Preparation and Characterization of Novolak Phenol Formaldehyde Resin from Liquefied Brown-Rotted Wood

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Received 8 September 2011; accepted 12 November 2011
DOI 10.1002/app.36476

ABSTRACT: The brown-rotted wood was liquefied in phenol with phosphoric acid as catalyst and the resulting liquefied products were condensed with formaldehyde to yield novolak liquefied wood-based phenol formaldehyde resin (LWPF). The results showed that brown-rotted wood could be more easily liquefied than sound wood in phenol. The residue content of liquefied wood decreased continually with the progress of brown-rot decay. Both water wash and neutralization and water wash slightly improved the thermofluidity and curing properties of LWPF with a small reduction of LWPF yield. An increase in phenol to wood (P/W) ratio from 2 to 3 slightly improved the flow property of LWPF, but with an accompanied by 20% deduction in the product yield. Increased liquefaction time from 30 min to 60 min showed no significant influence on the resulting LWPF. The moldings fabricated from LWPF yielded higher charpy impact, flexural and flexural modulus strength but yielded lower temperature deflection under load than that of the commercial novolak resin. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3142–3147, 2012

Key words: brown-rotted wood; phenol liquefaction; novolak PF resin; molding

INTRODUCTION

Wolfiporia cocos (Schwein.) Ryvarden & Gilbn., one species of brown-rot fungi, mainly degrades the hemicellulose and cellulose, with lignin modified or slightly depolymerized.[1] *W. cocos* has been cultivated on Masson pine wood (*Pinus massoniana* lamb) at large scale in many places in China for the production of sclerotia. The sclerotia of *W. cocos* is one of the most important crude drugs and has been used in Chinese traditional medicine for many centuries. After the sclerotia of *W. cocos* are harvested, a large amount of wood decayed by *W. cocos* is mostly underutilized due to a lack of an economically viable utilization process. Interest in converting the decayed wood residues into value-added products persisted. The success in the development of such products will benefit and enhance the rural economic development.

Wood liquefaction is a promising technique for effective utilization of woody biomass, by which the lignocellulose can be converted to reactive liquid materials. Phenol is one of the solvents commonly used for lignocellulose liquefaction, and the resulting liquefied product can be used as a raw material to prepare phenolic resin and foam.[2–5] It was reported that wood species showed a strong influence on the liquefaction behavior resulting in different chemical composition and structure.[6] The liquefaction rates of three wood components were also different; with hemicellulose and lignin susceptible to phenol liquefaction, and crystalline cellulose most difficult to be liquefied.[7] To obtain satisfactory liquefaction results, strong sulfuric acid was most often used as a catalyst.[8] Consequently, the liquefaction process requires a significant high cost of equipment because of the extremely corrosion nature of concentrated sulfuric acid. Therefore, weaker phosphoric acid[9] and oxalic acid[10] have been evaluated to replace sulfuric acid in wood liquefaction. However, the liquefaction rate of wood using the weaker acids was always lower than that with sulfuric acid under similar conditions. Thus, the necessary longer reaction duration has limited commercial applications for this approach.

In this study, we proposed to convert the decayed wood residues into liquefied wood as industrial raw material for the production of value-added products, such as resin adhesives, foam, and molding. This consideration was based on an expectation that the brown-rotted wood residue, with its higher content of lignin and lower wood crystallinity, could be liquefied with less amount of liquefied solvent

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Contract grant sponsor: National High Technology Research and Development Program of China (National 863 Project); contract grant number: 2010AA101703.

Contract grant sponsor: Central Public-interest Scientific Institution Basal Research Fund; contract grant number: CAFYBB2010003-4.

Journal of Applied Polymer Science, Vol. 125, 3142–3147 (2012)

under weaker acid catalyst. The advantage of using less amount of solvent and weak acidic catalyst will reduce significantly the costs of the production and enhance the economical viability of the process. Thus, the liquefaction of brown-rotted wood in phenol under phosphoric acid catalyst was examined. The overall objective is to develop and optimize the process for the preparation of novolak resin from liquefied decayed wood residue. The specific objectives were: (1) investigation of the effects of degree of wood decay on wood liquefaction and the properties of liquefied wood, (2) investigation of the effects of resin washing on the properties of LWPF, and (3) evaluation of properties of LWPF and the compression molded products fabricated with LWPF.

