Fungus-Modified Lignin and Its Use in Wood Adhesive for Manufacturing Wood Composites*

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Abstract

Organosolv lignins were modified with different fungal species. The modified lignins were used as raw materials for preparing lignin-phenol-formaldehyde (LPF) resins. Oriented strandboard (OSB) panels were produced with these laboratory-synthesized LPF resins for evaluating the bond performance of the LPF resins in the manufacturing of wood composites. Ultraviolet spectroscopy results show that the phenolic hydroxyl contents in the lignins were changed after the lignins were treated with fungi. The lignin modified with the brown-rot fungi extended the gel time of the LPF resin compared with the corresponding unmodified lignin, while the lignin modified with the white-rot fungi shortened the gel time. The OSB test results show that the internal bond strength and the bending properties of the panels bonded with the LPF resins containing the modified lignin were comparable to or better than those of the panels bonded with the commercial phenolic resin or the LPF resin containing the unmodified lignin. It is worth noting that the fungi-modified lignin reduced the thickness swell and water absorption of the OSB panels, implying the water resistance of the LPF resins was improved with the fungi-modified lignin. It is also suggested that up to 50 percent of phenol can be potentially replaced with fungi-modified lignin in phenolic resins used as wood adhesives.

The opportunity of any new glue for the wood composite industry is highly market dependent, particularly for the structural panel industry such as oriented strandboard (OSB) and plywood products. Free formaldehyde emission is of much less concern for OSB and softwood plywood compared with reducing the cost for petrochemical-derived resins such as phenol, melamine, and formaldehyde associated with rising costs of natural gas and petrochemicals. Any partial replacement of phenol by a lower cost product such as lignin, which is a renewable material, could result in a cost reduction for resin manufacturers and an increase of their profit with less negative impact on the environment.

Lignin is the dominant phenolic substance in biomass, especially in wood. It is mostly obtained as a residue from the pulp and paper industry and from wood acid hydrolysis. The polyphenolic structure of lignin combined with its abundant availability and low cost offer a potential for phenol replacement in resin synthesis, while its low cost contributes to its use as an adhesive component. Not all lignin has the same reactivity. In fact, the lignin available from cellulose production through the pulping process is a rather inert material, and the active phenolic groups are unfavorably changed for use as an adhesive after the pulping processes.

Fungi are the main decomposers of woody materials; they are able to get energy and nutrients from a large variety of organic compounds, such as lignin, by enzymatic activities. Three major extracellular lignin-modifying enzymes are commonly produced by fungi: laccase, manganese peroxidase, and lignin peroxidase. The majority of fungi produce more than one type of lignin-modifying enzyme in varying combinations. The enzymatic modification of lignin for its technical use can be realized by increasing the reactive

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* This article is part of a series of 10 selected articles addressing a theme of efficient use of wood resources in wood adhesive bonding research. The research reported in these articles was presented at the International Conference on Wood Adhesives, held on October 9–11, 2013, in Toronto, Canada. All 10 articles are published in this issue of the *Forest Products Journal* (Vol. 65, No. 1/2).

Forest Prod. J. 65(1/2):43–47.
doi:10.13073/FPJ-D-14-00034

functional groups of lignin by selected fungal activities. The wood-decomposing fungi can be divided into two groups according to their mode of action on wood materials: brown-rot and white-rot fungi. Brown-rot fungi can degrade wood polysaccharides and leave behind a brown, partially modified (oxidized) lignin residue. Some brown-rot fungi can also produce laccase in liquid culture, but the laccase produced by brown-rot fungi has a low redox potential that allows direct oxidation only of phenolic lignin units, which are often less than 10 percent of the total polymer. White-rot fungi can degrade both polysaccharides and lignin selectively or simultaneously and leave a cellulose-enriched white material. They often invade the lumens of wood cells and cause progressive lignin degradation between fibers. In this study, both brown-rot and white-rot fungi were selected for their enzyme activities on lignin modification for resin manufacturing

Materials and Methods

Modification of lignin by biotechnology

The selected fungal species, *Pycnoporellus alboluteus* (Ellis & Everh.) Kotl. & Pouz. (FTK 76A), *Phanerochaete cremea* (Bres.) Parmasto (FTK 332A), *Lenzites elegans* (Spreng.) Pat. (FTK 329A), and *Meruliopsis taxicola* (Pers.) Bondartsev (FTK 122B), were retrieved from the liquid nitrogen reservoir and grown on a 2 percent malt extract agar medium in petri plates at 25°C for 1 week. Mycelia plugs (5 mm in diameter) were cut from each fungal colony and transferred to 1-liter flasks (five plugs in each) containing 450 mL of a 2 percent Difco malt extract broth (Difco, BD, Sparks, Maryland) in distilled water. The pH of the medium was 5.5. The flasks were cultured on a shaker (125 rpm) at 25°C for 14 days.

