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PHENOL-FORMALDEHYDE PLYWOOD ADHESIVE RESINS PREPARED WITH LIQUEFIED BARK OF BLACK WATTLE (*ACACIA MEARNSII*)

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ABSTRACT

In this study, whole bark and tannin-free bark from black wattle were liquefied in phenol in the presence of sulfuric acid catalyst. The resulting solutions were reacted with formalin in basic solution to yield resol resins that had 33% of the phenol replaced by liquefied bark. Preparation of three-ply Southern Pine plywood showed that the resins made with liquefied whole bark performed better than those prepared with tannin-free bark. At low veneer moisture content, panels bonded with the best liquefied bark resin had properties similar to panels bonded with the commercially available phenol-formaldehyde resins that were tested.

INTRODUCTION

Tannin extracted from the bark of wattle is used commercially as a replacement for phenol in phenol-formaldehyde adhesives in Brazil, South Africa, and Australia. However, this process requires extraction of the tannin from the bark prior to resin synthesis and produces tannin-free bark that has no use other than as fuel. In addition, the resins produced from tannin are quite reactive, thus having a very short pot life and a negligible shelf life. Recent research in Japan suggests the feasibility of using whole wood[1-4] or bark[5] liquefied in phenol as a feedstock for the synthesis of resol resins.

In previous work,[6] tannin from black wattle (*Acacia mearnsii*, formerly *A. mollissima*) was liquefied in phenol. The product was used to prepare a resol-type resin, in which 33% of phenol was replaced by tannin, to bond Southern Pine (*Pinus taeda*) plywood. The results showed that phenolated tannin resin performs similarly to laboratory-made and commercial phenol-formaldehyde resins.

In the current study, we liquefied whole bark and tannin-free bark from black wattle in phenol. The liquefied bark solutions were used to prepare resol-type resins. The effects of tannin in the bark and the adhesion properties of resins using liquefied bark were evaluated in plywood specimens. If adhesive resins could be successfully prepared using the whole bark, the need to extract tannin from bark prior to resin preparation would be eliminated. Resins prepared with tannin-free bark would utilize a resource that is currently viewed as waste.

EXPERIMENTAL

The whole bark of black wattle (*Acacia mearnsii)* was collected from plantations in southern Brazil by Tanac S.A. Rio Grande do Sul - Brazil). Tannin-free bark was obtained after commercial extraction. The moisture content of the

whole bark was 1.6% and that of the tannin-free bark was 3.8%. Tannin content of the bark was reported by Tanac to be 15% to 20% for the whole bark and 0% to 0.5% for the tannin-free bark. Both types of bark were ovendried and then crushed in a hammer mill to reduce the particle size to 425 μm (40 mesh) or less. All chemicals and solvents were reagent grade and were used without further purification. Veneer for plywood preparation was rotary-cut 0.32-cm (1/8-in.) loblolly pine (*Pinus taeda*).

Liquefaction of Bark in Phenol

To liquefy the bark, phenol was heated to 50°C with constant stirring, and sulfuric acid was added as a catalyst. Bark was slowly added to the reaction vessel to give a phenol to bark ratio of 2:1 (wt/wt), and the temperature was increased to between 145°C and 150°C. Tannin weights are based on the ovendried weight of the bark. The reaction was carried out for five different times: 30, 60, 90, 120, and 180 min. The whole bark was liquefied with three different amounts of acid: 2.5%, 5.0%, and 7.5% (based on phenol weight) for each reaction time. The tannin-free bark was liquefied using only 7.5% acid for the five different reaction times. Each of the 20 different liquefied bark solutions was prepared in duplicate. At the end of the reaction time, the liquefied bark was cooled to 80°C. This solution was used for analysis and in the preparation of the resins.

