

Study on Modified Phenolic Resin. II. Modification with *p*-Hydroxyphenylmaleimide/Styrene Copolymer

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SYNOPSIS

The improvement of heat resistance and mechanical properties of phenolic resin was examined with the blend of novolac and copolymers prepared from *p*-hydroxyphenylmaleimide (HPMI) and styrene.

Copolymers of HPMI and styrene with various molecular weights were synthesized. Glass transition (T_g) and thermal decomposition temperatures of the copolymers were measured by differential scanning calorimetry (DSC) and thermogravimetry (TG), respectively. The miscibility of the copolymers with novolac was examined by DSC.

It was found that the copolymers had a good heat resistance and a good miscibility with novolac. Molding compounds were prepared by hot roll-kneading of mixtures that involved novolac, copolymer, hexamethylenetetramine (hexamine), and glass fiber. It was found that the test pieces prepared by transfer molding from the molding compounds showed a good heat resistance and better mechanical properties than phenolic resin modified with HPMI homopolymer.

INTRODUCTION

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

Many approaches have been tried to improve the heat resistance of phenolic resin. Fukuda et al.¹ improved the heat resistance of the phenolic resins by means of after-cure or an increase of hardening agent content. It was reported² that phenolic resins with good heat resistance were produced by the addition of modifier. But in these approaches mechanical properties of phenolic resin, e.g., flexural strength or impact resistance, were reduced. There are a few papers^{3,4} related to the modified phenolic

resins of which both heat resistance and mechanical properties are superior to those of unmodified phenolic resin.

In the previous paper,⁵ it was found that the modification of phenolic resin with *p*-hydroxyphenylmaleimide (HPMI) homopolymer improved the heat resistance, but didn't improve the mechanical properties so much. The reasons for these were as follows: (1) HPMI homopolymer had a stiff main chain, a high glass transition temperature, and a good heat resistance; (2) HPMI homopolymer had a higher molecular weight than that of novolac; (3) the modified phenolic resin could form a higher degree of crosslinking because HPMI homopolymer was miscible with novolac and reacted with hexamine. It is expected that the modified phenolic resin with HPMI/styrene copolymer has better mechanical properties than those of the modified phenolic resin with HPMI homopolymer because HPMI/styrene copolymer is more flexible than HPMI homopolymer.

In this study, HPMI/styrene copolymers with various molecular weights were synthesized and T_g and thermal decomposition temperatures of the copolymers were measured by DSC and TG, respec-

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tively. Then, the miscibility of the copolymers with novolac was evaluated from the DSC results. Thermal and mechanical properties of the test pieces from the compounds prepared from novolac, copolymer, hexamine, and glass fiber were investigated.

EXPERIMENTAL

Reagents and Materials

HPMI was supplied from Daihachi Chemical Industry Co. Ltd. and recrystallized from methanol (mp. 189°C). Styrene (St) was refined before use in the usual way. 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 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 were used without further purification.

Synthesis of HPMI/St Copolymers

The synthesis of HPMI/St copolymer-1 was as follows: HPMI 219.24 g (1.16 mol), St 120.61 g (1.16 mol), AIBN 12.66 g (0.078 mol), and DMF 2700 mL were charged in a 3-L four-necked flask fitted with stirrer, thermometer, N₂ inlet, and reflux condenser. The polymerization was carried out at 70°C for 6 h under N₂ atmosphere. The reaction mixture was poured into an excess amount of distilled water to precipitate the polymer. HPMI/St copolymer-2 was also synthesized in the same manner as HPMI/St copolymer-1 except the amounts of HPMI, St,

and AIBN used were 189.0 g (1 mol), 104.0 g (1 mol), and 63.33 g (0.389 mol), respectively. HPMI/St copolymer-3 was synthesized in the same manner as HPMI/St copolymer-1 except the amounts of HPMI, St, and AIBN used were 109.62 g (0.58 mol), 60.31 g (0.58 mol), and 6.333 g (0.039 mol), respectively. In this case, 55.0 g (0.273 mol) of *n*-lauryl mercaptan was also added as a chain transfer agent.

Properties of HPMI/St Copolymers

Molecular weight, T_g , and thermal decomposition temperature of these copolymers were measured by GPC, DSC, and TG, respectively.

Miscibility of Novolac with HPMI/St Copolymers

Novolac and HPMI/St copolymer were dissolved in tetrahydrofuran (THF). Blends of novolac and 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

The molding compounds were prepared by hot roll-kneading of mixture composed of the novolac and HPMI/St copolymer (100 phr), 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.