EXPERIMENTAL

Materials

Masson pine (*Pinus massoniana* Lamb.) woods with different degree of decay for the study of chemical analysis and wood liquefaction were prepared by exposing pine to brown-rot fungi *Wolfiporia cocos* (Schwein.) Ryvarden & Gilbn. for various periods of 0, 3, 7, 11, and 15 weeks according to the outdoor cultivation method of *W. cocos* sclerotium described in a previous study.[11] In addition, the brown-rotted Masson pine after harvest of *W. cocos* sclerotium were collected from a sclerotium farm for the study on evaluation of inter-relationships among wood liquefaction conditions, resin formulations, and performance of the moldings. All wood samples after oven-drying were ground to pass a 0.9 mm screen (20 mesh) for liquefaction, and a 0.4 mm screen (40 mesh) for chemical analysis, respectively. Tetrahydrofuran was the high-performance liquid chromatography (HPLC) grade reagent. All the other chemicals were of analytical grade and were used as received from the manufacturer.

Wood liquefaction and synthesis of liquefied wood-phenol formaldehyde resins

Figure 1 summarizes the experimental procedures for wood liquefaction reaction, liquefied wood-phenol formaldehyde resin synthesis, LWPF resin powder preparation, and fabrication of the molded specimens. The detailed procedures are described as follows:

Chemical analysis

Holocellulose, α-cellulose, and Klason lignin of the wood samples were determined in accordance with the TAPPI standard T 249-75, T 203 om-93, and T 222 as described in the previous study.[11] The relative crystallinity of wood was analyzed by a Philips X'Pert Pro X-ray Diffractometer and the crystallinity index (CrI) was calculated using the Segal method.[12]

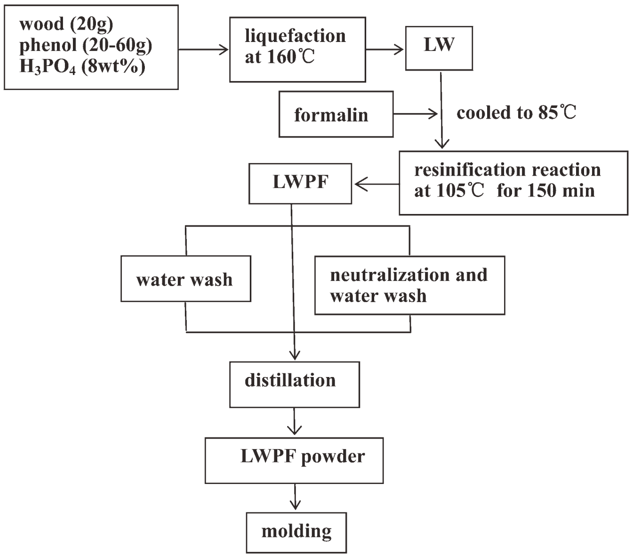

Figure 1 Flowchart of LW and LWPF resin preparation.

Wood liquefaction

Wood meal (20.0 g), phenol (20–60 g), and phosphoric acid catalyst (8 wt %, based on phenol) were mixed thoroughly in a 300-mL three-neck reaction flask equipped with a stirrer and a reflux condenser. Then, the reaction flask was immersed in an oil bath preheated at 160 ± 2°C. After various periods of 0.5, 1, and 2 h, the flask was immersed in cold water to quench the reaction to yield liquefied wood (LW).

Characterization of LW

LW was diluted with methanol and then filtered with a Toyo GA100 glass filter. The insoluble residue was dried to a constant weight in an oven at 105°C, and the residue content was calculated. The molecular weight and its distribution of LW were determined at 30°C with a Waters GPC 515-2410 system equipped with Styragel HR2, HR3, and HR4E columns in series and tetrahydrofuran as a mobile phase. The elution volume was 1.0 mL/min, and the monodisperse polystyrenes were used as standards.

