

Phenol–Formaldehyde-Type Resins Made from Phenol-Liquefied Wood for the Bonding of Particleboard

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ABSTRACT: Liquefaction of southern pine wood in phenol in 30–40 : 70–60 weight ratios resulted in homogeneous liquefied materials, which were directly used to synthesize phenol–formaldehyde (PF)-type resins. The synthesized resins showed good physical and handling properties: low viscosity, stability for storage and transportation, and resin applicable by a common sprayer. Particleboard panels bonded with the synthesized resins showed promising physical properties and significantly lower formaldehyde emission values than those bonded with the urea–formaldehyde resin control. One deficiency

observed for the synthesized resins was lower internal bond values, which might be overcome the use of a hot-stacking procedure. Overall, the process of wood liquefaction with limited amounts of phenol as a solvent was shown to have the potential of providing practical, low-cost PF-type resins with very low formaldehyde emission potentials. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1436–1443, 2009

Key words: adhesives; resins; synthesis; thermogravimetric analysis (TGA)

INTRODUCTION

Phenol–formaldehyde (PF) resin resins are thermosetting resins and are widely used as binders for exterior-grade wood composite boards, such as softwood plywood, oriented strand board (OSB), and other engineered wood composite products. PF resins are also used in various other applications, such as in the bonding of insulation materials and the molding of electrical and automotive parts. Cured PF resins have high strength properties, good thermal stability, and high moisture resistance.¹ Furthermore, it has been accepted that wood composite boards bonded with PF resins emit almost no formaldehyde gas.^{2,3}

Urea–formaldehyde (UF) resins are currently used for bonding interior-grade wood composite boards, such as particleboard, medium-density fiberboard, and hardwood plywood. UF resins are low cost and give adequate strength properties, but the boards have a formaldehyde emission problem, which has been proven to be difficult to resolve completely.⁴ The use of PF resins in place of UF resins could

resolve the formaldehyde emission problem,⁵ but there are two major disadvantages. The first disadvantage is the high price of phenol, which is derived from petroleum; a cheaper and readily available replacement is highly desirable.⁶ The other disadvantage is the slower curing speed of PF resins relative to UF resins; they require a significantly longer hot-pressing time for current board manufacturers. In this article, we present an approach using liquefied wood made in phenol to synthesize PF-type resins for interior-grade particleboard bonding composite applications. This approach will lower the bonding cost in comparison to the use of common PF resins.

Researchers have investigated the replacement of phenol in PF resins with carbohydrates,⁷ tannins,^{8,9} and lignins.^{10–12} Tannins are currently used as wood adhesive components in some parts of the world,¹³ but these three materials have not been used much as wood composite binder components in North America for various technical reasons. In particular, lignins are available in large quantities from wood pulping processes and have been found to be useful as partial replacement of phenol. Although the performance of lignin-modified PF resins has been reported to have slightly lower bonding performances,^{11,12} the limited availability of appropriate lignins currently prevents their utilization. Kraft pulping processes are the major source of large quantities of lignins, but the isolated products can be relatively expensive because of the extensive purification step necessary.

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Wood has been liquefied in various organic solvent systems with acid catalysts to give homogeneous liquid materials, which have been investigated for chemical transformation into various useful products.^{14–16} The organic solvents are typically phenol and polyhydric alcohols. Recently, liquefaction with cyclic carbonates was conducted at relatively mild temperatures and short reaction times.¹⁷ Wood and bark were also shown to be readily liquefied in a mixture of phenol with lower alcohols and polar solvents.^{18–20} These liquefied-wood materials are composed of many carbohydrate- and lignin-derived components, and therefore, the separation of certain components or purification attempts would be very expensive. Therefore, liquefied wood has been investigated to find useful applications without the need to go through such procedures.

Thus, liquefied wood has been investigated as a partial raw material for novolac and resol PF resins,^{21–24} epoxy resins,²⁵ and polyurethane resins.^{26,27} In these potential applications, the solvent used in the liquefaction step could be a roadblock. On the other hand, liquefied wood made in phenol as a solvent can be made into PF resol-type resins without the need for solvent removal.^{21,28} However, some bonding deficiencies of these PF-type resins are apparent compared to unmodified PF resins, and it was apparent that various PF resin synthesis parameters needed optimization to the target wood composite products, such as for softwood plywood, OSB face or core layers, and particleboard.

