

Physical Properties of Moldings from Liquefied Wood Resins

LIANZHEN LIN, MARIKO YOSHIOKA, YAOGUANG YAO, and NOBUO SHIRAISHI*

Department of Wood Science and Technology, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606, Japan

SYNOPSIS

The liquefied wood resins obtained by liquefying wood in the presence of phenol using phosphoric acid as a catalyst were applied to prepare the moldings by using hexamine as a hardener. The effects of the molding conditions and the moldings' compositions on flexural properties and water-sorption kinetics of the moldings were investigated. It was found that the liquefied wood resins had satisfactory and almost uniform curing reactivity, although they were composed of different kinds of wood components. The flexural properties of the liquefied wood moldings were enhanced with an increase in the amount of combined phenol within the liquefied wood and became comparable to those of the commercial novolak when the amounts of combined phenol were larger than 75%. Furthermore, it was also found that with an increase in the content of wood fillers the flexural properties of the liquefied wood moldings were enhanced more effectively than were the cases of the commercial novolak moldings, exhibiting that the liquefied wood resins could gain a greater reinforced effect from compounding with the wood fillers than did the commercial novolak resins, and the greater the amount of combined phenol, the higher the reinforcing performance of wood fillers. In addition, water-sorption measurements and the SEM observations of the moldings indicated that the liquefied wood resins had much greater hydrophilicity than that of the novolak and revealed a greater compatibility with wood fillers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Liquefaction of wood in the presence of phenol and the application of the resulting liquefied wood as novolaklike thermosetting resins has been intensively investigated recently.¹⁻⁴ Most of the efforts have been focused on the preparation of the liquefied wood resins, especially by using sulfuric acid as a catalyst. Few reports have been found in the literature concerning the relationships among the moldings' compositions, molding conditions, and the properties of the liquefied wood moldings. Because the constitution of the liquefied wood is significantly complicated and different from that of conventional phenolic resins,⁵ a comprehensive study on the properties of the liquefied wood resins is quite necessary. In previous articles,⁶ we studied the liquefaction of wood in the presence of phenol by using

a milder acid, phosphoric acid, as a catalyst. It was found that the obtained liquefied wood resins were quite different in several aspects from those obtained by the sulfuric acid-catalyzed method,⁷ i.e., the former has lower amounts of combined phenol, ranging from 40 to 90%, and retains chemical structures closer to those of original wood components. In this study, the moldings were prepared from these liquefied wood resins by using hexamine as a hardener, and the influences of the moldings' compositions and the molding conditions on the flexural properties and water-sorption of the moldings were investigated.

EXPERIMENT

Materials

The liquefied woods used as matrix resins for molding compounds were prepared according to the procedure described in a previous paper.⁶ Both the

* To whom correspondence should be addressed.

commercial novolak resin and the wood powders used as the filler (200 mesh past size) were supplied by Hitachi Co. Hexamine, as a hardener, was supplied by Mitsubishi Gas Chemical Co. All the other chemicals were of reagent grades and were used without further purification.

Preparation of Moldings from Liquefied Wood Resins

The general formula for the preparation of moldings is listed in Table I. Except for the resins (liquefied wood or novolak), all the other ingredients were premixed sufficiently in a mortar, followed by the addition of an acetone solution of the resins, and then the ingredients were mixed until a uniform mixture was obtained. The resulting mixture was dried in an oven at 70°C for 1 h and then reground into powder and kept in a desiccator before molding.

About 5 g of the compound powders mentioned above were compression-molded into test specimens with the dimensions of 80 × 10 × 4 (mm) in a Laboratory Molding Press. The molding was accomplished by a preheating for 1 min and a degassing, followed by a molding under a pressure of 38 MPa at 185°C for 2–45 min and a cooling under a certain pressure for 10 min.

Measurement of Mechanical Properties

The flexural test of the samples was conducted using a Shimadzu Autograph DCS-R-500 according to JIS K-6911 with a strain rate of 2 mm/min. The samples were conditioned at 20 ± 0.5°C and 60% RH for at least 48 h before being tested. The flexural strength and modulus were calculated following JIS K-6911. Additionally, in this article, the flexural toughness (or energy absorbed) was used to express the toughness of the moldings apart from the flexural strength and flexural modulus because the thermosetting resins such as phenolic resins are relatively brittle.

