

# Optimal Compositions of Molded Phenolic Resins and its Properties

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## Synopsis

Phenolic resins [commercial (CP), pure (PP), and woodflour-filled (WP)] containing different levels of hexamine, were evaluated in terms of curing behavior as well as thermal, electrical, and mechanical properties. The degree and rate of curing increase markedly with the rise of the hexamine content; however, the dielectric constant, dielectric loss, and dissipation factor decrease gradually. Dielectrical values decrease with the increase of the applied frequency. When the ratios of hexamine to phenolics are increased, samples become harder and experience increased molding shrinkage. With the increase of molding time or temperature, the surface hardness and molding shrinkage improve. The optimal hexamine contents of WP and PP are determined with respect to the above properties.

## INTRODUCTION

Phenolic resins were the first completely synthetic polymeric materials and have been widely used as engineering plastics because of their good moldability, mechanical and electrical properties, and economical merit. They are generally produced by compounding novolac resins with hexamethylenetetramine (hexamine), woodflour, lubricants, and pigments through a hot roll-milling process. During the production, their flow and curing characteristics, which are thought to dominate moldability and performance, are largely influenced by heating conditions in the roll-milling process. Phenolic resin performance is usually characterized by curing behavior, thermal analysis, and electrical and mechanical properties, which are dependent on curing time, molding pressure, molding temperature, and heat treatment.

An undercured molding, with a low degree of crosslinking, lacks optimal mechanical strength as well as heat and chemical resistance; however, overcured molding leads to embrittlement. Therefore, it is important to obtain the necessary information on conditions which will produce the proper degree of crosslinking.

Many test methods have been proposed for judging the degree of crosslinking.<sup>1</sup> They include water absorption at the boiling point, solvent extraction, recompression molding, electrical resistance, physical properties such as flexural strength and hardness at elevated temperature, and heat distortion temperature. Each method has its advantages and disadvantages; as a result, they are often used in combination depending on the resin type and molding shape.

The most popular method is solvent extraction, in which acetone and tetrahydrofuran (THF) are generally used for phenolics. The principle is based on the fact that the amount of extractable resin diminishes with curing.

However, this method has the disadvantage of being time consuming, not only in the extraction operation, but also in preparing a pulverized sample for molding.

Methods of measuring flow/curing characteristics may be roughly classified into three categories:<sup>2</sup> (a) tests using a molding press, which may include ASTM cup mold and JIS disk flow test; (b) orifice flow tests, which may include Koka, and Rossi Peakes, and the spiral flow test; (C) torque rheometry, which may include Brabender plastometry, curelastometry, Kanavec plastometry, and cone/plate or parallel-plate rheometer including eccentric rotating disk rheometer. The parallel-plate rheometer has an advantage of being able to rapidly heat a sample in a thin film; however, in practice it may show little correlation with moldability since curing during testing is done under slight pressure.

This article discusses several important properties of three kinds of phenolics: commercial, pure, and woodflour-filled that contain different levels of hexamine. Properties measured include curing behavior, thermal, electrical, and mechanical properties.

## EXPERIMENTAL

### Materials

The molded materials used included commercial phenolic resin (CP), pure phenolic resin (PP), and woodflour-filled phenolic resin (WP). The compositions of these three materials were as follows: (a) CP contained 46% novolac resin, 7% hexamine, 26% woodflour, 14% heat retarder, and 7% others (antioxidant, stabilizer, and pigments); (b) PP contained only novolac resin with different hexamine levels (phr): PP-15, PP-2 10, PP-3 15, PP-4 20; and (c) WP contained 60 phr woodflour, 4 phr stearic acid with different hexamine levels (phr): WP-1 9, WP-2 11, WP-3 13, WP-4 15, WP-5 17. Novolac and woodflour were made by Chang Chun Co. Ltd., Taiwan. The novolac composition was: ortho/para mol ratio 64/36, formaldehyde/phenol mol ratio 0.82, free phenol 3-5% (by iodometric titration), and moisture < 1% (by Karl Fischer titration).

### Processes and Methods

Materials were compounded by roll-milling and pulverized to pass a 45-mesh screen. The molded temperatures of CP ranged from 150 to 180°C and molded time lasted from 2 to 10 min. The molded conditions of PP and WP were 175°C, 4 and 7 min, respectively. Molded pressure was held constant at 150 kg/cm<sup>2</sup>. Molded specimens were cooled by water. Three kinds of samples were used: 100 × 100 × 2 mm for Izod impact test and extraction; 100 × 100 × 1 mm for electrical properties and thermal analysis; and 100 mm diameter and 3 mm thickness for shrinkage and hardness analyses.