Furthermore, because most carbohydrate-derived components in liquefied wood are expected to become extraneous materials in cured resins or, at best, a compatible filler, a more modest target of obtaining interior-grade wood composite binder resins, rather than exterior-grade ones, appears to be more appropriate. The interior-grade wood composite industry is currently searching for non-formaldehyde-emitting binder resins. Therefore, in this study, wood liquefaction was conducted with 60–70 wt % phenol, and the resulting homogeneous liquefied-wood products were used to directly synthesize PF-type resins; we evaluated them by bonding (interior-grade) particleboards and testing for free formaldehyde emission and other physical properties.

EXPERIMENTAL

Materials

Pine wood flour (100 mesh size) from American Wood Fiber Co. was used as raw material. Phenol ($\geq 99\%$, Sigma-Aldrich, Milwaukee, WI), sulfuric acid (95%, Fisher Scientific, Pittsburgh, PA), formaldehyde solution (50%, Georgia-Pacific Corp., Louisville, MS), sodium hydroxide (Aldrich Chemical), and other reagent-grade chemicals were used.

Liquefaction of wood

Liquefaction experiments were carried out with three different weight charge ratios of phenol to wood (70/30, 65/35, and 60/40) on the basis of the oven-dried wood weights. Sulfuric acid was used as a catalyst at three weight percentages on the basis of the phenol weight in all of the experiments. First, phenol was charged into a 2-L three-necked flask equipped with a stirrer, thermometer, reflux condenser, and heating mantle and heated to 60°C. Sulfuric acid was then added and thoroughly mixed; then, wood flour was slowly added with continuous stirring over a period of 30 min. After the completion of the wood flour addition, the reaction temperature was raised to 160–165°C over a period of 1 h, and this temperature was maintained for 45 min to complete the liquefaction. The liquefied wood was cooled to room temperature.

Determination of the formaldehyde reactivity of the liquefied wood

The formaldehyde reactivity of the liquefied wood was determined by a method described by Wooten et al.²⁹ as follows: 20 g of 50% NaOH solution, 158 g of water, and 158 g of 11.32% formaldehyde were charged into a 1-L three-necked flask equipped with a stirrer, thermometer, reflux condenser, and heating mantle. The reaction mixture was initially cooled to 30°C, and 50 g of liquefied wood was added; then, the temperature was increased to 60°C. This temperature was maintained, and samples (3.0 g) of the reaction mixture were taken at 30-min intervals for 5 h. The samples were transferred into a 150-mL beaker and dissolved in 20 mL of methanol and 30 mL of water. The pH of the sample solution was adjusted to 4.0 with 1.0N and 0.1N HCl solutions over a 5-min period of time, and then, 15 mL of 1.0M hydroxylamine hydrochloride (with the pH adjusted to 4.0 with 1N and 0.1N NaOH) was added to the sample solution. The sample was allowed to react for 8 min with stirring, and then, the generated acid was titrated to a pH of 4.0. The amount of free formaldehyde in the sample was calculated as equivalents of formaldehyde reacted per 100 g of liquefied wood.

Resin syntheses

The liquefied-wood solutions were used directly to prepare resins in the reaction flask used for liquefaction after the sulfuric acid used as a catalyst for liquefaction was first neutralized by the addition of a 50% sodium hydroxide solution. Three different resins resulted from the three liquefied-wood products from three different phenol/wood ratios: resin

TABLE I
Preparation Conditions of Liquefied-Wood PF-Type Resins

Resin 1	Resin 2	Resin 3
100 g of liquefied wood (70/30) + 17 g of NaOH Heat and hold at 70°C.	100 g of liquefied wood (65/35) + 18.5 g of NaOH	100 g of liquefied wood (60/40) + 20 g of NaOH
Add 104 g of formaldehyde (1.73 mol).	Add 96 g of formaldehyde (1.59 mol).	Add 88 g of formaldehyde (1.46 mol).
Charge dropwise and hold for 20 min at 70°C and then raise the temperature to 80°C until the G–H viscosity reaches J.		
Add 28 g of H ₂ O + 6 g of NaOH. Charge and heat and hold at 80°C until the G–H viscosity returns to J.	Add 33 g of H ₂ O + 6 g of NaOH.	Add 36 g of H ₂ O + 6 g of NaOH.
Add 48 g of H ₂ O + 15 g of NaOH. Charge and heat and hold at 80°C until the G–H viscosity returns to J and then cool the resin.	Add 53 g of H ₂ O + 15.5 g of NaOH.	Add 56 g of H ₂ O + 16 g of NaOH.