Test Pieces

Three kinds of test pieces were prepared by transfer molding from the molding compounds preheated by high-frequency dielectric heating. Molding conditions temperature, pressure, and time were 170°C, 100 kg/cm², and 10 min, respectively.

Table I Properties of HPMI/St Copolymers and HPMI Homopolymer

Feed				Product				
M1	M2	M1/M2 (mol/L)/(mol/L)	AIBN (mol/L)	Convsn. [%]	\bar{M}_n	\bar{M}_w	T_g (°C)	Temperature at Loss of 10 wt % (°C)
HPMI	St	0.43/0.43	0.029	97	2.5×10^4	1.5×10^5	211	395
HPMI	St	0.37/0.37	0.144	95	1.6×10^4	9.1×10^4	196	397
HPMI	St ^a	0.21/0.21	0.014	98	2.8×10^3	8.3×10^3	186	363
HPMI	—	1.19/—	0.200	95	4.8×10^3	1.2×10^4	267	377
HPMI	—	1.19/—	0.020	96	3.8×10^3	1.0×10^4	255	360

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

^a *n*-Lauryl mercaptan 0.100 (mol/L).

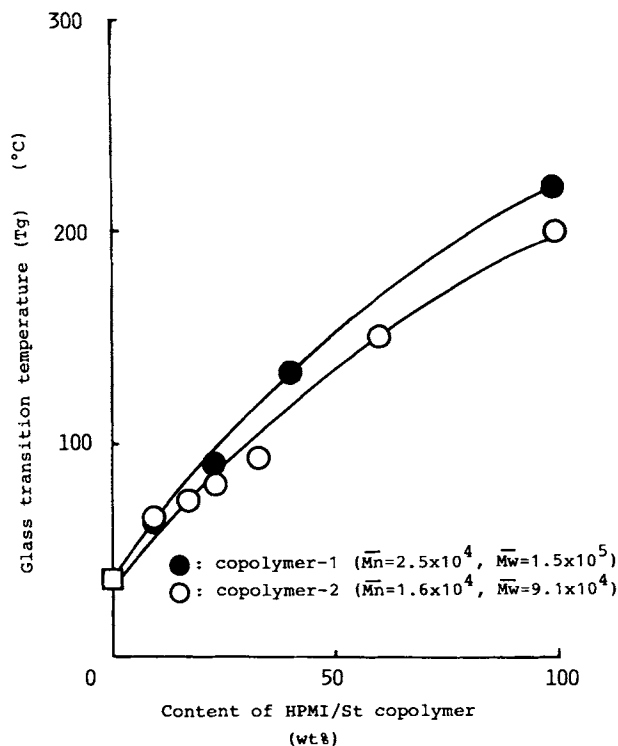


Figure 1 Relationship between T_g of the blends and wt % of HPMI/St copolymer in the mixtures.

Rectangular test pieces, $110 \times 12 \times 6$ mm, were used for the measurements of deflection temperature under a load and flexural properties. Notched rectangular test pieces, $88 \times 15 \times 15$ mm, were used

for measurement of impact strength. Disk test pieces, $50 \text{ mm}\phi \times 3$ mm, were used for the measurement of electrical properties and water absorption.

Testing Methods

1. Flexural properties: The flexural properties were measured for the rectangular samples according to JIS K 6911. The span between the two supports was 100 mm and the cross-head speed was 3 mm/min.
2. Impact strength: The impact strength was measured for 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: Deflection temperature under a load was measured for 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. The heating rate was $10^\circ\text{C}/\text{min}$. T_g was measured by DSC. The heating rate was $10^\circ\text{C}/\text{min}$.
4. Curing behavior: The curing behavior was measured by DSC thermogram according to JIS K 7122. The initial temperature (T_i), maximum temperature (T_p), and end temperature (T_e) of exotherm curve were read