Table I Compositions of the Compounds for Moldings

Ingredients	Weight Parts (g)
Liquefied wood resins or novolak resin	37.7
Wood powder	49.5–202
Hexamine	9.4
Calcium hydroxide	2.4
Zinc stearate	1.0

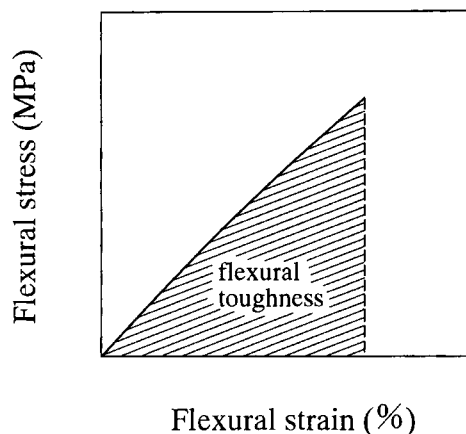


Figure 1 Flexural stress–strain curve and the flexural toughness.

The flexural toughness was calculated from the area under the flexural stress–strain curve, up to the breaking point, as shown in Figure 1.

Acetone Extraction of Cured Liquefied Wood Moldings

The cured liquefied wood moldings were ground with a grinder–mixer and then the 40 mesh-pass portion was taken. The ground powders were vacuum-dried at 60°C to constant weights. About 2 g of this powder was precisely weighed into a predried cellulose tube and then was extracted with acetone by a Soxhlet extractor for 60 h. The weight loss of the sample after drying was recorded. The extraction percentage was calculated as follows:

$$\text{Extracted amount (\%)} = \frac{W_0 - W_t}{W_0} \times 100$$

where W_0 and W_t are the weight of samples before and after extraction, respectively.

Test for Water Sorption

The molded specimens with the dimensions of 50 × 10 × 4 (mm) were used for the measurements of water sorption. After being vacuum-dried at 70°C to a constant weight, the specimens were immersed in the deionized water. The specimens were periodically taken out of the water, blotted with a Kimwipe to eliminate excess water from the surface, weighed, and immediately put back into the water. All the treatments were conducted in a conditioning room of 20 ± 0.5°C and 60% RH. The weights of the specimens were recorded until an equilibrium

value was reached. The amounts of water sorption (M_t) were calculated as follows:

$$M_t (\%) = \frac{W_t - W_0}{W_0} \times 100$$

where W_t and W_0 are the weight of specimen at a certain sorption time t and the initial dry weight of specimen, respectively.

Scanning Electron Microscopy Observation

Observations of the moldings' morphology were conducted using a JEOL JSM-T330A scanning microscope. The samples were mounted on brass stubs and were coated with a thin layer of gold using a JEOL JFC-1100E ion sputter coater. The water-sorbed samples were dried before coating to remove all the water sorbed.

RESULTS AND DISCUSSION

Effect of the Amounts of Combined Phenol on the Flexural Properties

The effects of the amounts of combined phenol within the liquefied wood resins on the flexural properties of the moldings are shown in Figures 2 and 3. It is obvious that all of the flexural strength, modulus, and toughness become progressively greater as the amount of combined phenol increases. These relationships are consistent with our previous findings in the cases of sulfuric acid catalytic and noncatalytic methods.⁵ These relations can be attributed to the fact that the liquefied wood resins

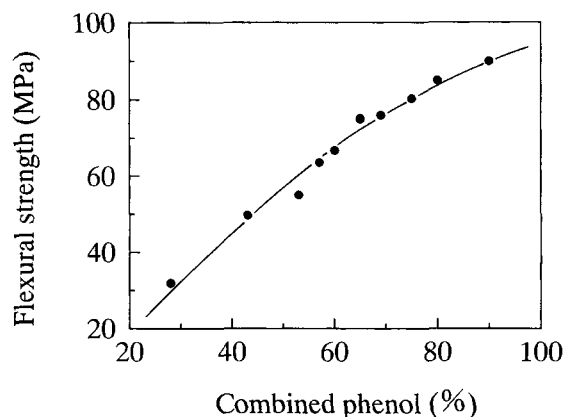


Figure 2 Effects of the amount of combined phenol on the flexural strength of the liquefied wood moldings with filler contents of 50%. The molding was accomplished by hot pressing for 2 min under the pressure of 38 MPa at 185°C.