### Measurement of Properties

#### *Curing Behavior*

Curing behavior was measured using infrared (IR) analysis, solvent extraction and rheology (Rheometer 100, Monsanto Co.). Compounded powder was used for IR and rheological measurements. Only PP was used for the IR and

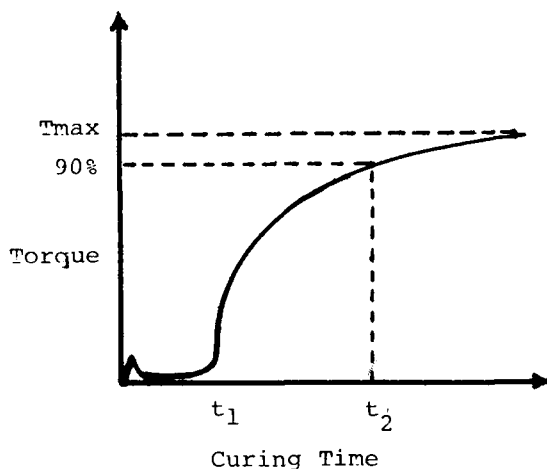


Fig. 1. Torque-curing time curve of phenolics.

solvent extraction measurement to eliminate any possible error that might arise from the simultaneous extraction of natural resins or other materials contained in the fillers. THF was used as an extraction solvent. The amount of the resin extracted was determined and plotted against the curing time. For the rheometer test, a sample (3 g) was charged into the lower die in which the temperature was previously set from 150 to 185°C. The lower disc was oscillated at 100 rpm through an arc of  $\pm 1^\circ$ . When the viscosity of the sample in the die increased to a certain value during the curing, the value was detected as a torque-curing time curve as shown in Figure 1, in which  $t_1$  was the beginning of a rapid increase in torque and  $t_2$  was a point at which the torque reached 90% of its maximum. These two points corresponded to the gel time of cure  $T_g$  and the cure time  $T_c$ , respectively.<sup>2</sup> Each value of  $t_1$  and  $t_2$  was the average of the figures obtained from more than three measurements.

#### *Electrical Properties*

Volume resistivity was measured by ASTM D257 and dielectrical properties were measured by ASTM D150 with frequency from 30 to 3M Hz.

#### *Thermal Analyses*

Thermogravimetric analysis (TGA) was made with a DuPont 1090B Thermal Analyzer equipped with TGA 951, and a heating rate of 20°C/min was used from 100 to 850°C. Differential scanning calorimetry (DSC) was determined by using a DuPont 1090B Thermal Analyzer equipped with DSC 910, and a heating rate of 5°C/min was used from 30 to 200°C. Nitrogen or air was used during the experiment.

#### *Mechanical Properties*

Two methods, Rockwell (R scall) and Shore D2, were used to test the surface hardness of different specimens at 22°C. Izod impact test was measured by ASTM D256. For mold shrinkage, compression molding according to ASTM D955 was used. The diameter was measured at eight different places

relative to the round sheet and the frame. To calculate the average mold shrinkage, the following equation was used:

$$\text{Mold shrinkage}(\%) = \frac{\text{frame diameter} - \text{measured sheet diameter}}{\text{frame diameter}} \times 100$$

## RESULTS AND DISCUSSION

### Curing Behavior

Three methods are used to evaluate the curing behavior: (1) IR analysis to monitor the changes after compounding; (2) solvent extraction to indicate the degree of crosslinking; and (3) rheological measurement to reveal the optimal conditions of molding time, temperature, and hexamine content.

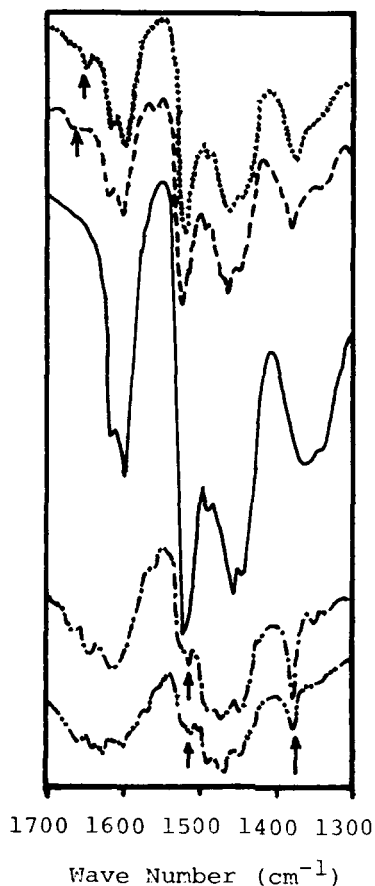


Fig. 2. Ir spectra of CP and PP with various hexamine contents after compounding or molding. CP(—); 5 phr after compounding(.....); 10 phr after compounding(-----); 15 phr after molding (-·-·-·-·-·-·-); 20 phr after molding (-·-·-·-·-·-·-).