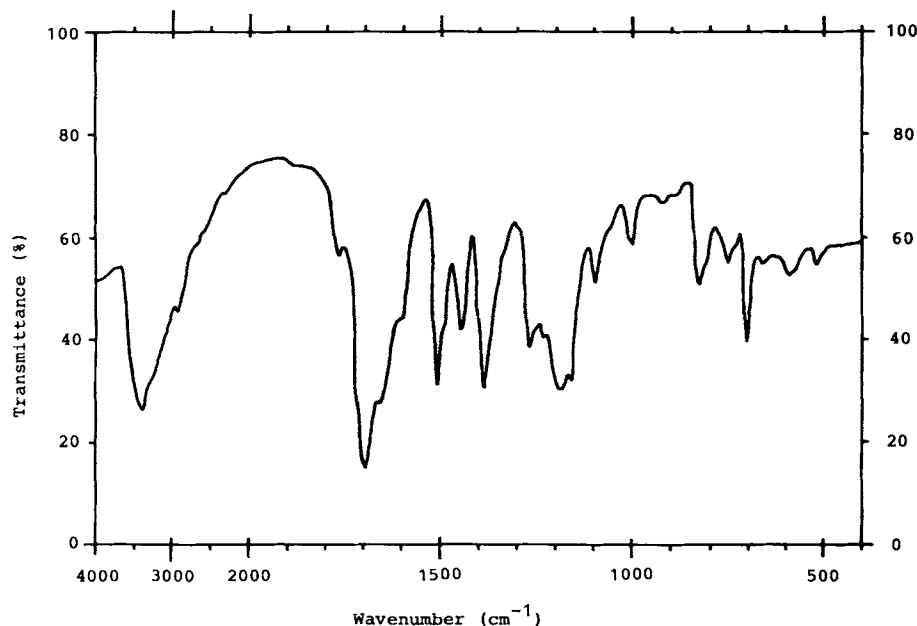


Figure 2 IR spectrum of THF insolubles.

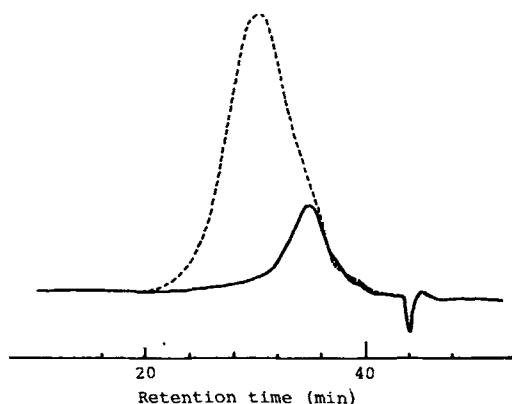


Figure 3 GPC curves of HPMI/St copolymer-1 and THF solubles.

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.

5. Electrical properties: Surface and volume resistivities were measured by a high-resistance meter (Yokogawa-Hewlett-Packard Co.).
6. Boiling tests: Test pieces (disk) were treated

in a boiled distilled water for 2 or 4 h and the water absorption and electrical properties of the treated disks were measured at room temperature.

7. 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 150°C).

RESULTS AND DISCUSSION

Thermal Properties of HPMI/St Copolymers

Properties of three kinds of HPMI/St copolymers and two kinds of HPMI homopolymers are shown in Table I. T_g for all copolymers was lower than that for HPMI homopolymers. Thermal decomposition temperature of two copolymers with higher molecular weight was higher than that of homopolymer. The number averaged molecular weight of the copolymers was between 2,800 and 25,000. The number was higher than that of novolac.

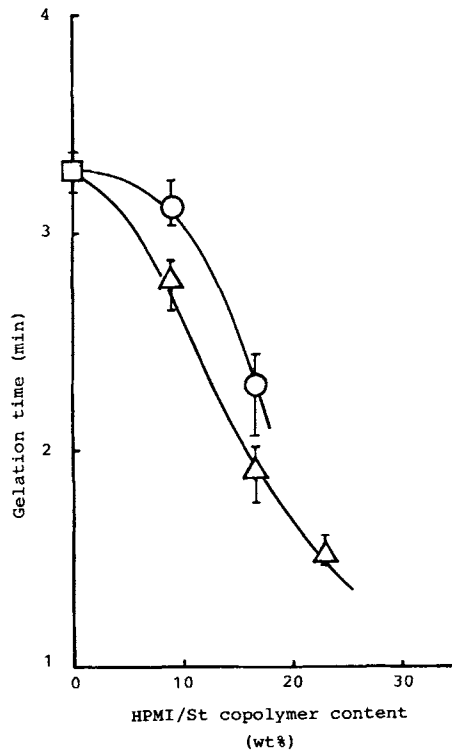


Figure 4 Gelation time of modified phenolic resin: (○) modified with HPMI/St copolymer-1 ($\bar{M}_n = 2.5 \times 10^4, \bar{M}_w = 1.5 \times 10^5$); (△) modified with HPMI/St copolymer-2 ($\bar{M}_n = 1.6 \times 10^4, \bar{M}_w = 9.1 \times 10^4$).