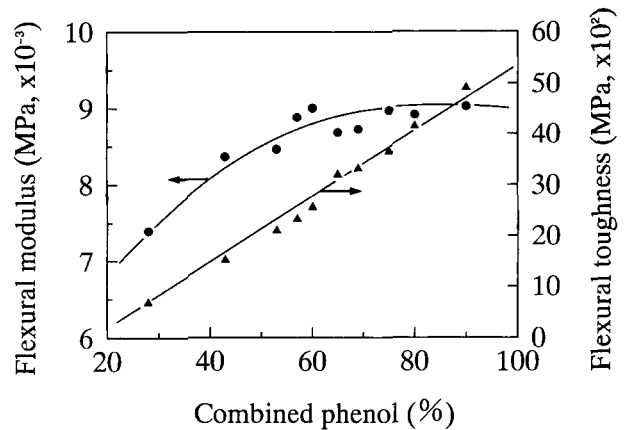


Figure 3 Effect of the amounts of combined phenol on the flexural modulus and toughness of the liquefied wood moldings with filler contents of 50%. The molding was accomplished by hot pressing for 2 min under the pressure of 38 MPa at 185°C.

with greater amounts of combined phenol have more crosslinking sites; therefore, with an increase in combined phenol, the network density of the matrix (i.e., liquefied wood resins) increases. On the other hand, as proposed in our previous article,⁶ an increase in the combined phenol could enhance the interaction (or wetting) between liquefied wood resins and wood fillers. In general, the performance of reinforcing strongly depends on the interfacial adhesion between the filler and matrix, and the stronger is the interfacial adhesion, the more effective becomes the reinforcement.⁸ In addition, better wetting between matrix and fillers permits better dispersion of fillers in the matrix.⁹ As a result, the flexural strength, modulus, and toughness of the liquefied wood moldings increase with an increase in the amount of combined phenol. Furthermore, it has been found that when the amount of combined phenol reaches 75% the flexural properties of the liquefied wood moldings become completely comparable to those of the commercial novolak moldings. When the combined phenol amount goes up to over that value, the influence of the combined phenol on the flexural strength and modulus become small, especially on the flexural modulus. This phenomenon indicates that the flexural properties except for the flexural toughness cannot be improved linearly by increasing the combined phenol after the latter reaches a reasonable value.

Effect of Filler Contents

Figures 4–6 show the effect of filler contents on the flexural strength, modulus, and toughness of the

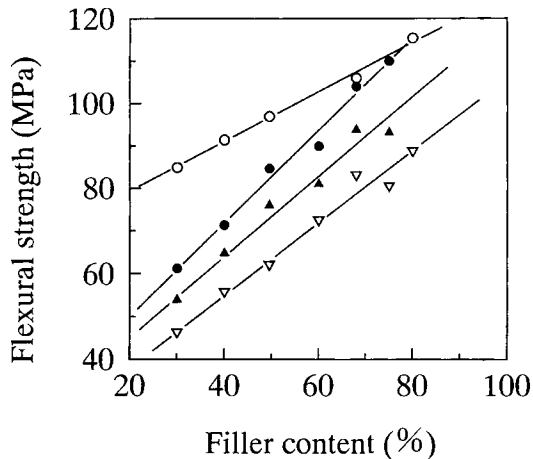


Figure 4 Effect of filler contents on the flexural strength of the moldings. Liquefied woods with combined phenol of (∇) 50%, (\blacktriangle) 60%, and (\bullet) 79%; (\circ) commercial novolak resin. The molding was accomplished by hot pressing for 2 min under the pressure of 38 MPa at 185°C.

moldings. It has been found that with an increase in the filler contents all the flexural properties increase linearly, and the greater is the amount of combined phenol, the larger becomes the slopes of curves except for the cases for the flexural modulus (Fig. 5). In other words, the liquefied wood resins can be more effectively reinforced by the addition of wood fillers as the amount of combined phenol becomes greater, which is in agreement with the result shown in Figure 2. It is worthwhile to notice

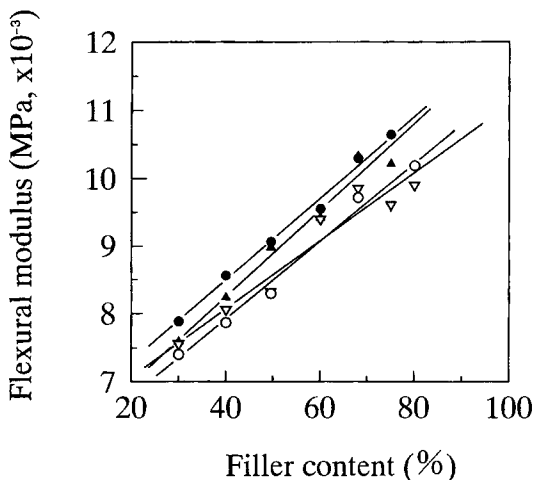


Figure 5 Effect of filler contents on the flexural modulus of the moldings. Liquefied woods with combined phenol of (∇) 50%, (\blacktriangle) 60%, and (\bullet) 79%; (\circ) commercial novolak resin. The molding was accomplished by hot pressing for 2 min under the pressure of 38 MPa at 185°C.