Separation of Residue From Dissolved Bark

While still at 80°C, the reaction product (50 g) was dissolved by stirring in 1,4-dioxane (100 mL). The mixture was brought to room temperature, then filtered through a glass fiber filter (Whatman GF/C, Whatman Ltd., Hillsboro, OR; 1.2 mm particle hold). The residue was rinsed with 1,4-dioxane, dried, and weighed to determine the amount of undissolved bark. The filtrate was concentrated under vacuum and stored at 4°C for further analysis.

Resin Preparation

All resins were prepared with bark (whole or tannin-free) that had been reacted with phenol for 90 min in the presence of 7.5% sulfuric acid, as described in previous paragraphs. The liquefied bark solutions, including the residue from the liquefaction, were used for preparing resins. While the liquefied bark (100 parts) was at 80°C, 47 parts of water and 18.2 parts of 50% aqueous sodium hydroxide were added. The resulting liquefied bark solution was stirred until it reached room temperature, then stored at 4°C until used to prepare the resins.

Resins 1, 2, and 3 were prepared with whole bark, and resins 4, 5, and 6 with tannin-free bark. Liquefied bark resins 1 to 6 had the same concentrations of reactants; however, they were reacted for different times and temperatures. A summary of reactants and reaction conditions for the resins is given in Table 1. In each case, 100 parts of the liquefied bark solution was combined with 98.6 parts of formalin (37% aqueous, by weight) in a reaction vessel furnished with a mechanical stirrer, thermometer, and condenser.

For resins 1 and 4, the liquefied bark-formaldehyde mixture was heated to reflux (97°C) and held for 10 min. It was then cooled to 80°C and held for 15 min, followed by the addition of 8.9 parts of 50% aqueous sodium hydroxide. The reaction was again held at 80°C for 20 min before 13.3 parts of 50% aqueous sodium hydroxide was added. Finally, the mixture was cooled to 75°C, and the reaction continued for 60 min before cooling to room temperature.

Resins 2 and 5 were prepared by heating the liquefied bark-formaldehyde mixture to 75°C for 60 min, followed by the addition of 50% aqueous sodium hydroxide (8.9 parts). The mixture was again held at 75°C for 60 min before making second addition of 50% aqueous sodium hydroxide (13.3 parts).

TABLE 1

Preparation conditions: resins 1, 2, and 3 were prepared with liquefied whole bark and resins 4, 5, and 6 were prepared with liquefied tannin-free bark.

Resins 1 and 4	Resins 2 and 5	Resins 3 and 6
100 parts liquefied bark	100 parts liquefied bark	100 parts liquefied bark
98.6 parts formalin (37% aq.)	98.6 parts formalin (37% aq.)	98.6 parts formalin (37% aq.)
Reflux 10 min	Hold at 75°C for 60 min	Hold at 90°C for 60 min
Hold at 80°C for 15 min	Add 8.9 parts NaOH (50% aq.)	Add 22.2 parts NaOH (50% aq.)
Add 8.9 parts NaOH (50% aq.)	Hold at 75°C for 60 min	Cool
Hold at 80°C for 20 min	Add 13.3 parts NaOH (50% aq.)	
Add 13.3 parts NaOH (50% aq.)	Hold at 75°C for 105 min	
Hold at 75°C for 60 min	Cool	
Cool		

Following the second addition, the reaction was continued for 105 min. Then, the solution was cooled to room temperature.

For resins 3 and 6, the liquefied bark-formaldehyde mixture was heated to 90°C for 60 min, then cooled to room temperature. Fifty percent aqueous sodium hydroxide (22.2 parts) was then added in one step.

Resin 1a was derived from resin 1. To 100 parts of resin 1, 7.3 parts of 50% aqueous sodium hydroxide was added. The mixture was slowly heated (60 min) to

60°C and allowed to react until the free formaldehyde decreased to approximately 0.5% (105 min).

Resins 7 and 8 were commercial phenol-formaldehyde resins, SP 5300D and SPC 52CF (Borden Chemical Inc., Borden Packaging and Industrial Products, Columbus, OH), specially formulated for Southern Pine plywood. These resins were used as the commercial standard for comparison with laboratory-prepared resins.

