Resol-Type Phenolic Resin from Liquefied Phenolated Wood and Its Application to Phenolic Foam

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ABSTRACT: A liquefied wood-based resol resin was prepared with excellent yield by a reaction of liquefied wood and formaldehyde under alkaline conditions. The effects of various reaction parameters on the extent of the yield of the resol resin, unreacted phenol content, and viscosity were investigated. Milder resol resinification conditions were required as compared to those used in conventional methods. The liquefied wood-based resol resin was successfully applied to produce phenolic foam using appropriate combinations of foaming agents. Diisopropyl ether with a relatively higher boiling temperature was suitable for the foaming of liquefied wood-based resol resin. Hydrochloric acid and poly(ethylene ether) of sorbitan monopalmitate were used as a catalyst and a surfactant, respectively. The obtained foams showed satisfactory densities and compressive properties, comparable to those of foams obtained from conventional resol resin. Foams with low density were obtained by the blending of liquefied wood-based resol resin and conventional resol resin. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 468–472, 2002; DOI 10.1002/app.10018

Key words: phenolic foam; resol resin; liquefied wood; formaldehyde; phenol; adhesives; plastics; blends; resins

INTRODUCTION

Of all foamed plastics, phenolic resin foam offers good thermal and acoustic insulation properties, qualifying it as a good insulation material for use in the construction industry.[1,2] An additional field in which phenolic foam is applied, which requires friability and low mechanical strength, is as a flower-pin material.

Phenolic foams are now commonly produced by an acid-catalyzed reaction of a resol-type resin. A resol-type resin can be prepared from the phenol liquefied lignocellulosic products with a phenolic functional group.[3,4] Pu et al. and Ono et al. re-

ported the liquefaction of wood and newspaper in phenol and its application to resol-type resin, respectively.[5,6] Maldas et al. also reported wood liquefaction in the presence of an alkaline catalyst and its application as a phenolic adhesive.[7] In their study, phenol was reacted with liquefied lignocellulosic materials, introducing a phenolic functional group. Thus, the resulting phenolated products could be reacted with formaldehyde the same way as with phenol. Here, we describe the preparation of resol-type phenolic resin from liquefied wood and its application to phenolic foam.

EXPERIMENTAL

Materials

Sawdust of radiata pine was dried in an oven at 105°C for 24 h before use. All chemicals used were

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reagent grade and obtained from commercial sources.

Preparation of Liquefied Wood and Liquefied Wood-based Resol Resin

Liquefaction was conducted using an acid catalyst method as described in a previous study.[8–10] After liquefaction, formalin (37% aqueous solution) was added into the liquefied products, and the pH of the mixture was adjusted with the addition of sodium hydroxide. The resinification of liquefied wood was conducted with constant agitation at 55–90°C; then, the resulting resin was cooled to 40°C, at which temperature it was neutralized by the addition of sulfuric acid. Finally, the resin was concentrated by pressure-reduced evaporation to remove volatile components.

The amount of unreacted phenol in the liquefied phenolated wood and in the resol resin was measured using a high-performance liquid chromatograph (Shimadzu LC-10A) equipped with a UV absorbance detector (SPD-10A). A STR ODS-II reverse-phase column (4.6 × 250 mm) was used and the mobile phase was methanol/water (1/2 v/v) using a flow rate of 1.0 mL/min. The yield of liquefied wood-based resol resin was expressed as the extent of condensed resol resin based on the weight of the starting phenol. The yield was calculated according to the following equation:

Yield of resol resin (%)

$$= \{(W_{\mathrm{LWR}} - W_{\mathrm{UP}})/W_{\mathrm{P}}\} \times 100$$

where W_{LWR} is the weight of the liquefied wood-based resol resin obtained by condensation of liquefied wood and formaldehyde (after distillation of the volatile component); W_{UP}, the weight of unreacted phenol in the resol resin; and W_{P}, the weight of the starting phenol in the liquefaction procedure. The viscosity of the resin was measured using a Brookfield viscometer (TOKMEC INC.) at 25°C and 60% RH.

Foam Preparation

The liquefied wood-based resol resin was rapidly mixed together with the poly(ethylene ether) of sorbitan monopalmitate as a sulfactant, hydrochloric acid (37%) as a catalyst, and diisopropyl ether as a blowing agent for 10–20 s. The resulting mixture was poured immediately into an open-top square wooden box (12 × 12 × 10 cm) and allowed to rise at room temperature. The
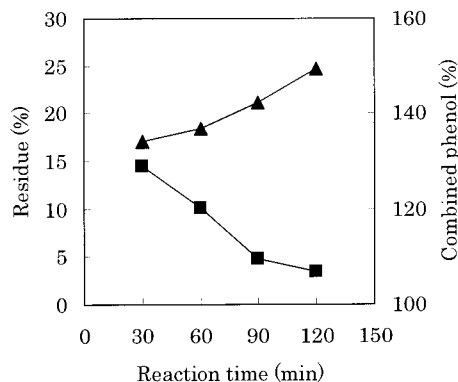

Figure 1 Effects of reaction time on the liquefaction of wood. Reaction temperature, 150°C; catalyst content, 3%; (■) residue; (▲) combined phenol.

foam obtained was cured at room temperature for 1 h before being removed from the box.