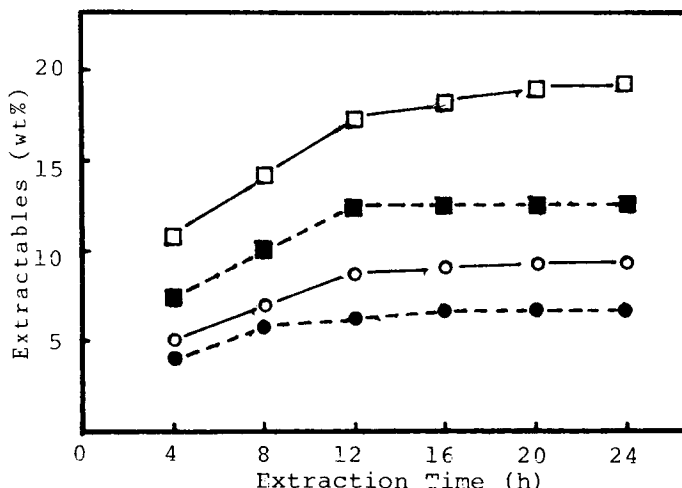


Fig. 3. Effect of hexamine content on the extraction of extractables. Hexamine content: (□) 5 phr; (■) 10 phr; (○) 15 phr; (●) 20 phr.

Figure 2 shows the IR spectra in the region of  $1300\text{--}1700\text{ cm}^{-1}$  for Novolac resin, PP after compounding, and PP after molding. Both PP after compounding and molding produce a new shoulder absorption peak at  $1640\text{--}1650\text{ cm}^{-1}$ , which is the stretching of the azomethine group ( $-\text{CH}=\text{N}-$ ).<sup>3</sup> The presence of this group is indicative of the existence of hexamine. The peak at the region of  $1500\text{--}1520\text{ cm}^{-1}$  is due to a phenolic ring substituted in ortho and para positions.<sup>4</sup> The intensity decreases with increasing hexamine and indicates that the depletion of mono- and disubstituted phenolic rings is brought about by crosslinking. The curing reaction enhances the intensity of the peak at  $1380\text{ cm}^{-1}$ , a fact attributed to methyl group ( $-\text{CH}_3$ ).<sup>4</sup> The increasing intensity also indicates that the PP compounding has started the curing reaction.

The results of THF solvent extraction are shown in Figure 3. PP powder, after being molded with a particle whose size passes through 80 mesh, was suitable for extraction. The percentage of extractables increases with extraction time and levels off in about 12 h, but decreases with the increase of the hexamine content. In other words, the degree of crosslinking rises with the increase of the hexamine content.

Figure 4 shows the effects of the molding temperature and hexamine content on the maximum torque and cure time of CP and PP. The cure time decreases markedly with the elevation of molding temperature or with the increase of hexamine content. However, the maximum torque increases with the elevation of the molding temperature or with the increase of the hexamine content. Thus, elevating the molding temperature or increasing the hexamine content not only shortens the cure time but also raises the maximum torque, a fact that reflects the increase in the degree of crosslinking. Figure 5 shows similar results for WP, but WP-3 with a hexamine content of about 13 phr turns out to possess an optimal composition on account of its shortest cure time and largest torque.

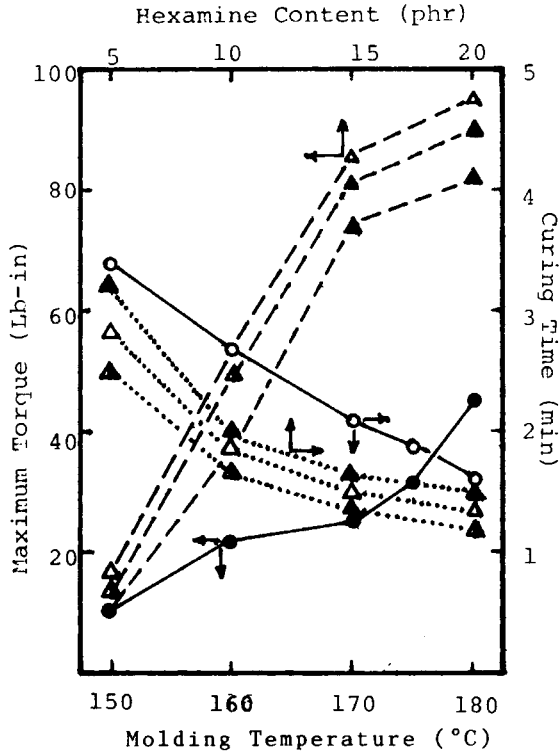


Fig. 4. Maximum torque and cure time of CP and PP at various molding temperatures. CP(O) (●); PP compounding conditions: 100°Cd, 20 min (▲); 100°C, 30 min (△); 110°C, 20 min (△).