Viscosity and Nonvolatile Determination

Viscosity of all resins was measured according to ASTM Method D1084, Method B[7] with a Brookfield Digital Viscometer model LVTD, using spindle LV2 at a rotation speed of 3 rpm. The nonvolatile contents were determined according to ASTM Method D4426.[8]

Differential Scanning Calorimetry

The reactivities of the liquefied bark resins were measured by differential scanning calorimetry (DSC). The DSC thermograms were produced by a Perkin Elmer DSC-7, at a scan rate of 10°C min^{-1}, using sealed stainless steel capsules. The samples weighed between 10 and 15 mg. Further details of the procedure can be found in Vick and Christiansen.[9]

Free Formaldehyde Determination

The percentage of free formaldehyde in the resins was determined using a modified version of Walker's[10] hydroxylamine hydrochloride method. Approximately 3 g of resin were diluted with 25 mL of water, and pH was adjusted to 4.0 using 0.1M HCl. Thirty milliliters of hydroxylamine hydrochloride (0.5 M, pH = 4) were added to the resin solution, and the mixture was stirred for

10 min. Free formaldehyde was determined by back titration to pH 4.0 using
0.1 M aqueous sodium hydroxide.

Panel Preparation

Loblolly pine (*Pinus taeda*) veneers measuring 17.8 by 17.8 by 0.32 cm were
stored at 32°C and 20% relative humidity (RH) to reach an approximate
equilibrium moisture content (EMC) of 4%; at 26.7°C and 30% RH to reach an
EMC of 6%; and at 26.7°C and 65% RH to reach an EMC of 12%. To bring the
veneer to room temperature, it was removed from the conditioning room and
stored in a plastic bag 1 hour prior to bonding. The veneer was laminated into
three-ply plywood panels. The adhesive was applied at a spread rate of 220 g m^{-2}
single glueline basis; thus, 6.75 g of resin was applied by brush to the inside
surfaces of the face veneers. The open assembly time was minimal, because the
veneers were assembled into panel construction immediately after the adhesive
was spread. Panels were prepressed at 1.07 MPa for 5 min. Finally, panels were
pressed at 1.31 MPa at 160°C for 6 min. Three panels were manufactured for
each treatment for a total of 81 panels. Temperature and pressure were selected to
typify industrial conditions used to bond Southern Pine with phenol-formaldehyde
resins. A relatively lengthy pressing time was used to ensure full reaction, because
a hot-stacking procedure was not used.

Evaluation of Adhesive Bonds

Six specimens were cut from each panel for wet testing in such a way as to
ensure that in half the specimens, lathe checks would be pulled in the open
direction; in the other half, lathe checks would be pulled in the closed direction.
The specimens were tested after a vacuum-pressure-soak test (VPS) as described
in U.S. Product Standard PS 1-83.[11] The wet specimens were tested in shear by

tension loading to failure with an Instron Model 1000 testing machine (Instron Corporation, Canton, MA) at a loading rate of 10 mm min^{-1}. Bond quality was evaluated from the visually estimated percentage of wood failure in the bond area and the shear strength of each specimen.

Statistical Analysis

The experimental design involved a factorial arrangement of three resin formulations, two bark types (whole and tannin-free) and two prepressing conditions. Analysis of variance (ANOVA), at the 95% level was performed separately on shear strength and wood failure. ANOVA was also used to evaluate the effects of veneer moisture content and resin modification. In each case, the Ryan-Einot-Gabriel-Welsch (REGW) multiple F-test[12] was used to separate data into significantly different groupings when the ANOVA indicated a statistical difference.