Mechanical Properties

Measurements of the mechanical properties of the foams are based on the JIS Standard (JIS K7220). The foams were cut into 50 × 50 × 50-mm specimens and conditioned for 48 h at 20°C and 60% RH. The density was determined using the dimensions and the weight of the foam. The strength measurements were conducted with a Shimadzu Autograph AGS-5kNG in the direction perpendicular to the foam rise at a constant crosshead speed of 5 mm/min. The compressive strength of the foams was determined as the stresses at 10 and 25% strain.

RESULTS AND DISCUSSION

Liquefied Wood-based Resol Resin

The progression of liquefaction over time was studied at 150°C in the presence of sulfuric acid as a catalyst, which is the general liquefaction condition used for lignocellulosics.[10–13] Figure 1 shows the effects of the reaction time on the amount of unliquefied residue and on the combined phenol of the phenolated wood. The unliquefied residue abruptly decreased to about 15% within a short liquefaction period (30 min) and then slowly decreased thereafter. Combined phenol also increased to 134% during the initial liquefaction period and then gradually increased thereafter.

After obtaining the liquefied product (residue 10%, combined phenol 136%) from wood, the obtained liquefied product was reacted with formaldehyde to obtain liquefied wood-based resol resin for preparation of the phenolic foam. The liquefied product had high miscibility with formaldehyde under alkaline conditions that permitted reactions in a homogeneous phase.

To determine the formaldehyde/unreacted phenol in a liquefied wood molar ratio, the resinification temperature and time were set 70°C and 2 h, respectively. Figure 2 shows the effects of formaldehyde/unreacted phenol in the liquefied wood molar ratio on the extent of yield and unreacted phenol content of liquefied wood-based resol resins. With increase in the amount of formaldehyde, the yield of resol resin increased and the unreacted phenol content decreased. It is natural that the reaction of formaldehyde with the unreacted phenol remaining after liquefaction should be enhanced by increasing the amount of formaldehyde, resulting in a higher yield and, consequently, a lower amount of unreacted phenol. Moreover, the added formaldehyde also reacts with the liquefied wood components during resinification.

Pu et al. and Shiraishi and Kishi reported that liquefied wood has a higher reactivity toward formaldehyde compared with phenol itself.[5,14] Phenol is introduced chemically into the side-
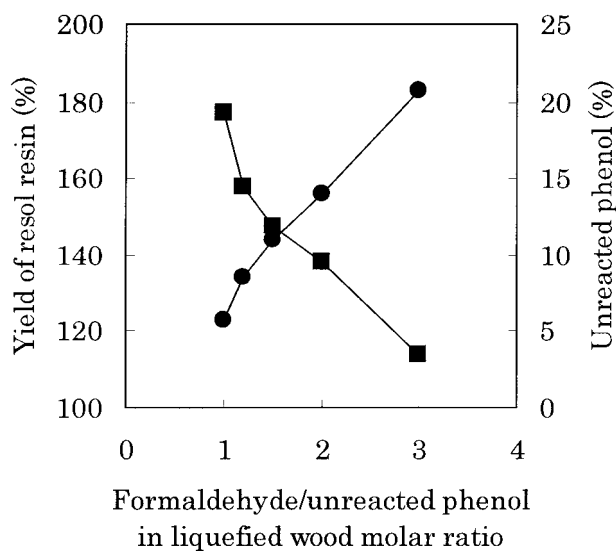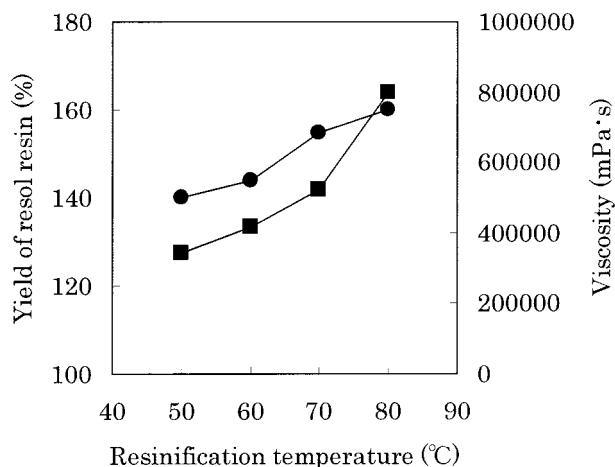