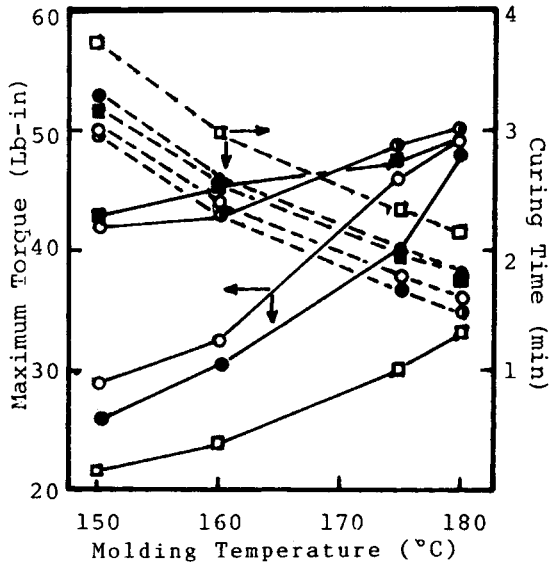


Fig. 5. Maximum torque and cure time of WP at various molding temperatures by rheometer. WP-1 (□); WP-2 (■); WP-3(○); WP-4 (○); WP-5 (●).

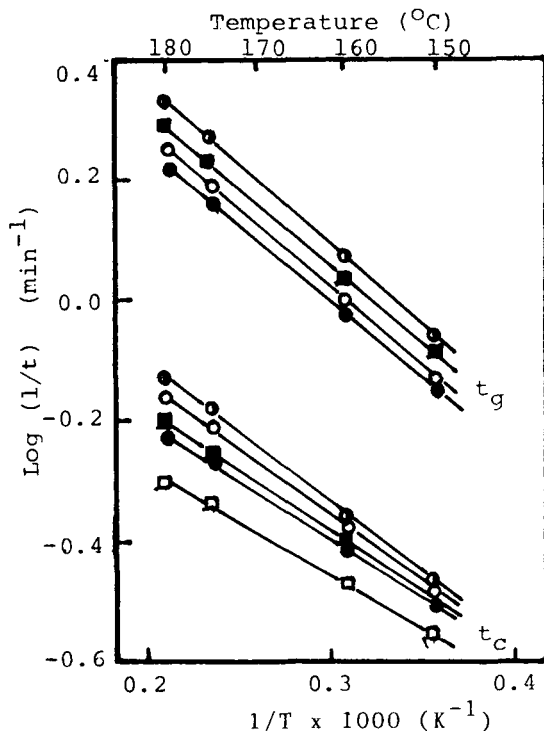


Fig. 6. Arrhenius plots for gel and curing rate of WP. WP-1 (□); WP-2 (■); WP-3 (○); WP-4 (○); WP-5 (●).

The gel time  $t_g$  and time  $t_c$  are shown in Figure 6. The Arrhenius form<sup>5</sup> between 150 and 185°C is :

$$\text{Log}(t/t') = H(1/T - 1/T') / (2.303R)$$

where  $t = t_g$  or  $t_c$  in min,  $H$  is the activation energy in kcal/mol,  $R$  is the gas constant of 1.987 cal/mol-K, and  $T$  is the molding temperature in K.  $H$  can be obtained from the slope of a plot  $\text{log}(1/t)$  versus  $(1/T)$  as shown in Figure 6. The activation energies of CP and WP are shown in Table I. The gel activation energies  $H_g$  of WP are smaller but the cure activation energies  $H_c$  of WP are larger than those of CP. Of the WP, WP-3 has the largest activation energy.

TABLE I  
Arrhenius Activation Energy of CP and WP Determined by Rheometry

Activation energy	CP	WP-1	WP-2	WP-3	WP-4	WP-5
$H_g$ (kcal/mol) <sup>a</sup>	13.50	9.02	9.50	9.82	9.68	9.08
$H_c$ (kcal/mol) <sup>b</sup>	6.71	6.83	7.35	8.46	7.87	7.32

<sup>a</sup>Activation energy of gel.  
<sup>b</sup>Activation energy of cure.

TABLE II  
Exotherm of Curing Reaction of CP, PP and WP Determined by DSC

	CP	PP-1	PP-2	PP-3	PP-4	WP-1	WP-2	WP-3	WP-4	WP-5
$H_c$ (J/g)	41.0	60.2	74.3	78.6	81.5	41.5	47.0	61.2	56.6	50.1

### Thermal Properties

Since the curing reaction is exothermic, DSC thermograms reveal the degree of crosslinking. The larger the exotherm of the reaction, the more the crosslinking. The results of the curing exotherm of CP, PP, and WP are shown in Table II. The curing exotherm of PP increases with the rise in the hexamine content; besides, PP-4 (hexamine content 20 phr) has the largest curing exotherm. However, the largest curing exotherm of WP is for WP-3 (hexamine content 13 phr). CP has the smallest curing exotherm in comparison with PP and WP because of its large amount of the filler.