Preparation of LWPF

After liquefaction, LW was directly cooled to 85 ± 2°C. Then, the calculated amount of formalin (the molar ratio of free phenol in LW to formaldehyde was 1/0.78) was added into LW and heated up to 105 ± 2°C. The resinification reaction was conducted for 150 min. The resulting resinified LWPF products was then treated according to the following methods

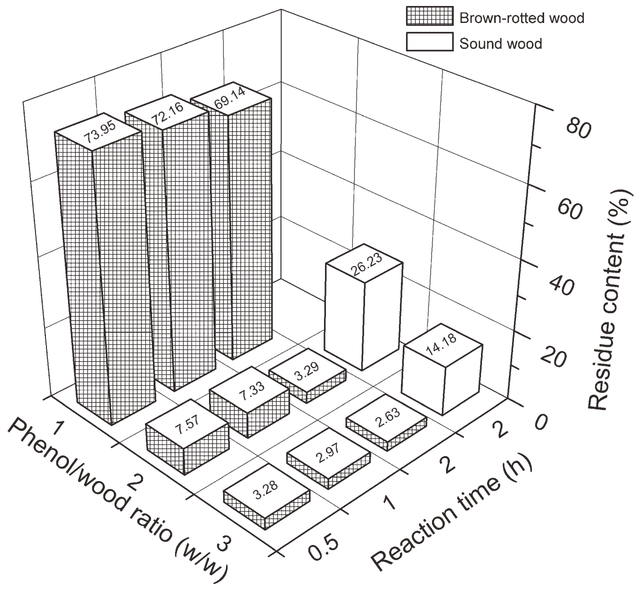

Figure 2 Comparison of the residue content between liquefied brown-rotted and sound wood under various conditions.

to yield three different LWPF products: (1) the resin was washed three times under constant stirring at 60 to 70°C for 10 min after water added into reactor and the supernatant was then sucked out, (2) the pH value was adjusted to 7.0 with sodium hydroxide solution, followed by water wash three times, and (3) without water wash. The resulting mixture was removed into the distillation flask with 150 mL mixed solvent of dioxane and water (dioxane/water = 8/2, by volume), and then concentrated by pressure-reduced evaporations at 55°C for 15 min and 150°C for 60 min to remove dioxane, water, and unreacted phenol, respectively. The obtained LWPF was removed into a container while still hot and was cooled in a desiccator. Finally, LWPF was ground and kept in a desiccator.

Characterization of LWPF

The product yield was calculated by the following equation: product yield (%) = $(W_r/W_p) \times 100$. Where W_r is the weight of LWPF and W_p is the weight of the starting phenol. The molecular weight and its distribution of LWPF were measured according to the same method as described above. Softening point and free phenol content of LWPF were measured using the ring and ball method and the bromine method according to JIS K6910-2007, respectively. To study the cure properties, LWPF and hexamethylene tetramine (HMTA) were homogeneously mixed in a weight ratio of 10/1. About 7 mg of the mixture was sealed in an aluminum capsule and heated from 30 to 300°C at a heating rate of 10°C/min under air atmosphere for DSC analysis (Shimadzu DSC-60). The mixture of LWPF and HMTA in a weight ratio of 9/1 was placed in a circular depressed portion of a hot metal plate maintained at 150°C, and the time required for the powder to gel was measured according to JIS K6910-2007.

Preparation of molded specimens and measurement of properties

LWPF, HMTA, wood fillers, $Ca(OH)_2$, and zinc stearate were mixed at a weight ratio of 22.4/3.4/1.5/1/70 to prepare the molded specimens. The specimens with a dimension of 80 × 10 × 4 mm and density of 1.3 g/cm^3 were made by compression molding using a temperature of 185°C for 5 min under a pressure of 30.6 MPa.

Charpy impact strength and temperature of deflection under load were measured according to ISO 179-1 and ISO 75-2 using an XJJ-5 Charpy impact tester and an XWB-300A deflection temperature under load tester, respectively. Flexural strength and flexural modulus were measured according to ISO 178 using an Instron 5582 universal testing machine. Results were statistically analyzed using two-factor with replication analysis of variance.