Figure 3 Effects of resinification temperature on the yield and viscosity of resol resin. Resinification time, 2 h; formaldehyde/unreacted phenol in liquefied wood molar ratio, 2; (●) yield; (■) viscosity.

chain portion of the lignin and the degraded polysaccharides during the phenolysis liquefying stage. Both these processes enhance the reactivity of the liquefied wood. The high degree of reactivity is also indicated by the fact that novolak-resin-type moldings can be prepared from liquefied wood.[9,10] Therefore, milder resinification conditions (e.g., lower reaction temperature or shorter reaction time) will be required for preparation of resol resin from liquefied wood as compared with the conventional methods.[1,2]

The effects of the resinification temperature and time on the yield and viscosity of the resol resin were investigated and the results are shown in Figures 3 and 4, respectively. In Figure 3, the yield and the viscosity of liquefied wood-based resol resins increased with increasing reaction temperature. However, the viscosity increased sharply with an increasing reaction temperature from 70 to 80°C. In resinification at 90°C, which is the conventional temperature used for resol resinification, gelation occurred during resinification. These observations indicated the high reactivity of the liquefied wood toward formaldehyde. Accordingly, a reaction temperature below 70°C was considered to be adequate for the resinification of liquefied wood.

The effects of resinification time are shown in Figure 4, in which the starting conditions were a resinification temperature of 70°C and formaldehyde/unreacted phenol in liquefied wood molar ratio of 2. On increasing the reaction time from 1 to 2 h, the yield and viscosity of the resol resin

Figure 2 Effects of formaldehyde/unreacted phenol in liquefied wood molar ratio on the extent of yield and unreacted phenol content of liquefied wood-based resol resins. Resinification temperature, 70°C; time, 2 h; (●) yield; (■) unreacted phenol of resol resin.

increased sharply and then gradually increased. The ranges of yields and viscosities were from 156 to 161% and from 538,400 to 661,000 mPa s, respectively, by changing the reaction time from 2 to 4 h. As a result, with regard to the yield and viscosity of the resol resin, the optimum conditions for resol resin preparation from liquefied wood were considered to be a reaction temperature of 70°C and a reaction time of 2 h.

Preparation of Phenolic Foam

Typical resol resins used in phenolic foam preparations contain about 80% solids. Volatile components consist mainly of water, formaldehyde, and unreacted phenol. After completion of the resinification of liquefied phenolated wood, the percentage of solid components was adjusted by distillation.

Foaming was conducted with a combination of foaming agents as shown in Table I. In general, blowing agents with a low boiling point and a corresponding low heat of vaporization are used in the foaming of phenolic resol resin. In this study, however, n-pentane, trichlorofluoroethane, diethyl ether, and cyclomethane, which boil at relatively low temperatures (35–50°C), were impractical because the control of volatilization was difficult. This may be attributed to a high reaction temperature by the high reactivity of liquefied wood-based resol resin. Among blowing agents examined in this study, diisopropyl ether with a boiling point of 68.4°C was most suitable for the foaming of liquefied wood-based resol resin. This agent began to volatilize almost from the start of

Table I   Combinations of Foaming Agents for Preparing Phenolic Foam

Agents	Combinations
Liquefied wood-based resol resin	100
Blowing agent (diisopropyl ether)	3–15
Surfactant (polyethylene ether of sorbitan monopalmitate)	0.1–2
Catalyst (hydrochloric acid)	2–10

the resin reaction and, hence, formed uniform cells within the foam. A suitable quantity of the blowing agent was from 3 to 15%, depending on the density of the resulting foam.

The surfactant plays a vital role in preparing phenolic foam by lowering the surface tension between the nonpolar blowing agent and the polar resol resin. The addition of too little surfactant fails to stabilize the foam and too much causes the cells to collapse. In this study, poly(ethylene ether) of sorbitan monopalmitate as a surfactant was added from 0.1 to 2%, which was considered to be suitable because the obtained foams did not show collapse.

Crosslinking of the resol resin was promoted by the addition of hydrochloric acid. A suitable quantity of hydrochloric acid as a foaming catalyst was from 2 to 10%, depending on the density and the foaming reaction rate.