The values listed in Table III are TGA data of PP after compounding at 100°C for 20 min and the molding at 175°C for 7 min. The weight loss reduces faster in air than in nitrogen, and the temperature of weight loss at 50°C in air is under 700°C. Therefore, the phenolic resins compounded with a high hexamine content or molded with a high temperature are still easily degradable in oxygen. As shown in Table III, PP-4 (in nitrogen) shows better thermal stability than the others in case of a 50% weight loss; also, PP-3 and PP-2 (in nitrogen) have better thermal stability when temperatures are higher than other PPs at the same weight loss. The curing rate of PP-4 is faster than the others because of its higher hexamine content, but the surface of the cured PP-4 will form a hard layer, inhibiting the elimination of small molecules. That is, the fast curing of the surface reduces the degree of crosslinking inside the molded specimen of PP-4 and decreases the thermal stability. However, PP-3 and PP-2 with lower curing rates can proceed to a high degree of crosslinking with the increase of thermal stability. Of course, the low thermal stability of PP-1 is due to its low degree of crosslinking.

TABLE III  
Thermogravimetric Analysis Data of PP

Phenolics	Temperature (°C) of remaining weight						Weight residue final (%)
	95%	90%	70%	50%	30%	10%	
PP-1 <sup>a</sup>	255.2	349.8	582.3	701.7	—	—	31.2
PP-2 <sup>a</sup>	275.3	433.6	592.3	734.9	—	—	35.0
PP-3 <sup>a</sup>	267.1	441.6	611.0	744.4	—	—	35.3
PP-4 <sup>a</sup>	332.1	432.1	593.2	716.8	—	—	34.1
PP-1 <sup>b</sup>	244.0	401.9	573.5	668.0	717.8	771.1	1.0
PP-2 <sup>b</sup>	268.6	436.8	586.7	685.9	753.4	825.5	4.5
PP-3 <sup>b</sup>	253.7	440.1	581.0	664.8	730.0	792.2	2.7
PP-4 <sup>b</sup>	320.8	422.6	555.7	654.8	720.2	773.3	1.1

<sup>a</sup>Measurement in nitrogen atmosphere.

<sup>b</sup>Compounded at 100°C for 20 min and measured in air atmosphere.



TABLE IV  
Thermogravimetric Analysis Data of PP and WP

Phenolics <sup>a</sup>	Temperature (°C) of remaining weight <sup>b</sup>				Weight residue final <sup>b</sup> (%)	IDT <sup>b</sup> (°C)	FDT <sup>b</sup> (°C)
	95%	90%	70%	50%			
PP-2	281.6	429.0	583.5	—	60.1	378.0	636.0
PP-3	266.8	414.3	580.3	—	58.9	391.5	642.5
PP-4	264.3	355.5	575.2	—	57.1	398.0	643.0
WP-1	269.9	341.5	447.8	626.6	44.1	304.0	608.5
WP-2	278.0	344.9	462.1	640.2	45.2	305.0	609.5
WP-3	281.9	345.8	461.0	666.0	46.3	310.0	611.0
WP-4	266.0	337.2	460.0	641.0	45.4	302.0	589.5
WP-5	265.1	335.1	457.0	639.0	45.3	296.0	595.0

<sup>a</sup>Phenolics are compounded at 100°C for 30 min.

<sup>b</sup>Measured in nitrogen atmosphere.

From Table IV, the initial decomposition temperature (IDT, 398°C) and final decomposition temperature (FDT, 643°C) of PP-4 are higher than the others, but the residue of PP-2 (60.1%) at the final stage has the highest in value. The data also show that both the temperatures of weight loss at any residual percentages and the final weight residue are greatest for WP-3, indicating that WP-3 (hexamine content 13 phr) has the best thermal stability. The IDT and FDT of WP are about 296–314°C and 595–611°C, respectively, compared to those of PP whose ranges are 370–400°C and 635–645°C, respectively.

### Electrical Properties

Untreated CP, which has a 1 to 100 mesh particle size, is molded directly. Its volume resistivity is about  $10^{12}$ – $10^{13}$  Ω-cm. Volume resistivity increases with an increase of molding temperature within 150–180°C, and there is a maximum value at a molding time of about 4 min [Fig 7(a)]. The treated CP is sieved through a 45-mesh screen and preheated at 60°C for 20 min. Its volume resistivities are at least 15 times as large as the values of untreated samples [Fig 7(a)]. The best results for volume resistivity are molded at 175°C for 4 min because the specimen will form a crosslinked layer on the surface at higher temperature, a characteristic that inhibits the release of small molecules during curing. The inhibition reduces the degree of crosslinking inside the specimen. However, increasing the hexamine content in PP or WP will cause a decreasing volume resistivity [Fig 7(b)]. The figure also indicates that the volume resistivity increases with heat treatment at 150°C. These results suggest that the specimen with 11 phr hexamine will be superior to the others after long heat treatment. The reasons for these improvements are<sup>6</sup>: (1) decrease in the hydrophilic nature of filler; (2) acceleration of volatilization of ionic compounds such as water, ammonia and amine; and (3) change of crosslinking from methylene amine to methylene.