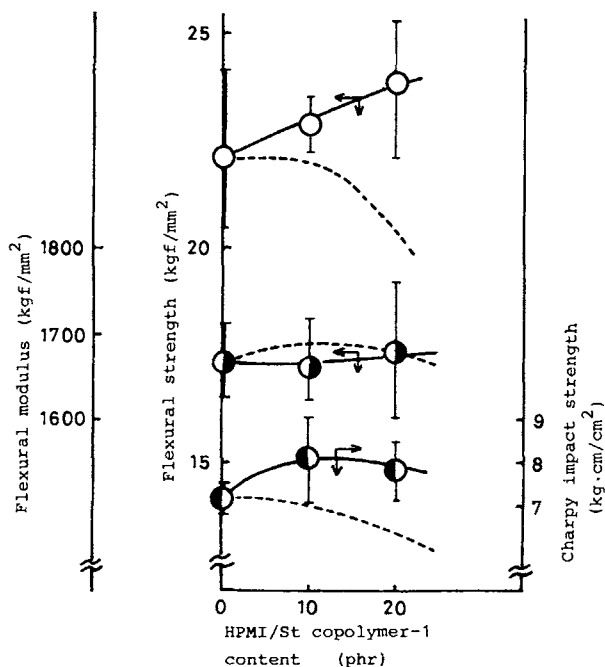


Figure 5 Mechanical properties of phenolic resin modified with HPMI/St copolymer-1 ($\bar{M}_n = 2.5 \times 10^4, \bar{M}_w = 1.5 \times 10^5$): (○): flexural strength; (●) flexural modulus; (●) Charpy impact strength; (---) phenolic resin modified with HPMI homopolymer ($\bar{M}_n = 3.8 \times 10^3, \bar{M}_w = 1.0 \times 10^4$).

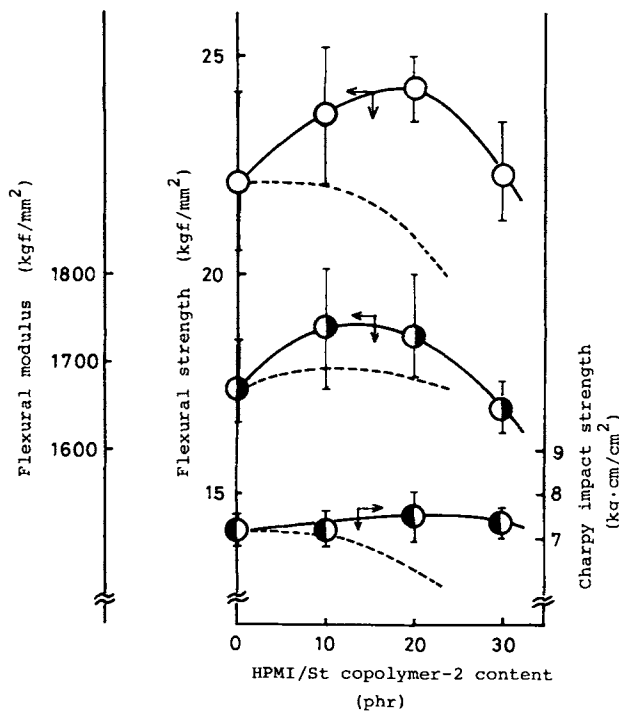


Figure 6 Mechanical properties of phenolic resin modified with HPMI/St copolymer-2 ($\bar{M}_n = 1.6 \times 10^4$, $\bar{M}_w = 9.1 \times 10^4$): (○) flexural strength; (●) flexural modulus; (●) charpy impact strength, (---) phenolic resin modified with HPMI homopolymer ($\bar{M}_n = 3.8 \times 10^3$, $\bar{M}_w = 1.0 \times 10^4$).

The results indicate that the copolymers with higher molecular weight have good heat resistance.

Modification of Two-Stage Phenolic Resin with HPMI/St Copolymer

Miscibility of Novolac and HPMI/St Copolymers

Since the copolymers have a phenolic group, it is expected that they react with hardening agent and change into a crosslinked structure; further, the copolymers are miscible with novolac. In addition, it is conceivable that HPMI/St copolymers are more flexible than HPMI homopolymers. We tried to improve the properties of the two-stage phenolic resin by the addition of the HPMI/St copolymer. First, 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 copolymer in the mixtures. For both copolymers, the T_g of the mixture increased with increasing the fraction of copolymer. The results suggest these copolymers are miscible with novolac. The miscibility was also recognized under the observation of optical microscope. When the temperature of the mixture was raised slowly, the samples flowed sharply at a specific temperature.

