15.5 (cal/cm³)^{1/2}, respectively. The difference between the SP value of no-

volac and that of the homopolymer was only 1.4. For comparison, SP values of polyphenyleneoxide and polystyrene, which are well known as miscible polymers, were 11.3 (cal/cm³)^{1/2} and 9.8 (cal/cm³)^{1/2}, respectively, according to eq. (1). Thus, it was concluded that these homopolymers should have good miscibility with novolac.

The Reactivity of HPMI Homopolymer and Hexamine

The reactivity of HPMI homopolymer and hexamine was examined. HPMI homopolymer-1 ($\bar{M}_n = 3800$) 10 g and hexamine 1.2 g were dissolved in DMF and refluxed at 150°C for 2 h. The reaction mixture was poured into an excess amount of distilled water to

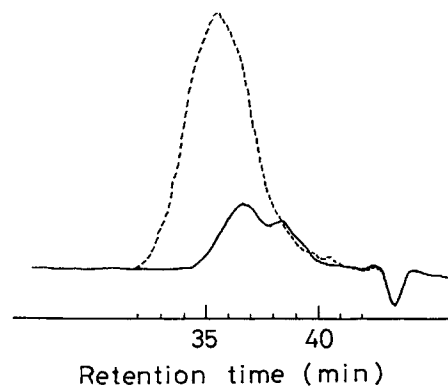


Figure 3 GPC curves of HPMI homopolymer-1 and THF solubles: (---) HPMI homopolymer-1 before reaction; (—) THF solubles in the reaction product from HPMI homopolymer-1 and hexamine.

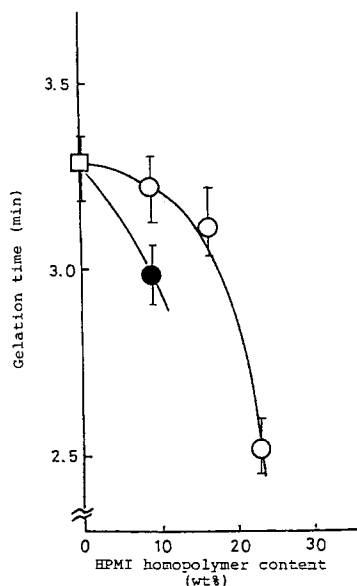


Figure 4 Gelation time of modified phenolic resin: (○) modified with homopolymer-1 ($\overline{M}_n = 3800$, $\overline{M}_w = 10,000$); (●) modified with homopolymer-2 ($\overline{M}_n = 4800$, $\overline{M}_w = 12,000$).

collect the products as precipitate. This precipitate consisted of a gel component (85 wt %) that was insoluble in THF and other compounds (15 wt %) that were soluble in THF. In Figure 2, the IR spectrum of the gel component showed the absorption bands of five-membered ring imide at 1700 and 1770 cm^{-1} and of C—N stretching vibration at 1190 and 1270 cm^{-1} . It was found that the HPMI homopolymer could react with hexamine without ring scission of the maleimide group to form the gel.

Table II Curing Behavior of Modified Phenolic Resin

HPMI Homopolymer Content (wt %) ^a	T_i ^b (°C)	T_p ^c (°C)	T_e ^d (°C)	ΔH ^e (kJ/kg)
0	124	145	168	57.5
9 ^f	120	140	171	64.2
17 ^f	118	140	176	83.8
23 ^f	111	139	177	87.6
9 ^g	122	141	174	62.8

^a Content of HPMI homopolymer in modified phenolic resin. Hexamine content: 12 phr of modified phenolic resin.

^b Initial temperature at exotherm curve.

^c Peak temperature at exotherm curve.

^d End temperature at exotherm curve.

^e Exotherm energy of curing.

^f Homopolymer-1 ($\overline{M}_n = 3800$).

^g Homopolymer-2 ($\overline{M}_n = 4800$).

In Figure 3, GPC curves of both HPMI homopolymer-1 and the component that was soluble in THF were shown. Those results suggested that its higher molecular weight components reacted with hexamine and its lower molecular weight components remained in the THF solution.¹¹

The results described above have led us to conclude that the HPMI homopolymer was miscible with novolac and reacted with the hardening agent changing into a cross-linked structure.