Properties of the Foams

With combinations of foaming agents shown in Table I, phenolic foams with a uniform fine cellular structure were obtained from liquefied wood-based resol resin. Table II shows the densities, compressive strengths, and elastic moduli of the obtained phenolic foams. The densities and compressive strengths at 10% strain and elastic moduli were in the range of 32–66 ($\times 10^{-3}$ g/cm^3), 96–212 KPa, and 3.4–12.8 MPa, respectively. These values were higher than those of the foam obtained from conventional resol resin. The higher compressive strength and modulus were considered to be due mainly to their higher density.

It was difficult to prepare a foam with a low density from liquefied wood-based resol resins because of their higher viscosity. Thus, the blending of liquefied wood-based resol resin and conventional resol resin was performed to obtain resol resin with low viscosity. Figure 5 shows the variation of viscosity in the blends as a function of the conventional resol resin content. An increasing
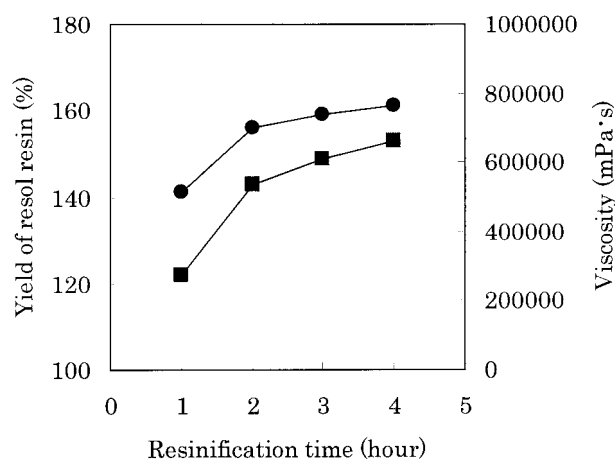

Figure 4 Effects of resinification time on the yield and viscosity of resol resin. Resinification temperature, 70°C; formaldehyde/unreacted phenol in liquefied wood molar ratio, 2; (●) yield; (■) viscosity.

Table II   Density, Compressive Strength, and Modulus of Phenolic Foams Obtained from Liquefied Wood-based Resol Resin, Conventional Resol Resin, and Their Blends

Samples	Density (kg/m^3)	Compressive Strength at 10% Strain (kPa)	Elastic Modulus (MPa)
Phenolic foam from liquefied wood-based resol resin	32–66	96–212	3.4–12.8
Phenolic foam from liquefied wood-based resol resin/conventional phenolic resol resin blends	19–45	25–160	0.78–7.82
Phenolic foam from conventional resol resin	17	49	1.47

amount of conventional resol resin decreased the viscosity of liquefied wood-based resol resin. Depending on the blending ratio, foams with relatively low density were obtained as shown in Table II. As a result, liquefied wood-based resol resin was successfully applied to produce phenolic foam, and the obtained foams showed satisfactory densities and compressive properties comparable to those of the foams obtained from conventional resol resin.

CONCLUSIONS

Wood was liquefied in the presence of phenol at 150°C and the obtained liquefied product was reacted with formaldehyde to obtain liquefied wood-based resol resin for preparing the phenolic foam. Milder resol resinification conditions were required as compared to those used in the conventional methods. With regard to the yield and viscosity of resol resin, the optimum conditions for

resol resin preparation were found to be a reaction temperature of 70°C and a reaction time of 2 h. Phenolic foams were successfully prepared from liquefied wood-based resol resin and the blends of liquefied wood-based resol resin and conventional resol resin with the combinations of a blowing agent, catalyst, and surfactant. The obtained foams showed satisfactory densities and compressive properties comparable to those of the foams obtained from conventional resol resin.

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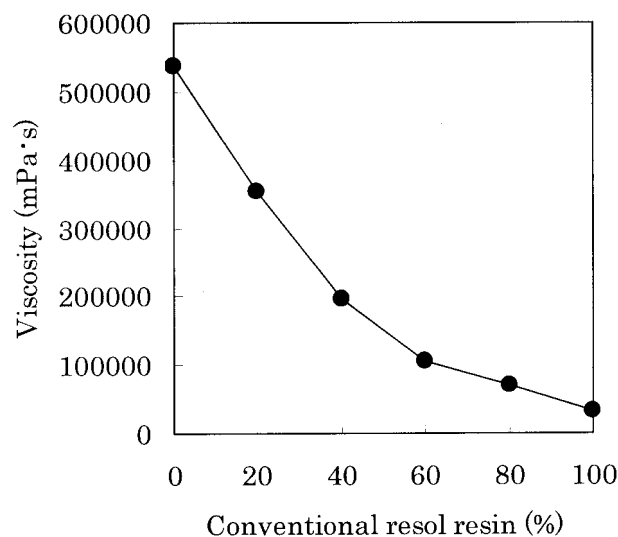**Figure 5**   Variation of viscosity as a function of conventional resol resin content.