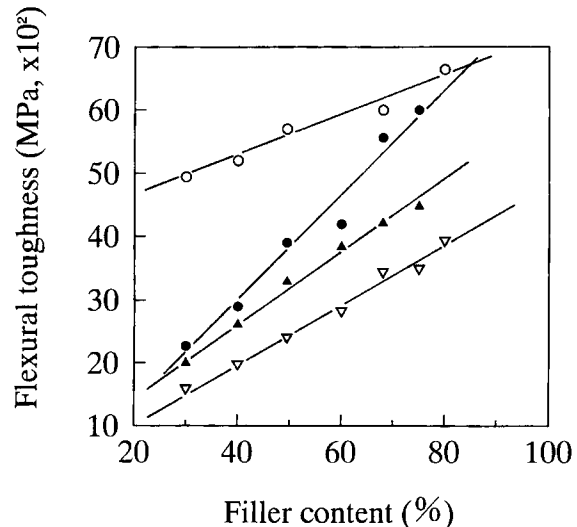


Figure 6 Effect of filler contents on the flexural toughness of the moldings. Liquefied woods with combined phenol of (∇) 50%, (\blacktriangle) 60%, and (\bullet) 79%; (\circ) commercial novolak resin. The molding was accomplished by hot pressing for 2 min under the pressure of 38 MPa at 185°C.

that the slopes of flexural strength or toughness vs. the content of wood filler for the liquefied wood moldings are greater compared with those for the commercial novolak moldings. These results suggest a stronger interaction or compatibility between the liquefied wood resins and the wood fillers than in the case of the novolak resin and the wood filler.

This finding has been further proved by comparing the fractured surface of the novolak moldings with that of liquefied wood moldings. Figure 7 shows the fractured surfaces of the novolak moldings with fillers of 50% weight. It is evident in Figure 7(a) that there exist a number of fibers being pulled out and smooth channels from which the fibers have been drawn out. By a closer observation at a high magnification [Fig. 7(b)], it can be seen that the pulled-out fibers are significant and there is no residual matrix resin adhering to the surface of the wood fibers. These results indicate weak interaction between the novolak matrix and wood fibers. Figure 8 shows the fracturing surfaces of liquefied wood moldings. It is demonstrated in Figure 8(a) that the drawn fiber length observed is relatively short and the smooth channels rarely appear. Besides, the closer observation at a high magnification [Fig. 8(b)] reveals severely broken fibers on the fractured surface and some degrees of matrix resin retention on the fiber surfaces, indicating a strong interaction existing between the liquefied wood matrix and wood fillers.

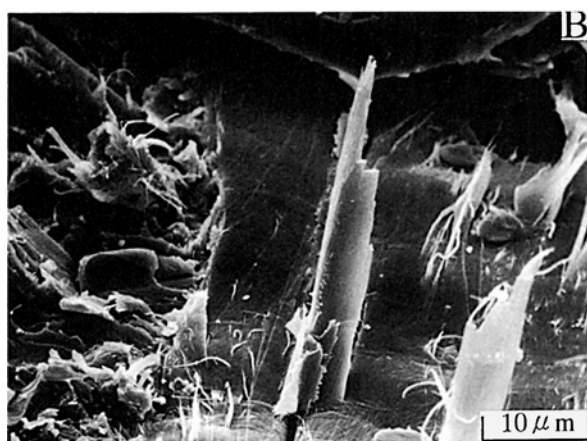


Figure 7 SEM micrographs of the fractured surfaces of the novolak moldings with filler contents of 50%.

Effect of Curing Time

The curing-time dependence of mechanical properties can be used as a measure to express the curing behavior or reactivity of thermosetting resins. Figures 9 and 10 show the relationships between curing time and flexural properties of the moldings. It can be seen that the curing-time dependencies of flexural properties for the liquefied wood moldings are similar to those for the novolak moldings. The flexural strength and modulus initially rise to the maximums with an increase in the curing time, followed by gradual decreases. The larger is the amount of combined phenol, the earlier the peak appears and the higher becomes the maximum. This result indicates that the liquefied wood resins with larger amounts of combined phenol have higher hardenability and a shorter curing time is required in order to obtain the optimum curing state. Compared with the commercial novolak, it can be pointed out that the liq-

uefied wood resins have somewhat lower hardenability.