Curing Behavior

In Figure 4 and Table II, the gelation time and the curing behavior of modified phenolic resins are shown, respectively. The gelation time shortens with an increase of the content of the homopolymer. The phenolic resin modified with homopolymer-2 ($\overline{M}_n = 4800$) has a shorter gelation time than that of resin modified with homopolymer-1 ($\overline{M}_n = 3800$). The initial temperature on the exotherm curve reduces with an increase of the content of the homopolymer. The exothermal energy of cure increases with increasing homopolymer content.

The results suggest that moldability of phenolic resin modified with HPMI homopolymer is influenced greatly by the content of the homopolymer, probably because the homopolymer consists of a stiff main chain and has high T_g .

It is considered that a suitable number-average molecular weight for HPMI homopolymer and content of HPMI homopolymer should be less than 5000 and less than 20 phr, respectively, to provide good moldability and good quality for the modified phenolic resin.

Properties of Modified Phenolic Resin

Mechanical Properties and Heat Resistance of Modified Phenolic Resin

Flexural strength, flexural modulus, and Charpy impact strength of modified phenolic resin are shown in Figures 5 and 6. In Figure 7, deflection temperature under load of modified phenolic resin is shown. It was found that the mechanical properties of phenolic resins modified with homopolymer-1 were almost the same as those of unmodified phenolic resin and the heat resistance of modified phenolic resins increased with an increase of the content of the homopolymer-1. Heat resistance of the phenolic resin modified with homopolymer-2 was superior to that of unmodified phenolic resin. But its mechanical properties were a little inferior to those of unmodified phenolic resin, because the phenolic resin

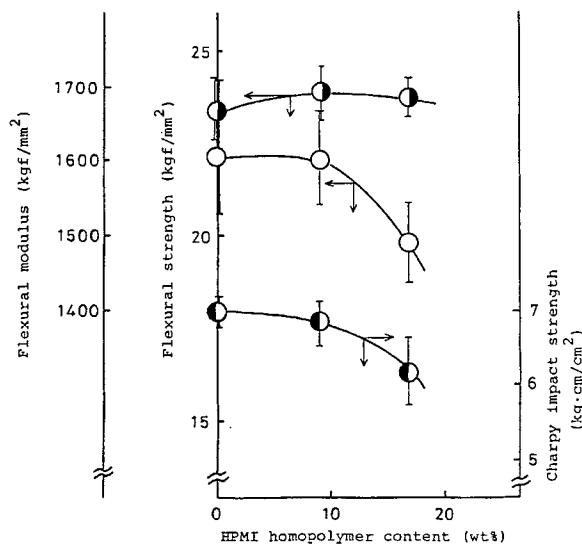


Figure 5 Mechanical properties of phenolic resin modified with HPMI homopolymer-1 ($\overline{M}_n = 3800$, $\overline{M}_w = 10,000$): (○) flexural strength; (●) flexural modulus; (●) charpy impact strength.

modified with homopolymer-2 has poorer moldability than does the phenolic resin modified with homopolymer-1, owing to its high T_g .

The reasons for both the improvement of the heat resistance of modified phenolic resin and the maintenance of the mechanical properties of modified phenolic resin are as follows: (i) HPMI ho-

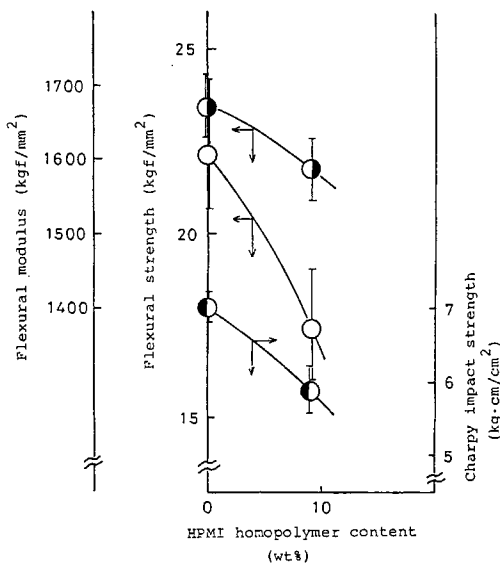


Figure 6 Mechanical properties of phenolic resin modified with HPMI homopolymer-2 ($\overline{M}_n = 4800$, $\overline{M}_w = 12,000$): (○) flexural strength; (●) flexural modulus; (●) charpy impact strength.