NaOH concentration = 50% aqueous solution. Formaldehyde concentration = 50%.
G-H, Gardner-Holdt scale.

1 came from a phenol/wood ratio of 70/30, resin 2 came from a phenol/wood ratio of 65/35, and resin 3 came from a phenol/wood ratio of 60/40. The resins were prepared according to a previously reported procedure;³⁰ the preparation conditions are summarized in Table I, and the typical synthesis procedure is described next for resin 1.

We started the preparation of resin 1 by adding 17.0 g of a 50% aqueous NaOH solution to 100 g of the neutralized liquefied wood and heating it to 70°C; we then added 104 g of a 50% formaldehyde solution (1.73 mol) over a period of 20 min. The temperature was then raised to about 80°C and maintained, and the viscosity measurements were carried out at 15-min intervals. When the viscosity reached J on the Gardner–Holdt scale, 28.0 g of H₂O and 6.0 g of 50% NaOH were added, and the temperature was reestablished to 80°C. When the viscosity reached again J, 48.0 g of H₂O and 15.0 g of 50% NaOH were added, and the temperature was reestablished to 80°C. When the viscosity again reached J, the finished resin was cooled to room temperature and kept in the refrigerator until use. Resin 2 and 3 were prepared similarly to resin 1, except different amounts of chemicals (formaldehyde, NaOH, and water) were used, as indicated in Table I. About 4 L of each resin was prepared. The viscosity, free formaldehyde content, resin solid content, and alkalinity percentage of the prepared resins were determined on the basis of standard analytical procedures.

Dynamic mechanical analysis (DMA) tests of the synthesized resins

DMA tests were performed on a DMA instrument (TA Instruments DMA model 983, New Castle, DE) according to reported procedures³¹ to investigate the curing behaviors of the synthesized resins. Approximately 25 mg of resin was evenly spread on a glass fiber braid (dimensions = 16.15 × 10.95 × 0.12

mm³), and the braid was clamped horizontally between two DMA arms. A fixed displacement mode with a 0.8-mm amplitude and a 1.0-Hz oscillation frequency was used with the chamber temperature ramped from ambient temperature to 180°C at a heating rate of 25°C/min; the chamber temperature was held for 20 min. The rigidity (G'), loss modulus (G''), and $\tan \delta$ curves were obtained, and the resin curing data were derived from the curves.

Particleboard panel manufacturing and performance tests

Test panels were bonded with the synthesized PF resins, and control panels were bonded with a commercial UF resin with the same hot-pressing parameters. The control UF resin and wood particles for the face and core layers were supplied by Forintek (Quebec, Canada) member particleboard mills. The wood particles for the face and core layers were dried and separately sprayed and blended with wax and resin. The synthesized resins were used as sole resins in the face layers but as 1 : 1 mixes with a commercial powder PF resin in the core layers. The powder PF resin was used to lower the mat moisture content (MC) in the core layer, that is, to improve the curing speed of the panel. The mat MC reached 11–12% for the face layer and 5–6% for the core layer. The resin-applied particles were formatted into mats with dimensions of 61 × 61 cm² and hot-pressed into panels in a Dieffenbacher laboratory press with a hot-press schedule developed at Alberta Research Council (Alberta, Canada) with Pressman software. The panel manufacturing parameters and hot-pressing conditions for the control and test panels are listed in Table II. The prepared panels were cut and conditioned for 7 days at 24 ± 2°C and 50 ± 5% relative humidity for the free formaldehyde test according to the desiccator method (ASTM D 5582-00). The other board test

TABLE II
Particleboard Manufacturing Conditions for the UF Resin Control and Three PF Resins

Parameter	Conditions
Panel dimension	12.7 mm (1/2 in.) × 610 mm (24 in.) × 610 mm (24 in.)
Panel construction	Three layers
Wood species	Particles from mill
Mass distribution in layers	20/60/20
Support	Caul plate at the bottom
Target mat MC	11–12% in the face and 5–6% in the core
Wax content	Slack wax: 0.5% in the face and 0.5% in the core
Air pressure for wax	30 psi
Resin content	UF resin: Hexion US 105, 8% (solid basis) in the face and 8% (solid basis) in the core Three PF resins: 8% (solid basis) in the face and 4% (solid basis) + 4% powder PF resin (Hexion)
NH ₄ Cl (catalyst)	UF resin: 0% in the face and 1.0% (solid basis) on liquid resin in the core Three PF resins: No catalyst
Air pressure for the resin	50 psi
Resin flow rate	150 mL/min
Target density	688 kg/m ³ (43 lb/ft ³ ; oven dry basis)
Blender	3 ft (diameter) × 3 ft (depth) or 914 × 914 mm ²
Blender rotation speed	11 rpm
Blending time	5 min
Press temperature	210°C
Total press time	150 s (daylight to daylight)
Press closing speed	Close hot press to target thickness in 20 s and hold for 100 s.
Degas	30 s