The acetone extraction test is a simple method for evaluating the curing degree of rigid thermosetting resins such as phenolic resins.¹⁰ By measuring the change in the amounts of extracts with molding time, the curing degree of liquefied wood resins can be roughly evaluated. In addition, the amount of extracts corresponding to the equilibrium value in the extraction curve can be used to evaluate the amount of the liquefied components lacking reactivity.

The results of the acetone extraction test for the cured liquefied wood compounds are shown in Figure 11. It was found that the extracted amounts went down to equilibrium values with curing time up to about 5 min, and the larger are the amounts of combined phenol, the earlier appear the equilibrium points. This result agrees well with the results for the curing-time dependencies of the flexural prop-

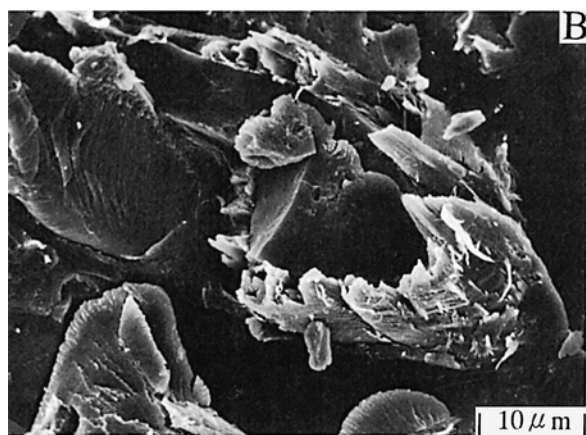
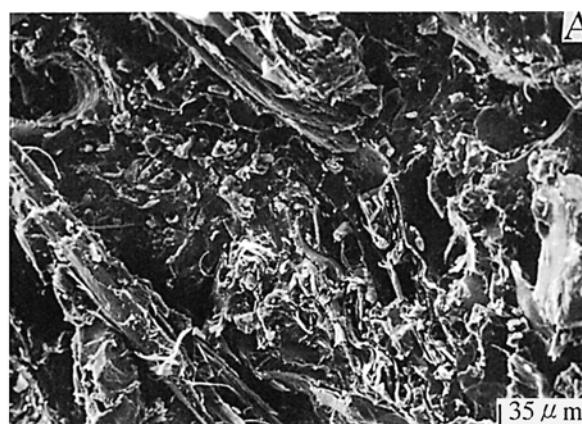


Figure 8 SEM micrographs of the fractured surfaces of the liquefied wood moldings with filler contents of 50%.

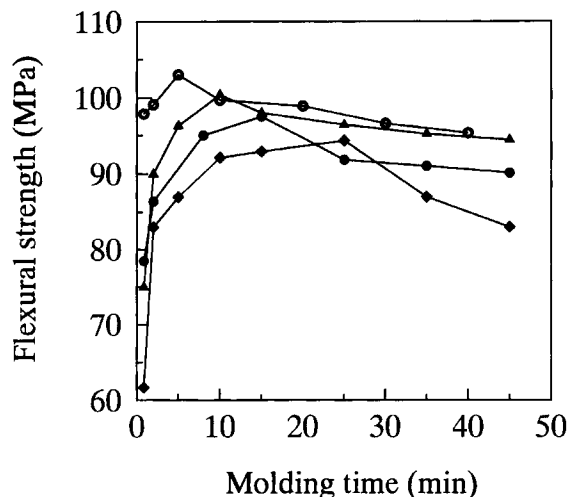


Figure 9 Effect of molding time on the flexural strength of the moldings. Liquefied woods with combined phenol of (◆) 60%, (●) 72%, and (▲) 81.6%; (○) commercial novolak resin. The filler contents of all the moldings were 60%.

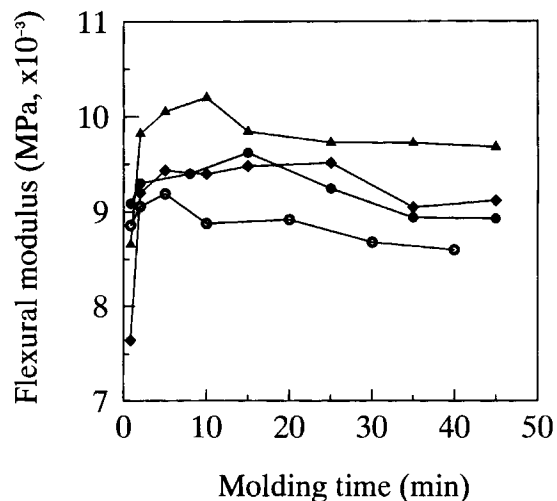


Figure 10 Effect of molding time on the flexural modulus of the moldings. Liquefied woods with combined phenol of (◆) 60%, (●) 72%, and (▲) 81.6%; (○) commercial novolak resin. The filler contents of all the moldings were 60%.