Table II Curing Behavior of Modified Phenolic Resin

HPMI/St Copolymer Content (phr) ^a	T_i^b (°C)	T_p^c (°C)	T_e^d (°C)	ΔH^e (kJ/kg)
0	124	145	168	57.5
10 ^f	121	141	176	74.1
20 ^f	118	141	180	72.6
30 ^f	122	141	188	71.1
10 ^g	121	141	176	81.7
20 ^g	124	142	177	63.9

^a Part of HPMI/St copolymer per hundred part of phenolic resin. Hexamine content, 12 phr modified phenolic resin.

^b Initial temperature at exotherm curve.

^c Maximum temperature at exotherm curve.

^d End temperature at exotherm curve.

^e Exotherm energy of curing.

^f Copolymer-2 ($\bar{M}_n = 1.6 \times 10^4$).

^g Copolymer-1 ($\bar{M}_n = 2.5 \times 10^4$).

Reactivity of HPMI/St Copolymers with Hexamine

The reactivity of HPMI/St copolymers with hexamine was examined. Ten grams of HPMI/St copolymer-1 ($\bar{M}_n = 2.5 \times 10^4$) and 1.2 g hexamine were dissolved in DMF and the solution was refluxed

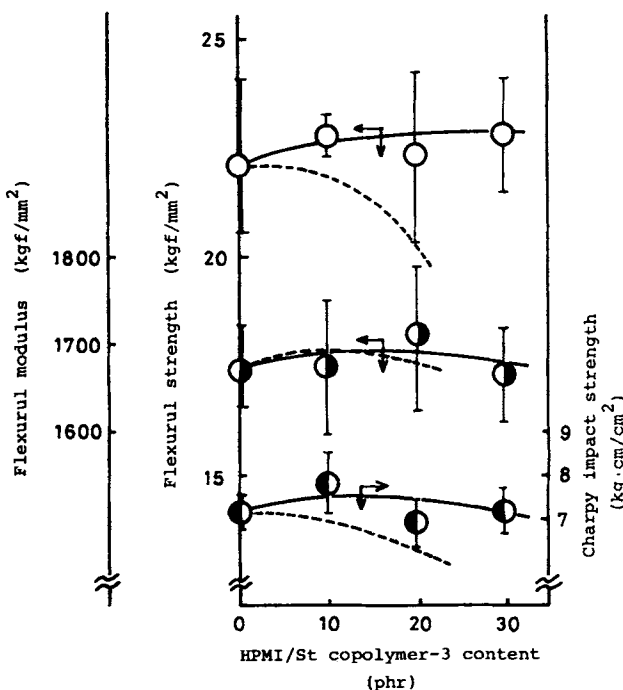


Figure 7 Mechanical properties of phenolic resin modified with HPMI/St copolymer-3 ($\bar{M}_n = 2.8 \times 10^3$, $\bar{M}_w = 8.3 \times 10^3$): (○) flexural strength; (●) flexural modulus; (●) charpy impact strength, (---) phenolic resin modified with HPMI homopolymer ($\bar{M}_n = 3.8 \times 10^3$, $\bar{M}_w = 1.0 \times 10^4$).