The organosolv lignin was first sterilized in an oven at 70°C for 2 hours. After cooling, 50 g of lignin was weighed in each flask that contained 14-day-old fungal cultures under sterile conditions. The concentration of lignin in fungal culturing flasks was approximately 10 percent (wt/wt). The flasks were put back on the shaker (125 rpm) for a further culturing period of 21 days at 25°C. After incubation, the fungal cultures and lignin in the flasks were filtered through a layer of cotton cloth. The fungal mycelia filtered on the top of the cotton cloth were discarded, and lignin in the liquid phase was collected. The collected lignin in liquid was poured into a shallow dish and dried in an oven at 50°C for 48 hours. The fungal modified lignin powder was collected from the dish. The modified organosolv lignins were coded OLEA (76A), OLEB (332A), OLEC (329A), and OLED (122B).

Ultraviolet spectroscopy offers a simple and rapid way of determining phenolic hydroxyl groups (Zakis 1994). Phenolic hydroxyl group and proportion of α-conjugated phenolics were calculated based on the absorbance values at 300 nm and 350 to 365 nm with different buffer solutions at pH 6, pH 12, and with 0.2 N NaOH (Zakis 1994).

Synthesis of biomodified lignin-phenol-formaldehyde (LPF) resin and wood composites made with resulting adhesives

Two fungi, *Pycnoporellus alboluteus* (76A) and *Phanerochaete cremea* (332A), were selected to conduct fungi modification based on the performance of lignin phenolic resins synthesized with fungi-modified organosolv lignin. The molar ratio of formaldehyde to phenol is in the range of 2.2 to 2.4 to 1, the phenol replaced by lignin is either 33 or 50 percent, the measured solid content of the final resin is around 40 percent, and the final pH of lignin phenolic resin is 10 to 10.5. Table 1 summarizes the different fungi used to modify the organosolv lignins.

EALPFA cooking procedure

The cooking procedure requires 170 parts by weight of phenol (98%), 89 parts of fungal-modified lignin (OLEA; moisture content of 6%, wt/wt), 146 parts by weight of paraformaldehyde (91%), 51 parts of sodium hydroxide (50%, wt/wt), and 452 parts of water.

In a 1-liter reaction kettle, phenol and modified lignin were loaded, and three-quarters of the water amount was mixed with them. After about 10 minutes, paraformaldehyde was loaded, and then part of the sodium hydroxide and some more water to make the solid content in the system around 50 percent were loaded. The mix was heated to around 70°C for 1.5 hours; then the remaining sodium hydroxide and all the remaining water were loaded, while maintaining the temperature at around 70°C for another one-half hour. After that, the temperature was increased to 80 to 90°C, until viscosity reached 150 to 200 cP. From practical experience, it is easier to control the synthesis of phenolic resin through lowering the temperature to 70 to 75°C when the viscosity reaches 80 to 100 cP and then monitoring the viscosity to the required level. The reaction was terminated by cooling down the system with cold water, to around 30°C, and the resulting reactants were transferred to a container and stored in a cold room (4°C) for further usage. The adhesive was coded EALPFA.

Nonvolatile content

One to two grams of resin was added to an aluminum pan and diluted with a few grams of water. It was then placed in an oven at 121°C for 2 hours, and the sample was weighed using an analytic balance. The nonvolatile content (NVC) was calculated as solid mass divided by resin total weight.

Gel time

To measure the gel time of the different lignin phenolic resins, a Sunshine 22A gel time meter was used. The gel time corresponds to the time to reach the point characterized

Table 1.—Lignin-based phenolic resin for oriented strandboard (OSB) application.

Code[a]	Lignin	Modified by fungi	Replacement of phenol (%)
LPFA	Organosolv	No	33
LPFB	Organosolv	No	50
EALPFA	Organosolv	76A	33
EALPFB	Organosolv	76A	50
EBLPFA	Organosolv	332A	33
EBLPFB	Organosolv	332A	50

[a] LPFA and LPFB (not shown) = lignin-phenol-formaldehyde (LPF) with 33 and 50 percent phenol replacement with lignin, respectively; EALPFA and EALPFB = LPF resin with 33 and 50 percent phenol replacement with lignin, respectively, in which lignin is organosolv lignin modified by 76A (OLEA); EBLPFA and EBLPFB = LPF resin with 33 and 50 percent phenol replacement with lignin, respectively, in which lignin is organosolv lignin modified by 332A (OLEB).

Table 2.—Oriented strandboard (OSB) panel manufacturing conditions.