erties as shown in Figures 9 and 10. Additionally, such a small amount of extracts as 0.1–0.2% after reaching the maximum curing demonstrates that the liquefied wood resins have a rather satisfactory and uniform reactivity, even though the liquefied wood resins are complicated mixtures which are composed of degraded and phenolated wood components.⁷

Effect of Concentrating Time

Similar to the preparation of the conventional novolak resin, the free phenol must be removed from the liquefaction products for obtaining the final product resins. For that purpose, the liquefied wood solution was concentrated at an elevated temperature (180°C) under reduced pressure as done in the usual novolak manufacturing process. However, because the liquefied wood components still have reactivity at high temperature, it can be expected that the concentration conditions affect the chemical structures of the components of the liquefied wood resins and, therefore, result in changes in the thermofluidity, moldability, and physical properties of the liquefied wood resins. In this study, an attempt was made to examine the effect of concentrating time on flow temperature and flexural properties. As shown in Table II, extending the concentrating time more than 40 min leads to decreases in the flexural strength, modulus, and toughness of the moldings prepared from the resulting liquefied wood resins and, in contrast, leads to an increase in the

flow temperature of the liquefied wood resins. Additionally, it was observed that when the concentrating time is too long the liquefied wood cannot show moldability any more, i.e., the molded specimens had many cracks and tended to stick on the surface of the molding die, probably resulting from the lack of occurrence of enough crosslinking. These results suggest that an overconcentration of the liquefied wood mixtures leads to too much condensa-

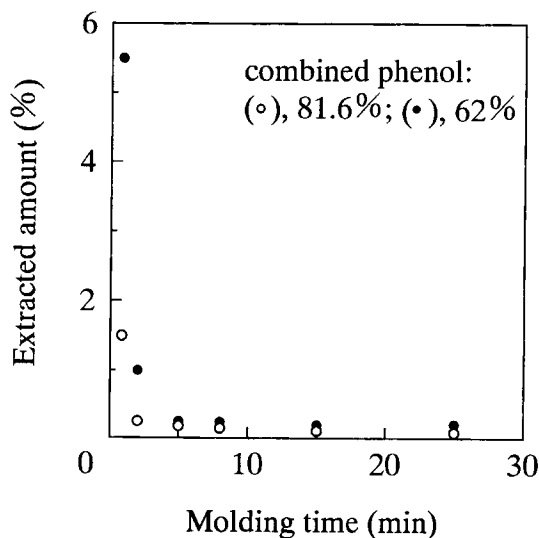


Figure 11 Effect of molding time on the acetone extracted amount for the liquefied wood moldings. The filler contents of all the moldings were 60%.

Table II Effect of the Concentrating Time of Liquefied Wood Solution on the Flexural Properties of Liquefied Wood Moldings and Flow Temperature of the Liquefied Wood Resins

	Concentrating Time (min)			
	40	60	80	90
Flexural strength (MPa)	94	85	79	77
Flexural modulus (MPa, $\times 10^{-3}$)	9.8	9.6	9.7	9.3
Flexural toughness (MPa, $\times 10^2$)	46.8	42.5	37.9	32
Flow temperature ($^{\circ}\text{C}$)	100	114	130	—

Liquefaction reaction conditions: wood/phenol/ $\text{H}_3\text{PO}_4 = 50/150/7.2$, 120 min, 160°C . Concentrating temperature 180°C . Wood filler content of the moldings 60%; the molding was accomplished by hot pressing for 2 min under the pressure of 38 MPa at 185°C .

tion of the liquefied wood resins and therefore results in decreases in the reactivity and moldability of the liquefied wood resins.

Kinetics of Water Sorption

For further evaluating the characteristics of the wood-based thermosetting moldings, the water-sorption behavior of the moldings was examined. As shown in Figure 12(a), the amount of water sorbed by the specimens (M_t) was plotted against the square root of time divided by the thickness of specimens ($t^{1/2}/\Delta x$). It can be seen that the water-sorption processes of the moldings follow Fick's law, i.e., the amounts of water sorption increase linearly with the square root of time and then gradually approach the equilibrium plateaus. Therefore, the apparent diffusion coefficients of water in the moldings can be calculated based on the slopes of the initial linear stages of the curves according to the following equation¹¹:

$$M_t/M_{\infty} = (4/\pi^{1/2})(1/\Delta x)(Dt)^{1/2},$$

where Δx is the thickness of the specimen, and M_t and M_{∞} , the water-sorption amounts of specimens at time t and an equilibrium sorption time, respectively. The values of diffusion coefficients (D) and the equilibrium water-sorption amounts (M_{∞}) are shown in Table III. It was found that an increase in the wood filler content leads to increases in both the diffusion coefficient and the equilibrium water sorp-

tion, being understandable because of the hydrophilic nature of wood fillers. In the meantime, the liquefied wood moldings with larger amounts of combined phenol reveal smaller diffusion coefficients and equilibrium water-sorption amounts, suggesting a decrease in the hydrophilicity of the liquefied wood resins and an increase in the crosslinking density of the moldings with increasing amounts of combined phenol.