Figure 8 shows the dielectric constant  $E'$  and dissipation factor  $\tan \delta$  of PP, heat-treated WP at different hexamine contents, and CP at different molding

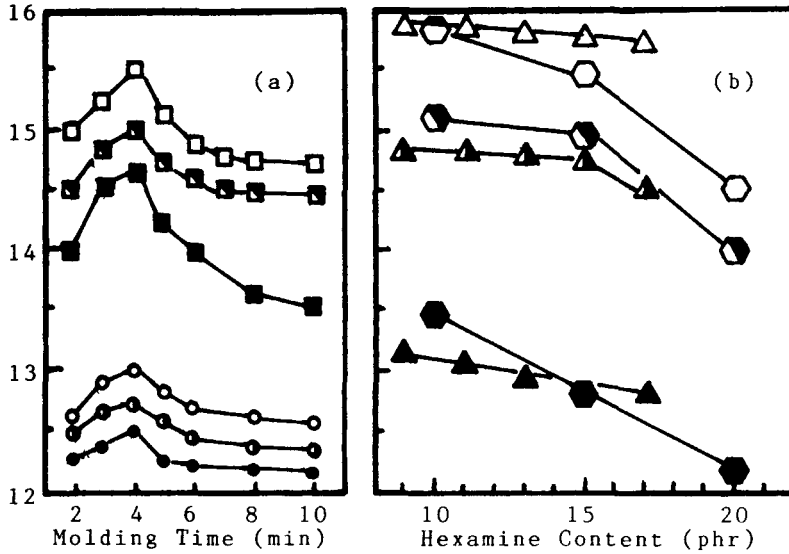


Fig. 7. Volume resistivities of phenolics under different processes, molding time, and hexamine content. (a) CP without sieved and preheated: molded at 180°C (○); 170°C (◐); 160°C (●). CP after being sieved and preheated: molded at 150°C (■); 185°C (◑); 175°C (◒). (b) without preheated: PP (●); WP (▲). Heat treatment at 150°C: PP 4 h (○); WP 8 h (Δ). Preheated and compounded: PP 100°C for 30 min (◐); WP 100°C for 30 min (Δ).

temperatures and times. The change indicates that  $E'$  and  $\tan \delta$  of PP and WP increase with hexamine content. For CP,  $E'$  decreases with the increase in the molding temperature, especially for longer molding time. Dependence of WP dielectric properties ( $E''$ ,  $E'$ , and  $\tan \delta$ ) upon the frequency within the range from 30 to 3M Hz is shown in Figure 9. Those properties all decrease with an increase in frequency. Each property of  $E''$ ,  $E'$  and  $\tan \delta$  of WP with different hexamine contents reach a constant value at higher frequency, but are significantly different at a lower frequency. The results of CP and PP reflect the same trend.

### Mechanical Properties

The results given in Figure 10 indicate that the shrinkage of phenolic resins will decrease with an increase in molding time, and the shrinkage of CP with the molding temperature at 170°C has the least value. The shrinkage of PP and WP increases with an increase in hexamine content, except that WP of the hexamine content is less than 11 phr. At a certain value of hexamine content, the shrinkage of PP is smaller than that of WP.

Figure 11 is a plot of hardness versus the molding time of CP as a function of the molding temperature. The greater the molding time, the harder the surface, except that the hardness levels off at about 6 min to a Shore D2 hardness of 90–92. For PP and WP, increasing the hexamine content raises hardness, though it levels off at about 13 phr to a Shore D2 hardness of 91–92.