samples were conditioned at 20°C and 65% relative humidity for 3 weeks and tested for internal bond (IB), modulus of elasticity (MOE), modulus of rupture (MOR), and 24-h water-soak thickness swelling (TS) and water absorption (WA) according to ASTM D 1037.

RESULTS AND DISCUSSION

Formaldehyde reactivity tests of the liquefied-wood samples

Lignins' reactivity for formaldehyde is determined to formulate resins in preparation of lignin-based PF resins for wood composite binder applications. The use of an optimum amount of formaldehyde can maximize the number of hydroxymethyl groups formed and improve the chance of lignin molecule incorporation into the PF resin structures. Formaldehyde reactivity is also essential to formulate resins with minimal amounts of free formaldehyde remaining in the resulting resins.^{10,32} The formaldehyde reactivity of the liquefied-wood samples as determined (Fig. 1) showed that about 1.9–2.0 mol of formaldehyde reacted with 100 g of liquefied wood in 2 h at 60°C. Because 60–70% of the liquefied-wood samples was phenol added as the liquefaction solvent, the amounts of formaldehyde consumed by the reaction were accounted for by the phenol, which had three reactive sites.

The formaldehyde consumption levels generally agreed with the phenol levels used in the liquefaction. However, the liquefaction of wood breaks down lignin and carbohydrates, and there is the possibility of some phenol reacting with lignin- and carbohydrate-derived carbocationic components. The exposed lignin molecules that have the phenolic structure with unreacted ortho carbons would react with formaldehyde to form hydroxymethyl groups. Thus, the formaldehyde reactivity of the wood-

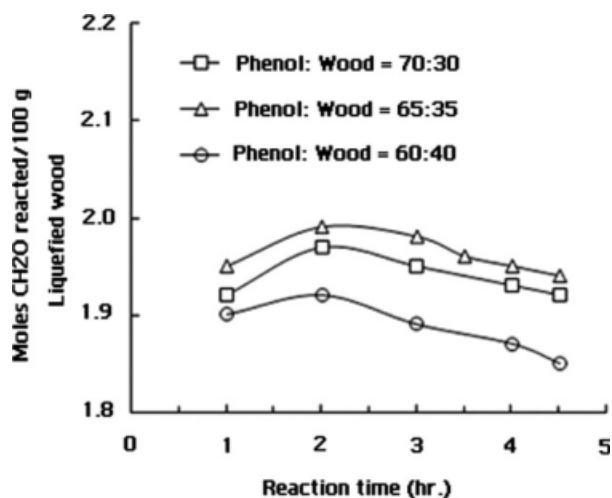


Figure 1 Results of the formaldehyde reactivity tests for liquefied wood.

TABLE III
Some Physical Properties of the Liquefied-Wood Phenolic Resins

	Resin 1	Resin 2	Resin 3
Solid content (%)	48.14	44.26	46.24
Free HCHO (%)	0.53	1.02	0.25
Alkalinity (%)	4.18	4.46	4.68
Viscosity (cP)	300	220	210

derived lignin components could not be differentiated from the overall reactivity because of the excess phenol present. Reaction times beyond 2 h showed decreased formaldehyde consumption, which did not agree with previous results observed from lignin reactions,^{10,33} but our results could be explained as due to the formation of methylene bonds by condensation reactions of the hydroxymethyl groups of phenol and liquefied-wood intermediates.^{34,35} The temperature used in the test, 60°C, is commonly known to favor the formation of hydroxymethyl groups, but methylene groups can also form at a low rate when the reaction time is extended. In the syntheses of PF resol resins under the full substitution conditions, two hydroxymethyl groups would react to form one methylene bond with the expelling of one formaldehyde molecule because there would be no unreacted site.³⁰ It is also apparent from Figure 1 that the 60 : 40 phenol/wood liquefaction product had a significantly lower formaldehyde reactivity than the other two liquefaction products, with more wood and less reactivity for the liquefaction products.