RESULTS AND DISCUSSION

Effects of reaction time and phenol/wood (P/W) ratio on liquefaction

Effect of reaction time and P/W ratio on residue content is shown in Figure 2. As expected, residue content decreased as the P/W ratio increased. It is interesting to note while decrease in residue contents

TABLE I
Effects of Degree of Wood Decay on Residue Content and Properties of Liquefied Wood

Decay time (week)	α-Cellulose (%)	Klason lignin (%)	CrI (%)	Residue content (%)	M_w	Polydispersity
0	47.14	27.85	40.3	26.23	3337	3.8
3	40.49	28.47	39.0	22.81	1859	2.1
7	26.35	30.52	37.6	16.43	2100	2.3
11	13.30	37.96	28.9	4.37	2376	2.4
15	3.08	53.88	16.1	2.30	2812	2.6

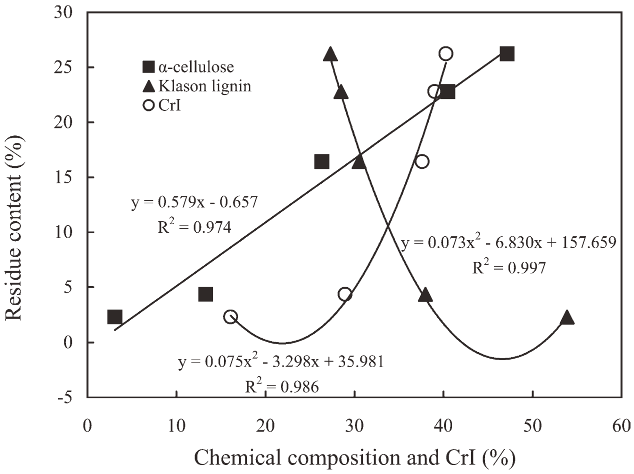

Figure 3 Effect of wood chemical composition and CrI on residue content.

between the P/W ratios at 2/1 and 3/1 was rather minor, but the decrease between the P/W ratios at 1/1 and 2/1 was almost exponential (i.e., average residue contents at P/W ratio of 2/1 was 13 times smaller than that at 1/1). While the average residue content value maintained as high as 70% at P/W ratio of 1/1 even after prolonging liquefaction time of up to 2 h, the results strongly suggest that the amount of phenol at P/W ratio of 1/1 appears to be insufficient to achieve a satisfactory liquefaction result. The residue content also decreased as the reaction time increased. However, it should be noted the low residue contents of 7.6% and 3.3%, respectively, for liquefying brown-rotted wood at P/W ratios of 2/1 and 3/1, were attained in very early reaction time of 0.5 h, and the effect of further increasing reaction time would be considered less significant as compared to that of P/W ratio. These results strongly suggest that the P/W ratio has a pronounced influence on wood residue contents.

The residue contents of sound wood liquefied for 2 h at P/W ratio 2/1 and 3/1 were 26.2% and 14.2%, respectively, which were substantially higher than that of 3.3% and 2.6% from liquefied brown-rotted wood. The above results show that the liquefaction rate of brown-rotted wood is at least four times faster than that of sound wood. This is because the brown-rotted wood has higher lignin content and lower cellulose content and wood crystallinity than sound wood. Therefore, brown-rotted wood could be more easily liquefied than sound wood in phenol as expected.

Effect of degree of wood decay on liquefaction

The residue contents and chemical compositions of the brown-rotted wood at various decay duration were summarized in Table I. In line with expectation, the residue content decreased steadily as wood decay progressed into 7 weeks, thereafter, decreases in residue contents accelerated as decay progressed further. The pattern of the decrease trends of residue content is very similar to that of change in chemical components of the brown-rotted wood. The α-cellulose and CrI decreased and klason lignin increased as decay progressed (Table I), and the accelerated rate of change occurred in/or next to 7 weeks of wood decay. It is generally agreed that the lignin and hemicellulose are easily to be liquefied and cellulose (particularly crystalline cellulose) is difficult and last to be liquefied in the presence of phenol,[7] indicating important effects of the cellulose in wood liquefaction. In this study, the effect of chemical compositions and crystallinity on liquefaction rate is further demonstrated by analyzing their quantitative correlations with residue contents (Fig. 3). There were good positive linear correlation between α-cellulose content and residue content ($R^2 = 0.974$) and curvilinear correlations between lignin with residue content ($R^2 = 0.997$) and CrI with residue contents ($R^2 = 0.986$). These results confirm that wood samples become more difficult to be liquefied in phenol with an increase in either α-cellulose content or CrI. There was a good negative correlation between Klason lignin content and residue content, which indicates that lignin is relatively easily liquefied in phenol.