RESULTS AND DISCUSSION

Liquefaction of Bark

Rate curves for bark dissolution in phenol in the presence of 2.5%, 5.0% and 7.5% sulfuric acid for whole bark and 7.5% for tannin-free bark reacted at 145°C to 150°C for 30 to 180 min are shown in Figure 1. The extent of dissolution increases with the amount of sulfuric acid used as a catalyst. After 90 min, the amount of residue stabilized near 12% and 38% for whole bark and tannin-free bark, respectively. At the 2.5% and 5.0% levels of sulfuric acid, an appreciable amount of whole bark residue was found. Therefore, these levels were not attempted for tannin-free bark. Based on these data, the conditions selected to liquefy bark for resin preparation were 7.5% of sulfuric acid and 90 min reaction
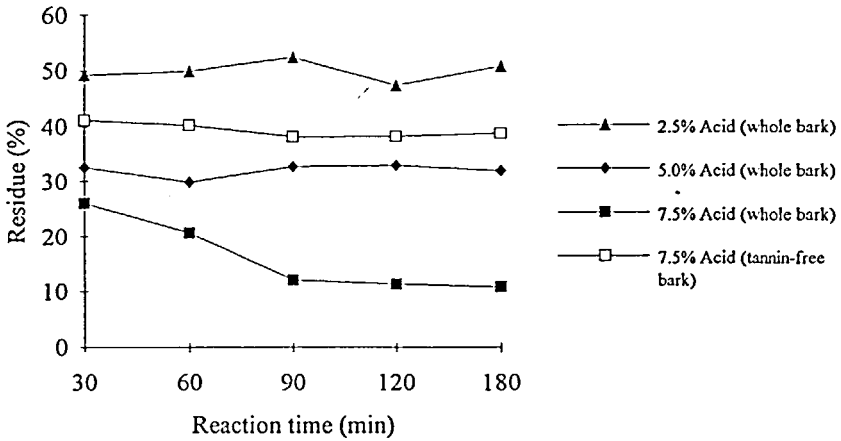
Figure 1. Dissolution rate curves for bark in phenol.

time. These conditions gave whole bark resins with approximately 12% residue and tannin-free bark resins with 38% residue.

It is known that the phenolation of lignin takes place under acidic condition at elevated temperatures.[13-16] It is also known that these same conditions dissolve wood or bark by means of phenolysis of lignin and hydrolysis of polysaccharides.[4] Therefore, it is assumed that both whole and tannin-free bark must have been liquefied in phenol by a similar mechanism.

Properties of the Resins

Properties of the liquefied bark and commercial resins are summarized in Table 2. All liquefied bark resins had 33% of the phenol replaced by bark. The pH, nonvolatile content, and percentage of free-formaldehyde are in the same range for resins 1 to 6, while viscosity is intentionally different. The modified resin 1a had a higher pH, because it contained a greater amount of sodium

TABLE 2

Properties of whole bark, tannin-free bark, and commercial phenol-
formaldehyde resins.

	Resin	pH	Non-volatile (%)	Free-formaldehyde (%)	Viscosity (mPa·s)
Whole bark	1	11.4	44.6	3.6	880
	1a	12.3	46.7	0.6	4,250
	2	11.4	44.6	3.9	1,480
	3	11.7	44.2	4.5	2,900
Tannin-free bark	4	11.1	46	3.5	1,900
	5	11.2	44.2	3.7	1,400
	6	11.8	43.7	5.3	2,400
Commercial phenol-	7	11.6	43.4	0.5	650
formaldehyde	8	11.7	41.9	0.6	5,300

hydroxide. It had a higher viscosity because it was allowed to react longer to
reduce the free-formaldehyde to the level found in commercial resins.

Table 3 shows the pH and the viscosity of resins 1 to 6 after being stored in a
freezer for 120 and 180 days. A comparison (Tables 2 and 3) reveals that the
largest increase in viscosity occurred in the first 120 days of storage, although still
in the range for plywood production. From 120 to 180 days, the resin viscosity
changed little. These results indicate that the liquefied bark resins are not as
reactive as unmodified tannin-formaldehyde resins, which typically cannot be
stored.

TABLE 3

Viscosity and pH of the stored bark resins.