Physical property tests of the synthesized resins

The resin synthesis parameters selected in this study, that is, the NaOH level, resin solids level, viscosity, and extent of polymerization, were designed for particleboard binder-type resins, which are also similar to PF resins used as core-layer binders in the manufacturing of OSB. In the preparation of the resins, the total used alkalinity was higher than the titrated alkalinity of the prepared resins. This phenomenon was due to the generation of organic acidic groups from the wood-derived liquefaction components, which generated more acids in the resin synthesis procedure. This acid generation could be troublesome in large-scale resin manufacturing, but the extent of acid formation appeared to be minimal. The physical test values of the synthesized resins are reported in Table III. All test values were in the acceptable range for the particleboard binder application. The synthesized resins showed low viscosities and good viscosity stabilities, expected resin solids levels, and good sprayability with a compressed-air sprayer.

DMA curing tests of the synthesized resins

The DMA scans of the synthesized liquefied-wood PF resins shown in Figure 2 are very similar to previous results reported for PF resol resins.³⁶ The DMA curing behavior of the liquefied-wood PF resins exhibited the four stages of viscoelastic property changes. In the first stage, up to 3.0 min of run time, the sample's G' and G'' curves did not change much because of the low sensitivity of the instrument in this near-zero G' region. From 3.0 to 6.0 min of run time, the sample's G' increased in small extents with increasing temperature, and G'' remained low; as a result, a remarkable decrease in $\tan \delta$ occurred. This second stage reflected the drying of the resin sample. In the third stage, between 6.0 and 10.0 min, the resin sample's G' increased to the maximum, which indicated that the resin curing occurred by polymerization, and the crosslinking reactions indicated the completion. G'' initially increased to the maximum, which reflected the rapid increase in G' , or the extended polymer structures formed and helped increase the energy dissipation through increased contacts with the uncured portion of the resin. As the uncured portion of resin started to decrease from extended curing of resin, G'' started to decrease from the maximum value³⁷ and reached a low value.

In the fourth stage of the test, after about 10 min, the G' curve leveled off, and the G'' curve decreased to a low very value, which indicated the completion of cure or the formation of a highly rigid material. In this final stage of postcuring, the two synthesized resins made from higher wood contents showed some small decreases in G' , which indicated the cured resins' tendency to weaken or degrade. This could have arisen from the wood-derived components that were not incorporated into the cured resin structure or some weaker bonds that broke down under the prolonged high-temperature heating condition. This type of degradation in the postcure period is more common for urea formaldehyde resins and is not very common at all for PF and phenol-resorcinol-formaldehyde exterior-grade wood adhesive resins.³⁸ The *DMA curing rate* of PF resins is commonly defined as the time taken to reach the maximum G' value under a controlled heating schedule. The curing rates of the three synthesized resins were similar to each other and comparable with those of common PF resins.

Manufacturing of the panels and performance tests of the manufactured panels

The panel manufacturing experiments went smoothly; particularly, the resin distribution by direct inspection appeared adequate. The viscosity values of the synthesized resins did not change much during