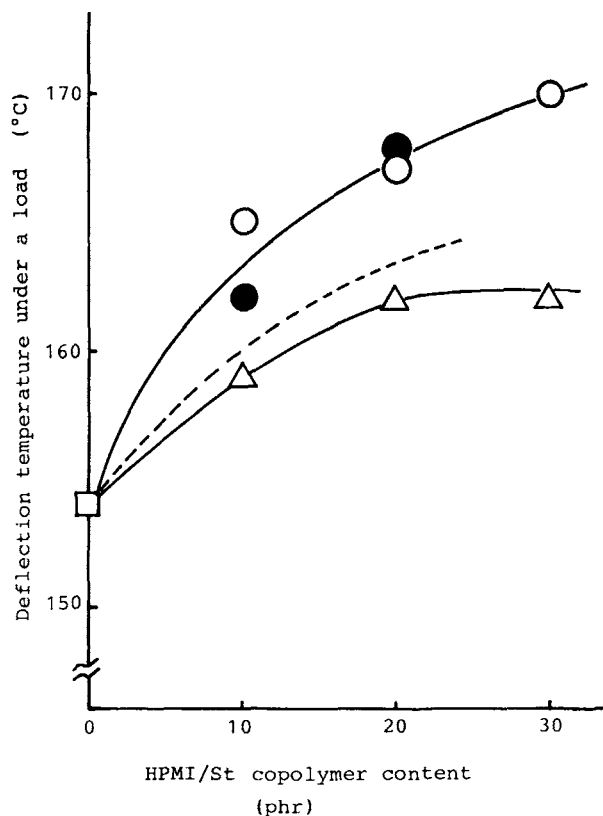


Figure 8 Heat resistance of modified phenolic resin. (●) modified with HPMI/St copolymer-1 ($\bar{M}_n = 2.5 \times 10^4$, $\bar{M}_w = 1.5 \times 10^5$); (○) modified with HPMI/St copolymer-2 ($\bar{M}_n = 1.6 \times 10^4$, $\bar{M}_w = 9.1 \times 10^4$); (△) modified with HPMI/St copolymer-3 ($\bar{M}_n = 2.8 \times 10^3$, $\bar{M}_w = 8.3 \times 10^3$); (---) modified with HPMI homopolymer ($\bar{M}_n = 3.8 \times 10^3$, $\bar{M}_w = 1.0 \times 10^4$).

at 150°C for 1 h. The reaction mixture was poured into an excess amount of ethyl ether to collect the products as precipitates. The precipitates were consisted of gel component (94 wt %) that was insoluble in THF and other compounds (6 wt %) that were soluble in THF. In Figure 2, IR spectrum of the gel component is shown. The absorption bands at 1,700 and 1,770 cm^{-1} correspond to the five-member ring imide.⁶ The results imply the HPMI/St copolymer can react with hexamine without ring scission of the maleimide group.

In Figure 3, GPC curves of both HPMI/St copolymer-1 and the component soluble in THF are shown. The results suggest that a large amount of HPMI/St copolymer reacts with hexamine and a small amount of HPMI/St copolymer remains in THF solution.⁷

Curing Behavior

Figure 4 and Table II show the gelation time and curing behavior of modified phenolic resins, respec-

tively. The gelation time shortens with an increase of the content of HPMI/St copolymer. The initial and maximum temperatures on the exotherm curves are not affected by the modification with HPMI/St copolymer, but the end temperature on the exotherm curves raises with an increase of the content of the copolymer. The exothermal energy of cure increases by the modification with the HPMI/St copolymer.

Properties of Modified Phenolic Resin

Mechanical Properties and Heat Resistance

Flexural strength, flexural modulus, and Charpy impact strength of modified phenolic resin are shown in Figures 5–7. In Figure 8, deflection temperature of modified phenolic resin under a load is shown. It was found that up to a copolymer content of 20 phr mechanical properties of phenolic resin modified with HPMI/St copolymer-1 or -2 were superior to those of unmodified phenolic resin and modified phenolic resin with HPMI homopolymer. Heat resistance of phenolic resin modified with HPMI/St copolymer-1 or -2 increased with an increase of the content of the HPMI/St copolymer-1 or -2. The results were almost similar to those for modified

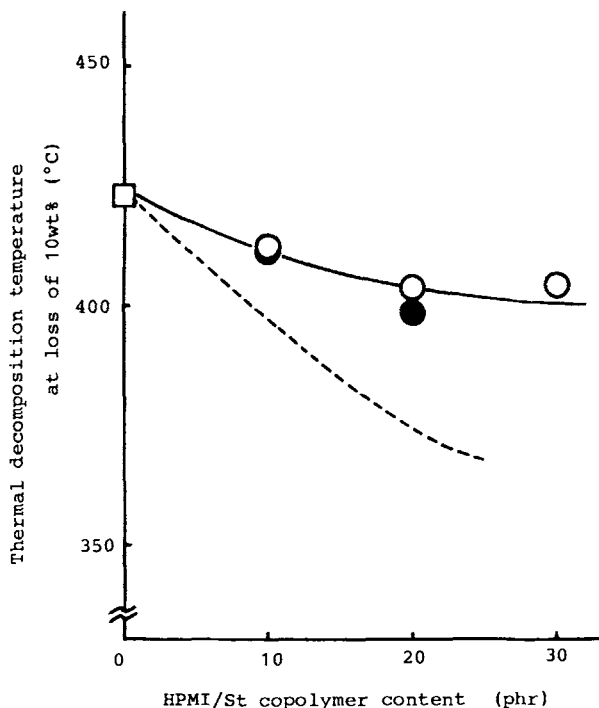


Figure 9 Thermal decomposition temperature of modified phenolic resin (●) modified with HPMI/St copolymer-1 ($\bar{M}_n = 2.5 \times 10^4$, $\bar{M}_w = 1.5 \times 10^5$); (○) modified with HPMI/St copolymer-2 ($\bar{M}_n = 1.6 \times 10^4$, $\bar{M}_w = 9.1 \times 10^4$); (---) modified with HPMI homopolymer ($\bar{M}_n = 3.8 \times 10^3$, $\bar{M}_w = 1.0 \times 10^4$).