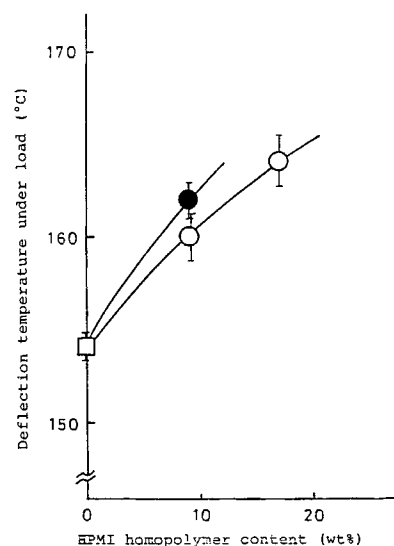


Figure 7 Heat resistance of modified phenolic resin: (○) modified with HPMI homopolymer-1 ($\overline{M}_n = 3800$, $\overline{M}_w = 10,000$); (●) modified with HPMI homopolymer-2 ($\overline{M}_n = 4800$, $\overline{M}_w = 12,000$).

mopolymer has a high glass transition temperature and good heat resistance, (ii) HPMI homopolymer has higher molecular weight than that of novolac, and (iii) the modified phenolic resin can form a higher degree of cross-linking because HPMI homopolymer is miscible with novolac and reacts with hexamine.

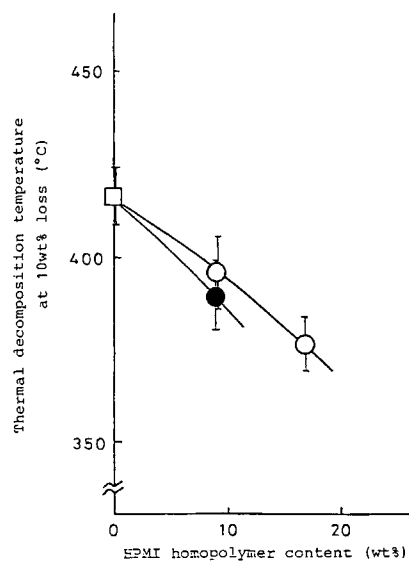


Figure 8 Thermal decomposition temperature of modified phenolic resin: (○) modified with HPMI homopolymer-1 ($\overline{M}_n = 3800$, $\overline{M}_w = 10,000$); (●) modified with HPMI homopolymer-2 ($\overline{M}_n = 4800$, $\overline{M}_w = 12,000$).

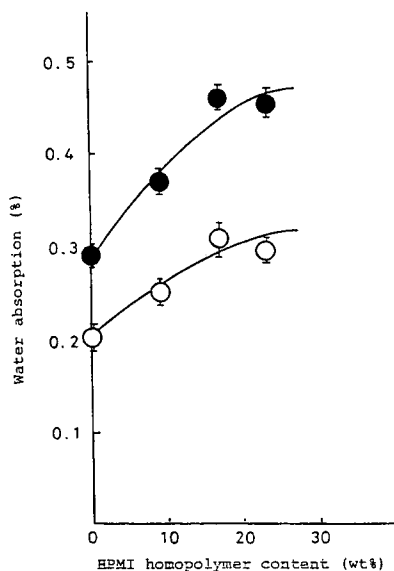


Figure 9 Water absorption of phenolic resin modified with homopolymer-1 after 2 h boiling (O) and 4 h boiling (●).

Thermal Decomposition Temperature of Modified Phenolic Resin

Thermal decomposition temperature was defined as the temperature at which the sample showed 10 wt

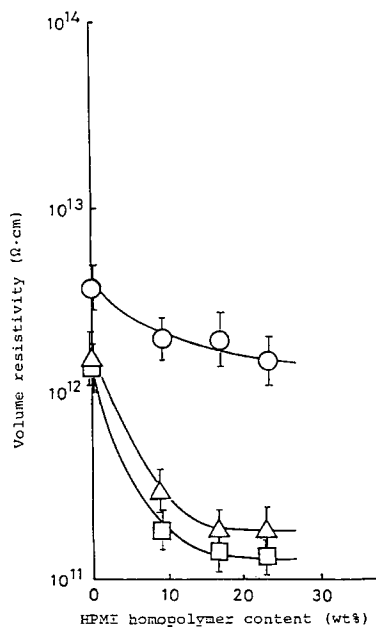


Figure 10 Volume resistivity of phenolic resin modified with HPMI homopolymer-1: (O) before boiling; (Δ) after 2 h boiling; (\square) after 4 h boiling.