In contrast to those of the liquefied wood moldings, especially in the cases for a lower amount of combined phenol and higher filler contents, the

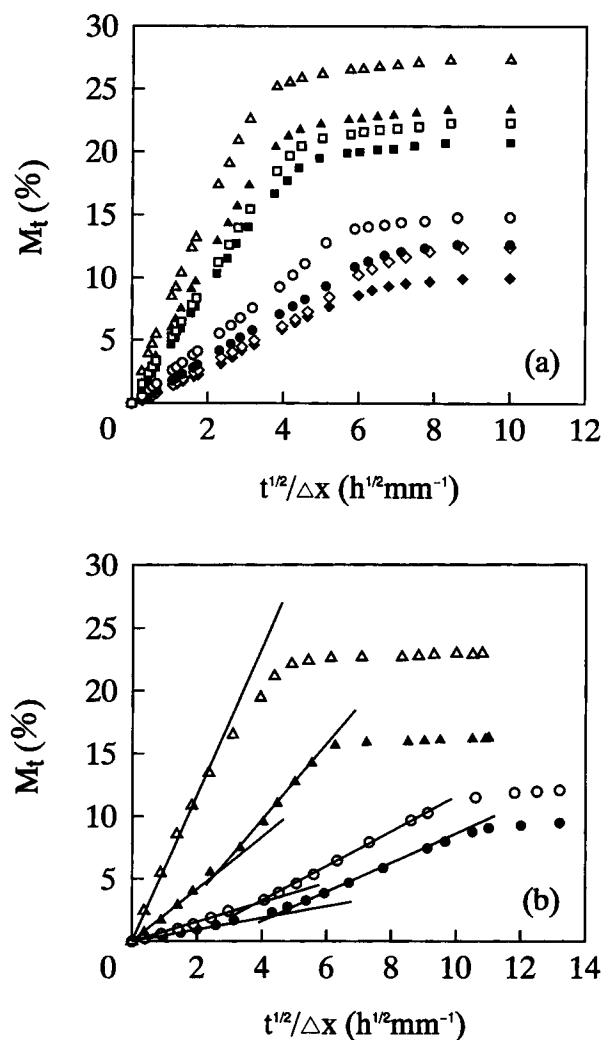


Figure 12 (a) Water-sorption curves for the liquefied wood moldings with filler contents: (\blacklozenge , \diamond) 40%, (\bullet , \circ) 50%, (\blacksquare , \square) 68%, and (\blacktriangle , \triangle) 75%. Solid and empty marks express the liquefied wood resins with combined phenol of 50 and 60%, respectively. (b) Water-sorption curves of the commercial novolak moldings with filler contents: (\bullet) 40%, (\circ) 50%; (\blacktriangle) 68%; (\triangle) 80%.

Table III Effect of Filler Contents and Combined Phenol on Diffusion Coefficients (D) and Equilibrium Water-sorption Amounts (M_∞) of Liquefied Wood Moldings

Content of Wood Filler (%)	Amount of Combined Phenol			
	50%		60%	
	$D \times 10^8$ (cm ² /s)	M_∞ (%)	$D \times 10^8$ (cm ² /s)	M_∞ (%)
40	1.26	12.2	1.24	9.9
50	1.52	14.5	1.27	12.7
60	2.19	19.2	—	—
68	3.01	21.4	2.67	20.7
75	3.94	27.4	3.29	23.4
80	4.63	31.4	—	—

equilibrium water-sorption amounts (M_∞) of the commercial novolak moldings are obviously smaller, as shown in Table IV. Additionally, it is worthwhile to notice that the linear stages in the water-sorption curves for the novolak moldings are composed of two sections with different slopes, as shown in Figure 12(b), and the intersection points of these two linear slope lines gradually reduce their values toward zero on the abscissa, as the wood filler content increases, i.e., the differences in the slopes between the two linear sections diminished with increasing the wood filler content up to 80%. When the filler content was 80%, only one linear stage is observed in the water-sorption curve. The diffusion coefficients for the novolak moldings were calculated based on the individual slopes of both the linear sections, and the results are also listed in Table IV. Compared with Table III, it can be seen that in the same filler content the water-diffusion coefficients for liquefied wood moldings are fairly greater than those of com-