	120-day storage		180-day storage	
Resin	pH	Viscosity (mP·s)	pH	Viscosity (mPa·s)
1	11.5	1,170	11.7	1,180
2	11.4	1,960	11.8	2,115
3	11.9	3.130	11.8	3,200
4	11.5	3,270	11.2	3,200
5	11.6	1,640	11.7	1,900
6	12	2,630	11.9	2,650

Plywood Bond Evaluation

Effects of prepressing and type of bark—Liquefied whole bark in phenol,

obtained after 90 min reaction time in presence of 7.5% sulfuric acid, was used to

prepare resol-type resins 1, 2, and 3. Veneer used for plywood in this step had a

moisture content of 4%. Liquefied tannin-free bark, obtained under the same

conditions, was used to prepare resins 4, 5, and 6. A total of 36 panels were

bonded, half with prepressing and the other half without. Shear strength and wood

failure percentages after VPS conditioning are reported in Table 4.

Our data show that both the average shear strength and wood failure were

better for the whole bark resin (1.92 MPa, 44%) than for the tannin-free bark resin

(1.67 MPa, 25%). These differences may be explained by the presence of tannin

in the whole bark and the larger amount of residue in the resin prepared with

tannin-free bark.

TABLE 4

Average shear strength and wood failure after VPS conditioning.

Resin	No prepressing[a]		Prepressing[a]		Average by bark	
	Shear strength (MPa)	Wood failure (%)	Shear strength (MPa)	Wood failure (%)	Shear strength (MPa)	Wood failure (%)
1	1.89	36	1.94	68		
2	1.88	50	1.97	35	1.92	47
3	1.92	34	1.94	39		
4	1.61	28	1.7	28		
5	1.86	11	1.86	25	1.67	32
6	1.45	15	1.53	43		
Average by prepressing condition	1.77	29	1.82	40		

[a]Each value represents an average of 18 specimens, 6 for each of 3 replications.

Whole bark contains 15%- to 20% tannin, and the tannin-free bark contains less than 0.5%. In our previous work,[6] we found that resins could be prepared from tannin liquefied in phenol under acidic conditions and that plywood prepared with the liquefied tannin resins was comparable in strength and wood failure to plywood prepared with commercial phenol-formaldehyde resins. Thus, in the current study, it is probable that the higher tannin content of the whole bark contributed favorably to its ability to bond the Southern Pine plywood. However, further research is needed to more rigorously characterize the performance of the liquefied tannin resins.

During the liquefaction process, the whole bark dissolved more completely than did the tannin-free bark, with only 12% residue remaining in the whole bark solution compared to 38% for the tannin-free bark. It is possible that this undissolved residue interfered with bonding in some way, because it was not removed from the liquefied bark solutions before they were used to make resins. Further work would be necessary in this area to determine if the residue does indeed interfere with the bonding.

The difference in shear strength between panels produced with prepressing (1.82 MPa) and without prepressing (1.77 MPa) was not significant. However, the percentage of wood failure was significantly greater for the prepressed panels (40%) than for the panels prepared without prepressing (29%).

A well-performed prepressing step transfers adhesive between the two veneer surfaces that are to be bonded, resulting in the consolidation of the panel to its approximate final thickness prior to final cure in the hot press. This step is routinely used in the production of plywood utilizing traditional phenol-formaldehyde adhesives, but cannot be used with unmodified tannin-formaldehyde adhesives because of their high reactivity. These results reveal that the liquefied bark adhesives performed better with prepressing than without, again indicating that they are less reactive than the unmodified tannin-formaldehyde adhesives currently in use.