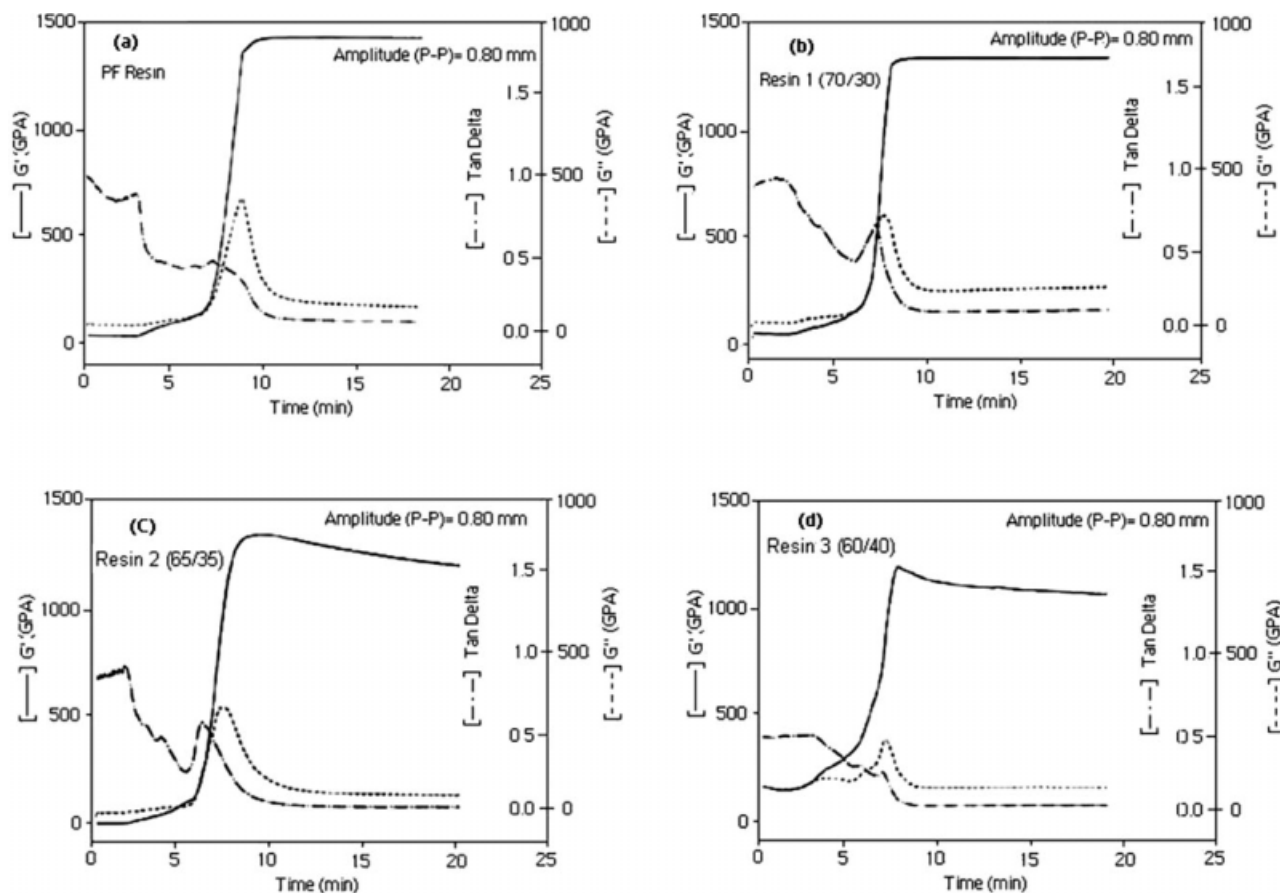


Figure 2 DMA analysis results of the (a) commercial PF resin, (b) resin 1 (70/30), (c) resin 2 (65/35), and (d) resin 3 (60/40). (P-P) = Amplitude (peak to peak).

the transportation and waiting period of about 2 months. The physical test performance panels bonded with the control and synthesized resins (Table IV) generally showed quite low panel density variations of about 2.3%, which indicated an adequate panel mat forming operation. Uniform mats are essential the comparison of the bonding performance of similar but different binder resins. Nevertheless, there were some density variations in the IB, MOE/MOR, and TS/WA measurement samples. To make the comparisons at equal densities, the IB, TS, and WA test values were normalized at a 750 kg/m³ (47 lb/ft³) density, whereas the MOE and MOR values were extrapolated to 750 kg/m³ (47 lb/ft³) density.

IB strength values of the panels

Generally, panels bonded with the synthesized PF resins had lower IB values than the panels bonded with the UF resin control. The IB of the UF resin-bonded control panels was similar to the commonly observed values of particleboard made in the laboratory.⁴ The IB values of panels bonded with the synthesized resins at resin loading levels of 8% were significantly lower than the those of the control and similar to the IB values of OSB bonded with PF resins at lower resin loading levels of about 4.0% and at a somewhat lower board density of 670 kg/m³ (42 lb/ft³). Also, because current OSB binder PF resins

TABLE IV
Panel Performance Test Results

	Control (UF resin)	Resin 1	Resin 2	Resin 3
Density (kg/m ³)	724	712	707	709
IB (MPa)	0.703	0.475	0.512	0.486
MOR (MPa)	14.81	15.47	17.24	15.94
MOE (MPa)	2392	2308	2558	2342
TS (%)	23.3	16.7	14.0	17.7
WA (%)	49.8	41.8	34.6	39.8
Free formaldehyde (ppm)	0.16	0.09	0.09	0.06

contain 5–10% urea as diluent solids,³⁹ the observed IB values for the synthesized resins can be considered that much lower.