Effects of resin washing on product yield and properties of LWPF

Table II summarizes the effect of washing method on product yield and properties of LWPF. Both washing methods resulted in a slight decrease in the product yield of LWPF, resulting mainly from the

TABLE II
Product Yield and Properties of LW and LWPF Obtained Using Different Washing Methods

Sample	Product yield (%)	Softening point (°C)	pH value	Before distillation		After distillation	
				M_w	Polydispersity	M_w	Polydispersity
LWPF	125.4	115.0	2.22	2409	3.4	3280	4.1
LWPF with water wash	116.1	106.3	2.96	2336	3.3	2829	3.8
LWPF with neutralization and water wash	115.4	110.3	7.03	2693	3.8	3029	4.3

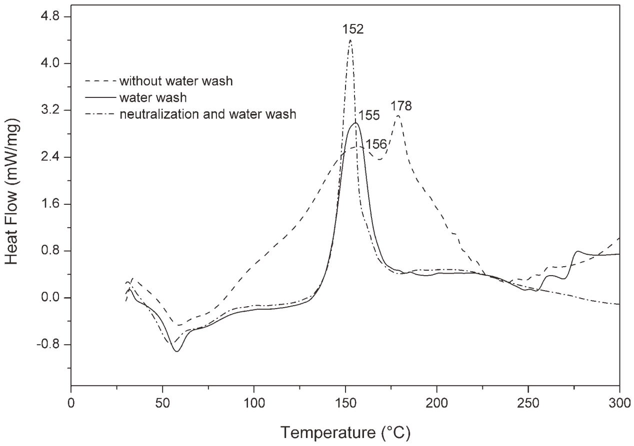

Figure 4 DSC curves of LWPF obtained using different washing methods.

removal of unreacted phenol and some soluble low molecular weight materials during the washing process.

On average, M_w and polydispersity of the resulting LWPF after distillation were consistently greater than those of LWPF before distillation due to the occurrence of further condensation during the distillation process. As expected, the LWPF without water wash has the biggest increase in M_w (i.e., from 2409 to 3280), whereas the LWPF by neutralization and water wash has the smallest increase in M_w (i.e., from 2693 to 3029). It is interesting to note that even though the M_w of LWPF before distillation by neutralization and water wash increased slightly, the M_w of LWPF after distillation is lower than that of LWPF without water wash due to a lower H-ion concentration (i.e., higher pH) as a result of neutralization. The proportional effect of the H-ion concentration on the overall phenol-formaldehyde reaction rate is well recognized.[13]

It is also noticed that the washing method has a significant influence on the curing behavior of LWPF, as seen in Figure 4. In general, the thermograms consist of three exothermic curing reactions at the temperature ranges of about 76°C to about 124°C, 135°C to 170°C, and 170°C to 189°C. The first exothermic peak seems to be the result of the initial methylolation reactions of free formaldehyde to phenol. The exotherm appears as a broad peak for the LWPF without water wash in comparison to the minor shoulder peak for the LWPF from neutralization and water wash, due mainly to the greater availability of formaldehyde and phenol for the addition reactions as compared with that of LWPF with water wash. The second exothermic peak for the three LWPFs appear almost in the same range of 135°C to 170°C and is attributed to the formation of the methylene linkage between phenolic rings for chain extension and cross-linking, together with various amine, amide/imide, imine, and methyl phenol, benzaldehyde, and other structures.[14] The third exothermic peak for LWPF without water wash can be due to the formation of the methylene linkage from the more stable intermediates at relatively high temperatures, such as the thermal decomposition of the benzoxazine structure.[15] It is probable that the initial methylolation reactions of free formaldehyde to phenol facilitate the formation of more stable intermediates during the curing process of LWPF without water wash.

It is further noticed that the DSC curve for LWPF with water wash looks identical to that of LWPF with neutralization and water wash, despite the remarkable difference in pH value of the two resins. The results indicate that the molecular structure and composition of LWPF play a more important role than pH value in LWPF curing under those conditions studied in this article.