Effect of veneer moisture content—Resins 1 and 2 from whole bark and resins 4 and 6 from tannin-free bark were used to bond panels with veneers having 6% and 12% moisture content. The results were compared with panels previously bonded with the same resins and veneers having 4% moisture content. For comparison, two commercial phenol-formaldehyde resins (7 and 8) were used to bond panels with veneers having 4%, 6%, and 12% moisture content. A total of 42 panels were
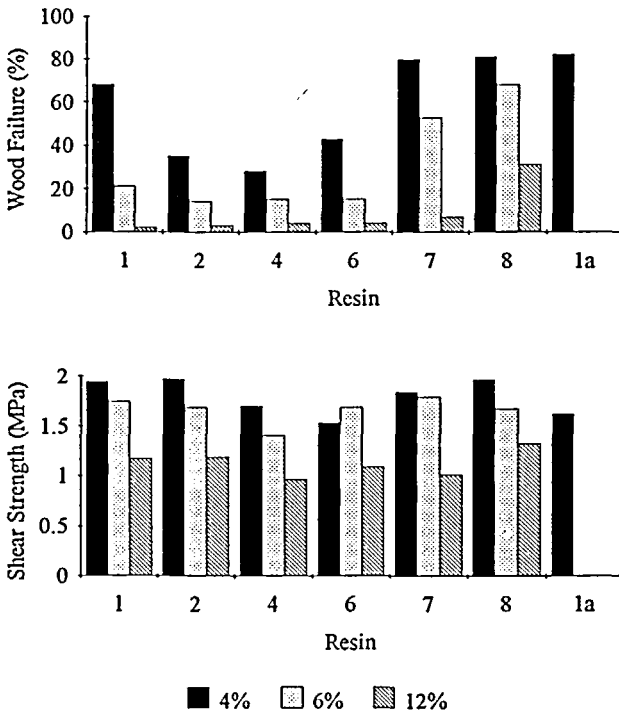
Figure 2. Effect of veneer moisture content on wood failure and shear shrength.

prepared in this phase. Wood failure and shear strength results are presented in Figure 2.

When the effect of moisture content was analyzed, we found that in both wood failure and shear strength, all six liquefied bark resins differed significantly, with the 4% moisture content veneer generally yielding better results (Fig. 2). The wood failure results for commercial phenol-formaldehyde resins do not differ significantly for 4% and 6% moisture content, which agrees with the range of 3% to 7% recommended by the adhesive suppliers of most phenolic adhesive systems for Southern Pine.[17] For the bark resins, wood failure results for 4% moisture

content were significantly better than for the 6% or 12%, indicating that the liquefied bark resins appear to be more sensitive to moisture content than commercial phenolics.

Statistical analysis of the panels bonded with the individual resins showed statistical differences among the resins at all three levels of veneer moisture content. However, in shear strength measurements, resin performance was significantly different only with 12% moisture content veneer. The significant difference among means is shown in Table 5. At 4% moisture content, the analysis shows that wood failure for resins 1, 7, and 8 does not differ significantly. Therefore, resin 1 (prepared with whole bark) is equivalent to both of the commercial phenol-formaldehyde resins tested.

Effect of bark resin modification—Based on results previously discussed, resin 1 was similar to commercial phenol-formaldehyde resins, although for American standards it gave a low percentage of wood failure (68%) and its free-formaldehyde content was too high (3.6%) when compared to commercial phenol-formaldehyde resins (0.5%). The modified resin 1a, with decreased free formaldehyde, was prepared by gently heating resin 1 after adding extra sodium hydroxide.

The reactivity of resins 1 and 1a were measured by differential scanning calorimetry (DSC). The DSC thermograms (Fig. 3), revealed two different exothermic reaction peaks for resin 1. The first is a sharp peak at 124°C, generally associated with the reaction of free-formaldehyde in the resin. The second is a broad peak at 144°C, associated with the condensation reaction of the hydroxymethyl groups. For resin 1a, only one broad peak was found at 148°C, which is associated with the condensation reactions.

TABLE 5

Statistical grouping of means for panels bonded with different veneer
moisture content after VPS conditioning.