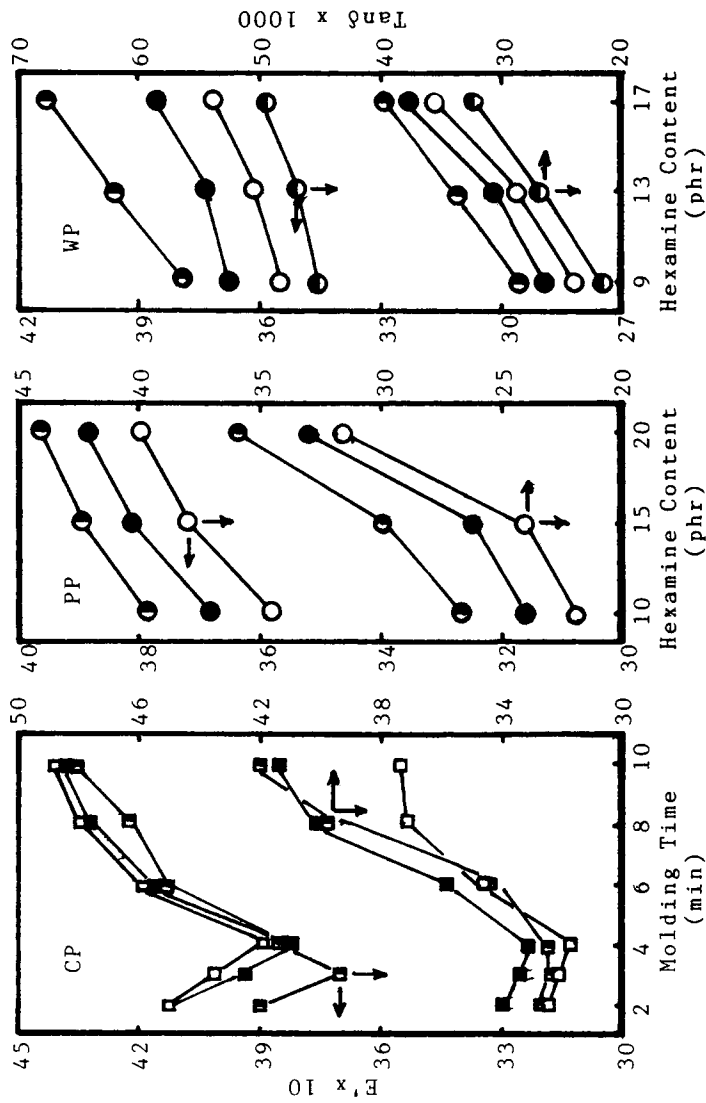


Fig. 8. Dielectric constant  $E'$  and dissipation factor  $\tan \delta$  of phenolics under different process, molding time, and hexamine content. CP: molded at: 150°C (□); 160°C (■); 170°C (▣). PP: compounded at: 100°C, 30 min (○); 110°C, 20 min (●); 100°C, 20 min (⊙). WP: without preheating (⊖); preheated at: 60°C, 20 min (⊕); 150°C, 4 h (⊗); 150°C, 8 h (⊘).

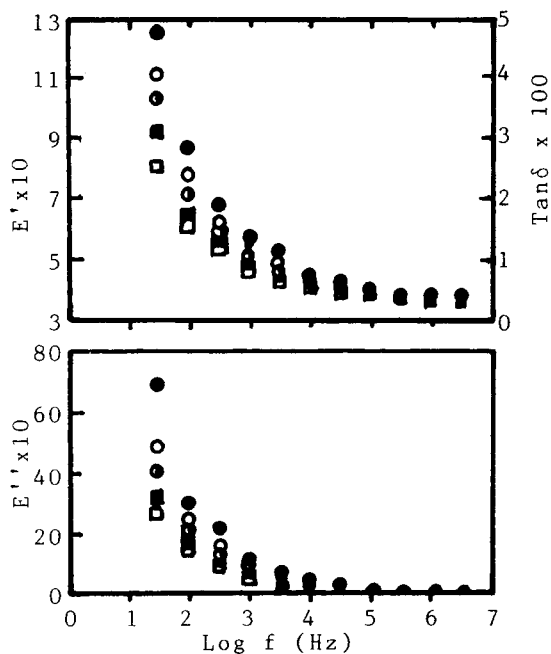


Fig. 9. Effect of frequencies on dielectric constant ( $E'$ ), dissipation factors ( $\tan \delta$ ) and dielectric loss ( $E''$ ) of WP. WP-1 ( $\square$ ); WP-2 ( $\blacksquare$ ); WP-3 ( $\bullet$ ); WP-4 ( $\circ$ ); WP-5 ( $\bullet$ ).

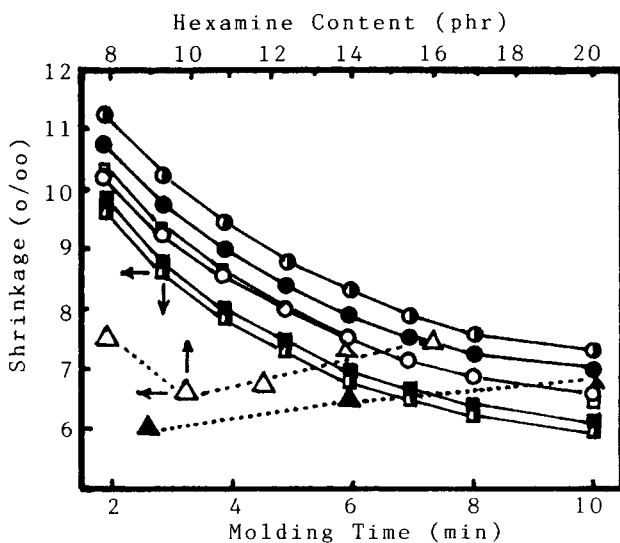


Fig. 10. Shrinkage of phenolic resins vs. hexamine content and molding time. WP ( $\Delta$ ) PP ( $\blacktriangle$ ); CP molded at: 150°C ( $\square$ ); 160°C ( $\blacksquare$ ); 170°C ( $\square$ ); 175°C ( $\circ$ ); 180°C ( $\bullet$ ); 185°C ( $\circ$ ).