Table IV Effect of Filler Contents on the Diffusion Coefficients (D) and Equilibrium Water-sorption Amounts (M_∞) of the Commercial Novolak Moldings

Content of Wood Filler (%)	$D \times 10^8$ (cm ² /s)		M_∞ (%)
	Step 1	Step 2	
40	0.18	0.71	9.5
50	0.27	0.77	12.0
68	1.17	1.88	16.8
80	—	2.8	22.5

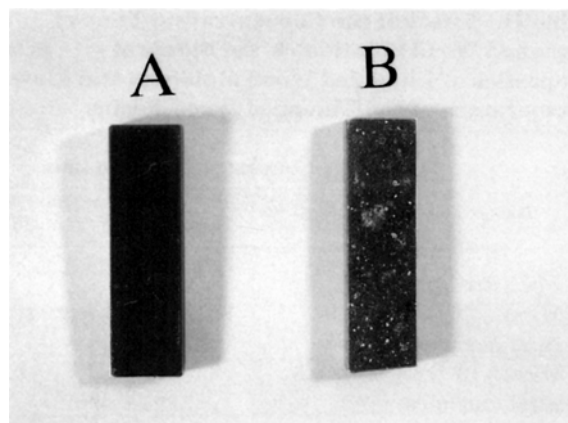


Figure 13 Photographs of the appearances of the moldings with 60% filler contents after sorbing water: (A) a liquefied wood molding; (B) a novolak molding.

mercial novolak moldings, especially compared with those of step 1. These results indicate that the liquefied wood resins have higher hydrophilicity than that of the commercial novolak. This character of the liquefied wood resins makes them obtain stronger interaction with hydrophilic wood fillers, as having been proved by the flexural properties (Figs. 4 and 6) and SEM observation (Figs. 7 and 8). It can be said that the presence of two different diffusions in the sorption processes for the commercial novolak moldings can be attributed to the poor compatibility and weak interfacial bonding between the matrix resin and fillers, i.e., the diffusion of water proceeded initially slowly through the novolak matrix and, after a certain swelling, the microcracking of the specimens occurs, which would speed up the

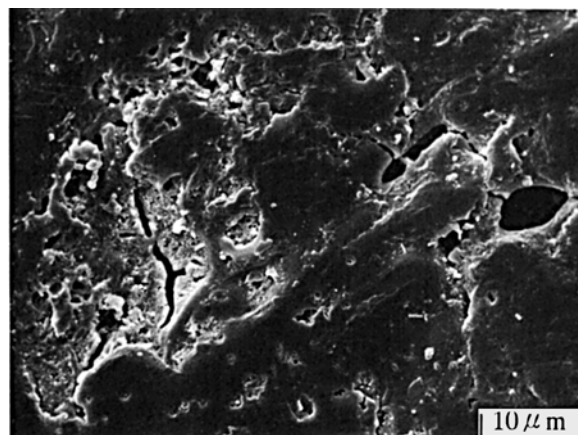


Figure 14 SEM micrograph of the specimen's surface of the novolak molding with 60% filler contents after sorbing water.

diffusion. This interpretation can be proved by the observation of the swelled specimens, as shown in Figures 13 and 14. It can be seen that the surface of the swelled novolak moldings is characterized by the formation of a lot of bumps (Fig. 13) and cracks and holes (Fig. 14). The above results suggest that the moldings from the liquefied wood resins are good in the dispersion of the filler and in the compatibility between the fillers and matrix resins.

CONCLUSION

The liquefied wood resins, which are obtained from the liquefaction of wood in the presence of phenol by using phosphoric acid as a catalyst, can be applied successfully to moldings as a substitute of novolak moldings. The liquefied wood resins reveal satisfactory and regular curing reactivity at the molding conditions used for the conventional novolak molding. The flexural properties of the moldings increase with an increase in the amount of combined phenol and the content of the wood filler. When the amount of combined phenol is more than about 75%, the mechanical properties of the liquefied wood moldings are comparable to those of the moldings from the commercial novolak. The water-sorption measurement and the SEM observation of the moldings indicate that the liquefied wood resins have greater hydrophilicity and reveal greater compatibility with wood fillers compared with the commercial novolak. Consistently, the liquefied wood resins show a

greater reinforced effect by the wood fillers than in the case with the commercial novolak.

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