Effects of P/W ratio and liquefaction time on resin properties and moldings

The product yield and other properties of LWPF are summarized in Table III in comparison with those of the commercial novolak resin. On average, the product yield at the P/W ratio of 2 is consistently higher than that at the P/W ratio of 3, indicating that the product yield of novolak resin based on phenol weight increases with the reduction of P/W ratio. Comparing the product yield of industrial novolak resin (not to exceed 105%),[13] the high product yield of the LWPF offers a clear advantage. The LWPF from the P/W ratio of 2 also shows a slightly higher softening point compared with that of LWPF from

TABLE III
Effect of P/W Ratio and Liquefaction Time on Product Yield and Properties of LWPF and Commercial Novolak PF Resin

P/W ratio	Liquefaction time (min)	Product yield (%)	Nonvolatility (%)	Free phenol (%)	Softening point (°C)	Gel time (s)
2	30	139.0	98.27	3.61	114.1	55
2	60	144.1	98.48	3.71	112.7	43
3	30	122.1	99.37	3.00	107.3	61
3	60	116.0	99.04	4.16	101.5	68
Commercial novolak PF resin		—	98.74	4.91	99.2	80

TABLE IV
Mechanical and Thermal Properties of Moldings Prepared from LWPF and Commercial Novolak PF Resin

P/W ratio	Liquefaction time (min)	Charpy impact strength (KJ/m^2)	Temperature of deflection under load (°C)	Flexural strength (MPa)	Flexural modulus (GPa)
2	30	6.35 (6.00)[a]	165 (0.90)	82.75 (6.91)	7.81 (2.16)
2	60	6.08 (7.10)	179 (2.37)	65.63 (6.79)	7.45 (4.53)
3	30	6.65 (8.18)	185 (3.82)	88.98 (7.14)	7.77 (3.75)
3	60	6.42 (8.59)	174 (1.63)	84.76 (6.65)	8.20 (4.99)
Commercial novolak PF resin		5.58 (8.88)	193 (4.43)	80.60 (8.41)	7.58 (5.53)

[a] Each values in parentheses is coefficient of variation (C.V., %).

the P/W ratio of 3, showing that LWPF from a higher P/W ratio has a slightly better thermofluidity than that from a lower P/W ratio. The results indicate that an increase in P/W ratio can improve the flow property, but reduce the product yield of novolak resin. It is also noticed that the commercial novolak resin has a lower softening point than LWPF, which means that the thermofluidity of LWPF is slightly inferior to that of the conventional phenol-formaldehyde resin.

The properties of moldings prepared using LWPF and commercial novolak resin as the matrix resin are listed in Table IV. The analysis of variance shows that both P/W ratio and liquefaction time have no significant effect on Charpy impact strength and temperature of deflection under load, but have significant influence on flexural strength at 5% level. Moreover, P/W ratio has a significant effect on flexural modulus. These results seem to indicate that the performance of molding can be improved by changing P/W ratio and liquefaction time. The moldings prepared from resin synthesized from LW of the P/W ratio of 2 at 60 min liquefaction time have significantly lower flexural strength than the others. This result might be related to gel time of LWPF. With gel time of 43 s, significantly faster than those of the other LWPF ranging from 55 s to 68 s (Table III), it is possible that uniform resin flow cannot be obtained due to the fast curing, which in turn led to the inferior mechanical strength. In this case, it is necessary to adjust the molding compound formulations and conditions for compression molding, such as increasing the proportion of LWPF and mould pressure.

In general, the moldings fabricated from LWPF yield higher charpy impact, flexural and flexural modulus strength but result in lower temperature deflection under load than that of the commercial novolak resin. Similar results have also been reported and the reason has been attributed to better interactions of wood fillers with LWPF than with the commercial resin by Lin et al.[2]

CONCLUSIONS

The novolak phenol formaldehyde resin could be prepared from brown-rotted wood according to the developed wood liquefaction method. It was found that brown-rotted wood could be more easily liquefied than sound wood in phenol. The higher the degree of wood decay, the easier the wood is to be liquefied. The resin washing method had an effect on the product yield and properties of the resulting LWPF. Unlike liquefaction time, P/W ratio had an effect on the product yield and thermofluidity of the resulting LWPF. The molded specimens prepared from LWPF had inferior thermal properties and superior mechanical properties to those from the commercial resin.

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