The lower IB values indicated that the synthesized PF resins had not fully cured in the hot-pressing step in the core layers of the panels; that is, the hot-press time was too short for the synthesized resins. Also, the fact that the three different synthesized resins showed somewhat different IB values did not have much significance because of the incomplete curing of the resins attained in the panels. The IB values for the synthesized resins would probably be improved by the hot stacking of the panels, a method used in the OSB industry, and further optimization of the resin synthesis formulation, especially an increase in the sodium hydroxide content for the core-layer resin. Ideally, hot-stacking experiments in the future might show the expected differences in IB, that is, in relation to the wood use levels and the formaldehyde reactivity.

MOR and MOE values

The MOE and MOR values of the panels bonded with the synthesized PF resins were at least comparable with or slightly better than those of the panels bonded with the UF resin control. Because the MOE/MOR values of panels greatly depend on the quality of the face layers of the panels, this result indicates that the synthesized resins cured adequately when they were used in the face layers. Among the panels, somewhat better MOE/MOR values were obtained for the synthesized resins made with 35% wood substitution, which was in line with the formaldehyde reactivity test results. This result appears to indicate that, by adjusting the resin formulation, we can improve the panel strength values to some extents.

TS and WA values in the 24-h water-soak tests

Panels bonded with the synthesized resins generally showed lower TS and WA values than the panels bonded with the UF resin control. This result is encouraging because the values appeared to be improvable further when the core-layer bond strength can be improved in the future, as discussed previously. Among the manufactured panels, those bonded with the synthesized resin with 35% wood substitution resulted in the lowest TS and WA values. This result is in agreement with MOE/MOR values and indicated again that the more solid panel, especially in the face layers, showed lower TS and WA values. On the other hand, the TS/WA values for the UF control resin were somewhat higher than the values commonly obtainable for UF resin-bonded industrial particleboard. It appears that the lay-up procedure used in the laboratory was not as

efficient as that used in industry. Better TS/WA performance was found in the synthesized resins than in the UF resin control.

Free formaldehyde emission values

The free formaldehyde emission of all the panels met the ANSI A208.2 standard value of 0.30 ppm (Table IV). Panels bonded with the synthesized resins showed lower formaldehyde emission values than panels bonded with the UF resin control by 40–60%. This extent of formaldehyde emission reduction appears to be significant, and this was achieved, despite the sizable amounts of free formaldehyde present in the synthesized resins before use in board manufacturing. Because the free formaldehyde content in the PF resins could be reduced to very low levels by the adjustment of the amount of formaldehyde used in resin synthesis and also by the addition of a low level of urea,³⁹ a further reduction in formaldehyde emission would be possible for PF-type synthesized resins. The low formaldehyde emission values observed for synthesized resins were expected, similarly to common PF resin resins.

CONCLUSIONS

Liquefaction of southern pine wood in phenol in 30–40 : 70–60 weight ratios with a sulfuric acid catalyst and at a mildly elevated temperature gave homogeneous liquefied materials, which were directly used for the synthesis of PF-type resins. Neither distillation of the solvent nor generation of wastes was involved. The synthesized resins showed good physical and handling properties, which were comparable with common PF resins made without the substitution of part of the phenol, including low viscosity, good stability for storage and transportation, and possible resin application with a common spraying mechanism. Furthermore, particleboard bonded with the synthesized resins showed promising strength properties and significantly low formaldehyde emission values compared to the UF resin control.

One deficiency observed was the lower IB values from the slower curing of the synthesized resins in the core layers, which would be overcome with the application of a hot-stacking procedure. Overall, the process of wood liquefaction by the use of limited amounts of phenol as a solvent appears to offer an avenue for fruitful research toward the production of PF-type resins that are low cost and have a very low formaldehyde emission potential. The current price of PF resins is about two to three times higher than UF resins, and the need for such low-cost PF resins is very high in the industry. Further research on overcoming the slower curing speed of resins,

using lower resin loading levels in panel manufacturing, and using other resin cost-lowering additives such as urea³⁸ needs to be carried out toward this goal in the future.