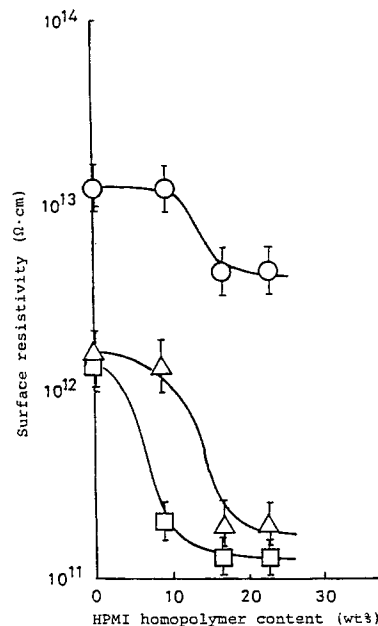


Figure 11 Surface resistivity of phenolic resin modified with HPMI homopolymer-1: (O) before boiling; (Δ) after 2 h boiling; (\square) after 4 h boiling.

% loss on heating at $10^\circ\text{C}/\text{min}$ (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 of the content of the homopolymer. The reason for this phenomenon is as follows: Above 350°C , the maleimide group of the HPMI homopolymer begins gradual thermal decomposition.

The results described above lead to the conclusion that phenolic resins modified with HPMI homopolymer have good heat resistance and mechanical properties simultaneously, but that above 350°C , the modified phenolic resins can decompose easier than can unmodified phenolic resin.

Water Absorption and Electrical Insulation

The water absorption of the test pieces was measured after boiling for 2 and 4 h. The results are shown in Figure 9 [(O) 2 h; (●) 4 h]. The amount of water absorption increases with an increase of the content of the HPMI homopolymer, due to its hydrophilic maleimide group.

The volume and surface resistivity of samples changed with the contents of HPMI homopolymer-1 as shown in Figures 10 and 11. These properties of modified phenolic resin after 2 and 4 h boiling are also shown in the same figures. The volume re-

sistivity of the samples shows a similar tendency to that of surface resistivity. The reasons for these phenomena are as follows: (i) Electric resistivities of modified phenolic resins are decreased by introduction of the maleimide unit into the HPMI homopolymer, and (ii) absorbed water promotes this tendency because water can combine with hydroxy groups of the phenol or carbonyl group of maleimide by hydrogen bonding.

In our next paper, we will report on phenolic resin modified with copolymers of HPMI with vinyl monomer.

CONCLUSIONS

Homopolymer of HPMI and copolymers of HPMI with some vinyl monomers were obtained by radical polymerization. These polymers had high T_g . It was found that the homopolymer was miscible with novolac by measuring the T_g of the mixture. Modification of phenolic resin with the homopolymer improved the physical thermal resistance of phenolic resin, but did not improve the mechanical properties so much. On the other hand, water absorption of the modified phenolic resin with the homopolymer

has increased and electric resistivity has decreased with an increase of the content of the homopolymer.

REFERENCES

1. A. Fukuda, K. Hasegawa, and H. Horiuchi, *Kobunshi Ronbunshu*, **40**(5), 329 (1983).
2. Jpn. Pat. 88,086,746 (April 18, 1988) (to Japan Synthetic Rubber Co., Ltd., Japan Kokai Tokko Koho).
3. DE-PS 1,233,606 (1960) (to Dynamit Nobel AG).
4. US-PS 2,258,218 (1941) (to General Electric Co.).
5. B. Helferich and K. G. Schmidt, *Chem. Ber.*, **92**, 2051 (1959).
6. DE-AS 1,816,241 (1968) (to Nord-Aviation Soci t  Nationale de Constructions A ronautiques).
7. M. Yamada, I. Takase, T. Tsukano, and Y. Ueda, *Kobunshi Kagaku*, **26**, 401 (1969).
8. M. Yamada, I. Takase, T. Tsukano, Y. Ueda, and N. Koutou, *Kobunshi Kagaku*, **26**, 593 (1969).
9. H. Aida, K. Ikou, A. Watanabe, S. Suzuki, and A. Tomokane, *Kobunshi Kagaku*, **29**, 643 (1972).
10. R. F. Fedors, *Polym. Eng. Sci.*, **14**, 147 (1974).
11. A. Fukuda, K. Hasegawa, and H. Horiuchi, *J. Appl. Polym. Sci.*, **31**, 7 (1986).

Received June 4, 1990

Accepted November 27, 1990