Moisture content (%)	Resin	Shear strength[a] (MPa)	Group -ing	Resin	Wood failure[a] (%)	Grouping
4	2	1.97	A	8	81	A
	8	1.96	A	7	80	A
	1	1.94	A	1	68	AB
	7	1.84	A	6	43	BC
	4	1.7	A	2	35	C
	6	1.53	A	4	28	C
6	7	1.79	A	8	68	A
	1	1.74	A	7	53	AB
	2	1.69	A	1	21	BC
	6	1.69	A	6	15	C
	8	1.67	A	4	15	C
	4	1.41	A	2	14	C
12	8	1.32	A	8	8	A
	2	1.19	AB	7	7	B
	1	1.17	AB	6	4	B
	6	1.09	AB	4	4	B
	7	1.01	AB	2	3	B
	4	0.97	B	1	2	B

[a]Each value represents an average of 18 specimens, 6 for each of 3 replications.

The modified resin 1a was used to bond three panels with 4% moisture
content. The results were compared with the results from panels bonded with the
unmodified resin 1 and commercial phenol-formaldehyde resins (Table 6). Again,
no significant difference was found for wood failure and shear strength, but resin
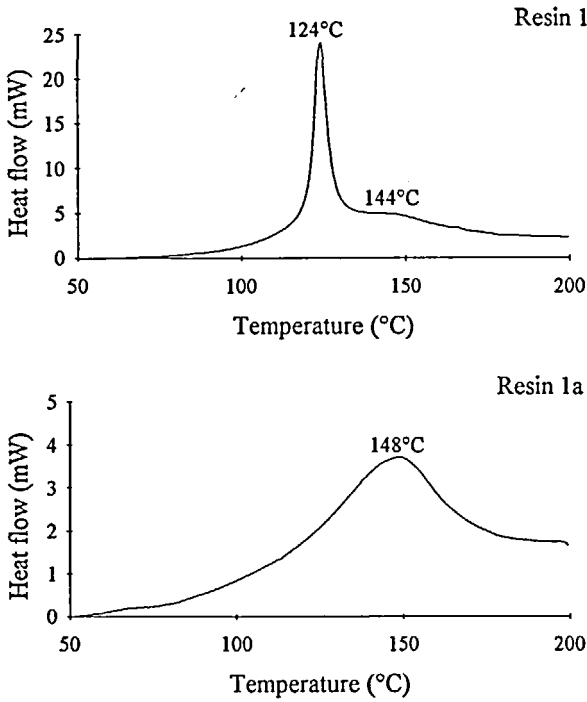1a gave much greater wood failure than the other bark resins.

Figure 3. DSC thermograms for resins 1 and 1a.

TABLE 6

Shear shrength and wood failure for specimens bonded with 1, modified 1a, and commercial phenol-formaldehyde resins.[a]

	Resin			
	1	1a	7	8
Shear strength (MPa)	1.94	1.62	1.84	1.96
Wood failure (%)	68	82	80	81

[a]Each value represents an average of 18 specimens, 6 for each of 3 replications.

In the United States, exterior grade plywood must average 85% wood failure when tested in shear after VPS conditioning.[11] For the conditions and veneer used in this study, 85% of wood failure was not achieved, either with the bark resins or with the commercial phenol-formaldehyde resins. However, all resins were applied neat. The addition of fillers and extenders probably would have improved the resin properties. Results obtained for resin 1a, 7, and 8 of 82%, 80%, and 81% wood failure, respectively, are very close to the minimum required by PS 1-83.

CONCLUSIONS

The present investigation on the use of liquefied bark to prepare resol-type resin shows that whole bark dissolves more completely in phenol than does tannin-free bark. Adhesive resins were prepared with 33% of the phenol replaced by bark. Although both types of liquefied bark can be used to prepare resins, whole bark gave better wood failure and shear strength results than tannin-free bark. The liquefied bark resins performed better when the plywood panels were prepressed, and they were critically affected by veneer moisture content—4% moisture content gave the best results. Resins 1 and 1a, in terms of wood failure and shear strength, were similar to the commercial phenol-formaldehyde tested, although none met the 85% wood failure required in PS1-83. Further research is needed to characterize and optimize the performance of the liquefied tannin resins.

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