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References

1. Knop, A.; Scheib, W. *Chemistry and Application of Phenolic Resins*; Springer-Verlag: Berlin, 1979.
2. Park, B.-D.; Riedl, B. *J Appl Polym Sci* 2000, 77, 841.
3. Tonge, B. Y.; Hodgkin, J.; Blicblau, A. S.; Collins, P. J. *J Therm Anal Calorim* 2001, 64, 721.
4. Kim, M. G.; Wan, H.; No, B. Y.; Nieh, W. L. *J Appl Polym Sci* 2001, 82, 1155.
5. Emery, J. A. *American Plywood Association Report SPE-1040*; American Plywood Association: Tacoma, WA, 1992.
6. Conner, A. H.; Lorenz, L. F. *J Wood Chem Technol* 1986, 6, 591.
7. Christiansen, A. W.; Gillespie, R. H. *Forest Prod J* 1986, 36, 20.
8. Coppens, H. A.; Santana, M. A. E.; Pastore, F. J. *Forest Prod J* 1980, 30, 38.
9. Sowunmi, S.; Ebebele, R. O.; Connere, A. H.; River, H. *J Appl Polym Sci* 1996, 62, 577.
10. Cetin, N. S.; Ozmen, N. *Turk J Agric Forestry* 2003, 27, 183.
11. Olivares, M.; Aceituno, H.; Neiman, G.; Rivera, E.; Sellers, T. J. *Forest Prod J* 1995, 45, 63.
12. Seller, T. J. R.; Kim, M. G.; Miller, G. D.; Haupt, R. A.; Strickland, R. C. *Forest Prod J* 1994, 44, 63.
13. Pizzi, A. In *Wood Adhesives Chemistry and Technology*; Pizzi, A., Ed.; Marcel Dekker: New York, 1983.
14. Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *Wood Sci Technol* 1998, 32, 297.
15. Shiraishi, N. In *Plasticization of Wood and its Application*; Shiraishi, N.; Kajta, H.; Norimoto, M., Eds.; Elsevier Applied Science: London, 1993.
16. Yao, Y.; Yoshioka, M.; Shiraishi, N. *Mokuzai Gakkaishi* 1993, 39, 930.
17. Yamada, T.; Ono, H. *Bioresour Technol* 1999, 70, 61.
18. Hassan, E. M.; Mun, S.-P. *J Ind Eng Chem* 2002, 8, 359.
19. Mun, S.-P.; Hassan, E. M. *J Ind Eng Chem* 2004, 10, 473.
20. Mun, S.-P.; Hassan, E. M. *J Ind Eng Chem* 2004, 10, 722.
21. Alma, M. H.; Basturk, M. A. *Ind Eng Chem Res* 2001, 40, 5036.
22. Lee, S.-H.; Teramoto, Y.; Shiraishi, N. *J Appl Polym Sci* 2002, 83, 1473.
23. Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *J Appl Polym Sci* 1995, 55, 1563.
24. Ono, H.; Yamada, T.; Hatano, Y.; Motohashi, K. *J Adhes* 1996, 59, 135.
25. Kobayashi, M.; Tukamoto, K.; Tomita, B. *Holzforchung* 2000, 54, 93.
26. Kurimoto, Y.; Koizumia, A.; Doia, S.; Tamuraa, Y.; Ono, H. *Biomass Bioenergy* 2001, 21, 381.
27. Wei, Y.; Cheng, F.; Li, H.; Yu, J. *J Appl Polym Sci* 2004, 92, 351.
28. Lee, W.-J.; Liu, C.-T. *J Appl Polym Sci* 2003, 87, 1837.
29. Wooten, A. L.; Sellers, T.; Tahir, P. M. *Forest Prod J* 1988, 38, 45.
30. Kim, M. G.; Amos, L. W.; Barnes, E. E. *Ind Eng Chem Res* 1990, 29, 2032.
31. No, B. Y.; Kim, M. G. *J Appl Polym Sci* 2005, 97, 377.
32. Jin, L.; Sellers, T.; Schultz, T. P.; Nicholas, D. D. *Holzforchung* 1990, 44, 207.
33. Gardner, D. J.; McGinnes, G. D. *J Wood Chem Technol* 1988, 8, 261.
34. Lin, L.; Nakagame, S.; Yao, Y.; Yoshioka, M.; Shiraishi, N. *Holzforchung* 2001, 55, 625.
35. Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *Holzforchung* 1997, 51, 333.
36. Kim, M. G.; Nieh, W. L.; Meacham, R. M. *Ind Eng Chem Res* 1991, 30, 798.
37. Follensbee, A. R. Ph.D. Thesis, University of Wisconsin, Madison, 1990; p 40.
38. Kim, M. G. In *Wood Adhesives*; Forest Products Society: Madison, WI, 2005; p 149.
39. Lee, S. M.; Kim, M. G. *J Appl Polym Sci* 2007, 105, 1144.