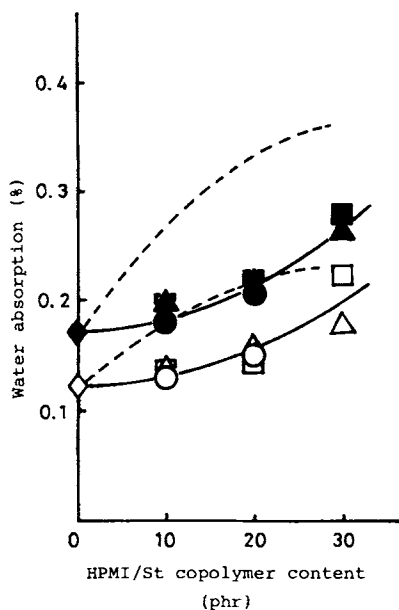


Figure 10 Water absorption of phenolic resin modified with HPMI/St copolymer after 2 (○, △, □) and 4 h boiling (●, ▲, ■). (○, ●) modified with HPMI/St copolymer-1 ($\bar{M}_n = 2.5 \times 10^4$, $\bar{M}_w = 1.5 \times 10^5$); (△, ▲) modified with HPMI/St copolymer-2 ($\bar{M}_n = 1.6 \times 10^4$, $\bar{M}_w = 9.1 \times 10^4$); (□, ■) modified with HPMI/St copolymer-3 ($\bar{M}_n = 2.8 \times 10^3$, $\bar{M}_w = 8.3 \times 10^3$); (---) modified with HPMI homopolymer ($\bar{M}_n = 3.8 \times 10^3$, $\bar{M}_w = 1.0 \times 10^4$).

phenolic resin with HPMI homopolymer. Mechanical properties of phenolic resins modified with HPMI/St copolymer-3 were almost similar to those of unmodified phenolic resin. Heat resistance of phenolic resins modified with HPMI/St copolymer-3 increased with an increase of the content of the HPMI/St copolymer-3, similar to the case of phenolic resins modified with HPMI/St copolymer-1 or -2.

The reasons for both the improvement of the heat resistance and mechanical properties of modified phenolic resin with HPMI/St copolymers are considered as follows: (1) HPMI/St copolymer has a high T_g and good heat resistance; (2) phenolic resin modified with HPMI/St copolymer can form a higher degree of crosslinking structure because it is miscible with novolac and reacts with hexamine; (3) although HPMI/St copolymer consists of stiff main chain, it is more flexible than HPMI homopolymer.

It is found that there is suitable molecular weight and content of HPMI/St copolymer for the modification of phenolic resin. HPMI/St copolymer-1 ($\bar{M}_n = 2.5 \times 10^4$, $\bar{M}_w = 1.5 \times 10^5$) and copolymer-2 ($\bar{M}_n = 1.6 \times 10^4$, $\bar{M}_w = 9.1 \times 10^4$) have a suitable molecular weight, and content of the modifier in the mixture should be less than 30 phr. When the num-

ber-averaged molecular weight was higher than 2.5×10^4 , the modified phenolic resin did not provide good flowability and moldability due to high T_g of the HPMI/St copolymer. When the number-averaged molecular weight was less than 1.0×10^4 , the modified phenolic resin did not provide better mechanical properties than unmodified phenolic resin.

Thermal Decomposition Temperature

Thermal decomposition temperature was defined as the temperature at which the sample showed 10 wt % loss on heating at $10^\circ\text{C}/\text{min}$ (Fig. 9). The samples used for this measurement were the modified phenolic resins that did not contain glass fiber. It was found that thermal decomposition temperature decreased with an increase of the content of the copolymer. The HPMI/St copolymer begins gradual thermal decomposition at 360°C , but the degree of decrease of thermal decomposition temperature is less than that of phenolic resin modified with HPMI homopolymer. It is considered that this phenomenon is due to the existence of St unit as comonomer.