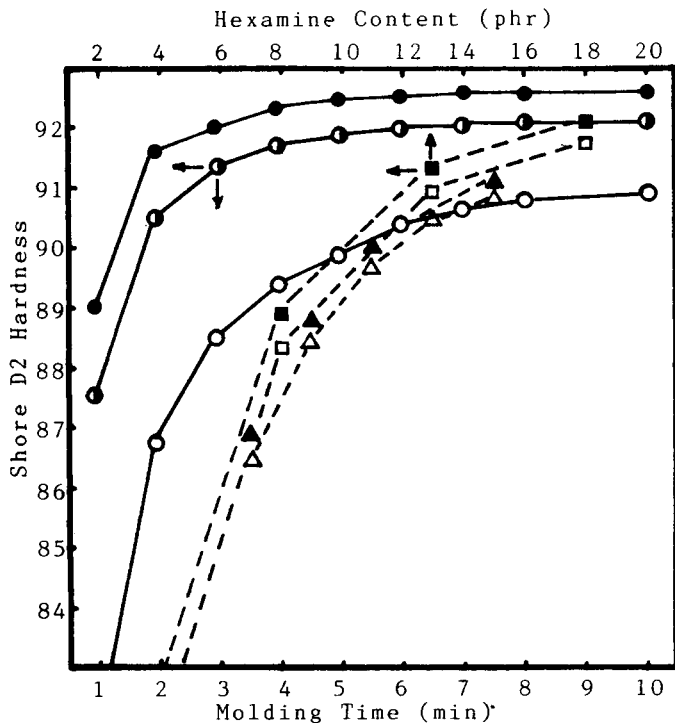


Fig. 11. Shore D2 hardness vs. molding time and hexamine content. CP molded at: 150°C (○); 175°C (●); 185°C (○). PP molded at: 175°C, 7 min (■); 175°C, 4 min (□). WP molded at 175°C 7 min (▲); 175°C, 4 min (△).

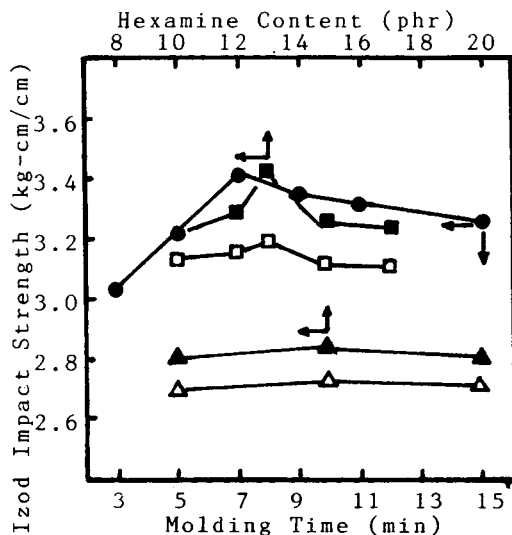


Fig. 12. Effect of molding time on Izod impact strength of CP and hexamine content on Izod impact strength at a molding temperature of 175°C. CP (●); WP 7 min (■); WP 4 min (□); PP 7 min (▲); pp 4 min (△).

Figure 12 shows the effects of the molding time on the Izod impact strength of CP, and the hexamine content on the Izod impact strength of PP and WP using molding time as a parameter. There is a maximum Izod impact strength of WP at a hexamine content of 13 phr. This observation is in agreement with what is observed from scanning electron micrographs, in that the best compatible phase is with this hexamine content composition. For CP, the Izod impact strength at a molding time of 7 min has the highest value. However, molding time and hexamine content have little effect on the Izod impact strength of PP.

### CONCLUSIONS

There are some differences in the IR absorption peaks between 1300 and 1700  $\text{cm}^{-1}$  among the novolac and molded specimens as a result of the hexamine crosslinking. The percentages of the residue after solvent extraction indicates that the degree of crosslinking increases with an increase in the hexamine content.

The gel activation energies of WP are smaller, but the cure activation energies of WP are larger than those of CP. The largest activation energy of WP is WP-3 with a hexamine content of 13 phr. Based on the DSC thermogram, the largest thermal stability is for WP-3.

The IDT and FDT of PP are about 370–400°C and 635–654°C, respectively; however, the IDT and FDT of WP are smaller, being at 295–310°C and 590–615°C, respectively. Volume resistivity of sieved and preheated samples is at least 15 times larger than that of untreated samples. The greater the hexamine content, the lower the volume resistivity. The dielectric constant, dielectric loss, and dissipation factor decrease with the increase in frequency and the decrease in hexamine content.

The presence of woodflour improves the Izod impact strength and decreases shrinkage. Increasing the hexamine content of WP will increase hardness and shrinkage. The best molding conditions for the Izod impact strength are 175°C, 7 min for CP, and about 11–13 phr of the hexamine content for PP and WP.

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