The results described above lead to the conclusion that phenolic resins modified with HPMI/St co-

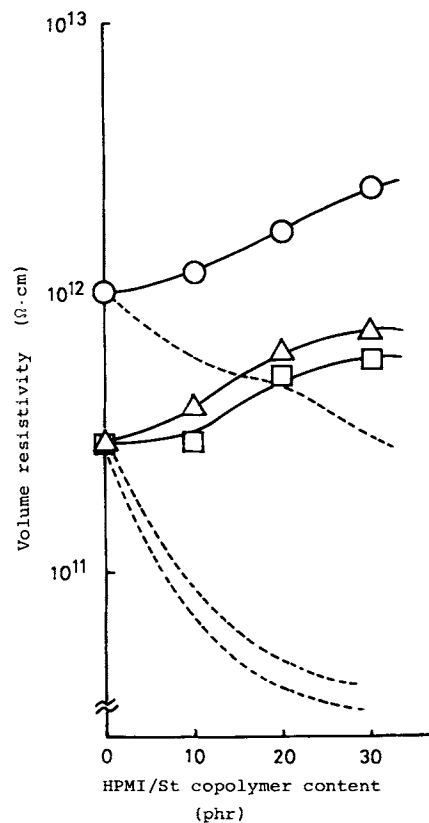


Figure 11 Volume resistivity of phenolic resin modified with HPMI/St copolymer-3 (○) before boiling; (△) after 2 h boiling; (□) after 4 h boiling; (---) modified with HPMI homopolymer ($\bar{M}_n = 3.8 \times 10^3$, $\bar{M}_w = 1.0 \times 10^4$).

polymer have good heat resistance and mechanical properties simultaneously, and that the resistance of thermal decomposition of phenolic resin modified with HPMI/St copolymer is superior to that of phenolic resin modified with HPMI homopolymer.

Water Absorption and Electrical Insulation

The water absorption of the test pieces was measured at room temperature for samples treated in boiling water for 2 and 4 h. The results are shown in Figure 10. The amount of water absorption increases with an increase of the content of the HPMI/St copolymer due to the increase in the number of hydrophilic phenol and maleimide groups in the mixtures.

However, the value of absorption for phenolic resin modified with HPMI/St copolymer is less than that for phenolic resin modified with HPMI homopolymer. HPMI/St copolymer has a hydrophobic nature due to the existence of St, which might reduce the water absorption.

The volume and surface resistivities of these samples changed with the content of HPMI/St copolymer-3 are shown in Figures 11 and 12. These properties of modified phenolic resin after 2 and 4 h boiling are also shown. The volume resistivity of the samples shows similar tendency to that of the surface resistivity. The volume and surface resistivities of HPMI/St copolymer are increased with an increase of the content of the copolymer. These phenomena are opposite tendency to the case of phenolic resin modified with HPMI homopolymer.⁵ The reason for these phenomena is supposed as follows: Although maleimide unit in HPMI/St copolymer causes the decrease of the electric resistivities, St unit in the copolymer contributes to the increase of the electric resistivities. After boiling, electric resistivities of modified phenolic resins decreases gradually. This phenomenon is the same as the case of phenolic resin modified with HPMI homopolymer owing to absorbed water.⁵ Even after boiling, electric resistivities of phenolic resin modified with HPMI/St copolymer are superior to those of unmodified phenolic resin.

CONCLUSIONS

Modification of phenolic resin with the HPMI/St copolymer led to improvement of both mechanical properties and thermal resistance. Although water absorption of phenolic resin modified with HPMI/St copolymer increased with an increase of the content of the copolymer, the increase was less than

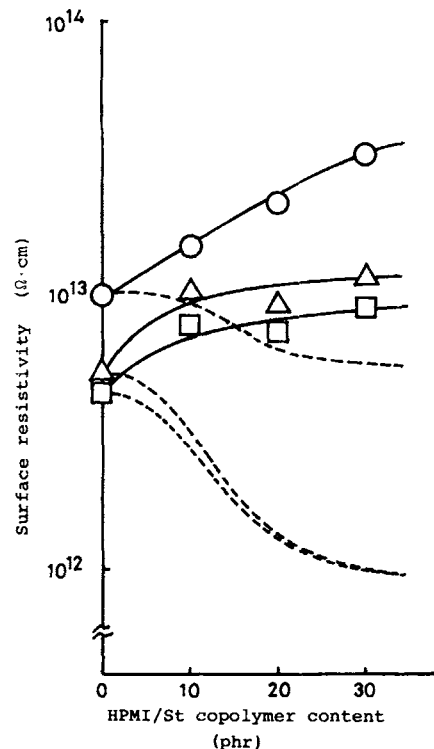


Figure 12 Surface resistivity of phenolic resin modified with HPMI/St copolymer-3 (O) before boiling; (Δ) after 2 h boiling; (□) after 4 h boiling; (---) modified with HPMI homopolymer ($\bar{M}_n = 3.8 \times 10^3$, $\bar{M}_w = 1.0 \times 10^4$).

the case of phenolic resin modified with HPMI homopolymer. The electric resistivity increased with an increase of the content of the HPMI/St copolymer in contrast to the case of phenolic resin modified with HPMI homopolymer.

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