Item	Value
Target panel density (ovendry basis) (lb/ft^3)	40
Mat dimensions (in.)	20 by 23
Target panel thickness, mm (in.)	11.1 (7/16)
Mat composition: face/core/face	25/50/25
Resin dosage	
Face (%)	3
Core (%)	3
Wax dosage	
Face (%)	1
Core (%)	1
Face water moisture before resin and wax (%)	~2
Core water moisture before resin and wax (%)	~2.5
Core mat moisture after resin and wax (%)	~3.5
Face mat moisture after resin and wax (%)	7–8
Press temperature (°C)	220

by a sudden increase in the viscosity of the resins. To determine gel time, a standard test procedure was followed: a glycerol bath was heated to a constant temperature of 120°C, the spindle (glass rod) was loosely inserted into a 13-mm-diameter test tube containing 5.0 g of each resin (size/cap: 16 by 150 mm), the test tube and samples were placed into a bath, and the spindle was connected to the driving assembly by means of magnetic coupling. Gel time was recorded in seconds from the start of the test to the point at which the two rods touched each other. Five duplicates were tested for each resin.

DSC measurement

A TA Instrument 2900 high pressurized cell differential scanning calorimeter (DSC) was used in this study. For each specimen, around 5 mg of resin was weighed using the analytic balance, and the pan was then sealed. The pan was placed in a pressurized cell, after which we closed the cell and increased the pressure to 400 kPa. The heating rates were 2.5, 5, and 10°C/min from 25°C to 250°C.

OSB panel manufacturing and testing

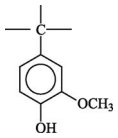
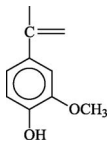
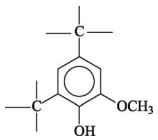
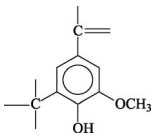
The OSB panel manufacturing conditions are listed in Table 2. All OSB panels were evaluated for average density, moisture content (MC), internal bond (IB) strength, modulus of rupture (MOR), modulus of elasticity (MOE), 24-hour thickness swelling (TS), and water absorption (WA). IB was tested according to ASTM D1037-99 (ASTM International 1999). The MOR and MOE were tested according to ASTM D1037-99 standard (static bending) with deformation rate of 5.328 mm/min.

Results and Discussion

Modification of lignin by biotechnology

The phenolic hydroxyl group changes by ultraviolet spectroscopy are listed in Table 3. The table shows that lignin structure is changed after biomodification and amount of phenolic hydroxyl groups. Phenolic hydroxyl number increased for Types I and II. That would increase the sites to

Table 3.—Phenolic hydroxyl group of unmodified and biomodified organosolv lignin.

	Unmodified lignin	OLEA		OLEB		OLEC		OLED	
		Value	Change (%)[a]	Value	Change (%)	Value	Change (%)	Value	Change (%)
Total phenolic hydroxyl group	2.052	1.597	−22.8	1.628	−20.7	2.711	32.1	2.412	17.5
I 	0.717	0.736	2.7	1.102	53.7	0.961	34.0	1.194	66.5
II 	0.180	0.160	11.1	0.208	15.6	0.196	8.9	0.254	41.1
III 	1.100	0.682	−38.0	0.329	−70.1	1.455	32.3	0.924	−16.0
IV 	0.054	0.019	−64.8	0	−100.0	0.099	83.3	0.041	−24.1

[a] The change percentage was calculated as followed: Change (%) = (value of biomodified organosolv lignin samples − value of original organosolv lignin)/value of organosolv lignin. A minus sign indicates that the value of change is decreasing.

react with formaldehyde, resulting in increasing the activity with formaldehyde.

Characterization of modified lignin phenolic resin

Gel time of modified lignin phenolic resins was also investigated. It gives comparable indication of how fast the lignin phenolic resin becomes the gel (Table 4).

Lignin-phenol-formaldehyde resin with 50 percent of phenol replaced by lignin (with/without biomodification, such as LPFB, EALPFB, EBLPFB) gives longer gel times than those of lignin-phenol-formaldehyde with 33 percent of phenol replaced by lignin (such as EALPFA, EBLPFA, and LPFA). It can be seen that the solid content of EALPFB resin is higher than others. This could imply that EALPFB could have a lower molecular weight than the other two resins because all resin synthesis resins are terminated at a similar viscosity.

The DSC curves under a heating rate of 10°C/min are depicted in Figures 1 and 2. The activated energy is calculated by the Ozawa method and the Kissinger method through different DSC curves under 2.5°C/min, 5°C/min, and 10°C/min. The peak temperatures under different heating rates and the activated energy are depicted in Table 5.

Table 4.—Nonvolatile content (NVC) and gel time of lignin phenolic resin.

Code[a]	NVC (%wt)	Gel time (s)
EALPFA	40.69	690 ± 11
EALPFB	41.70	877 ± 31
EBLPFA	39.31	644 ± 16
EBLPFB	39.66	756 ± 25
LPFA	40.20	656 ± 19
LPFB	40.94	792 ± 17

[a] See Table 1 for definition of codes.

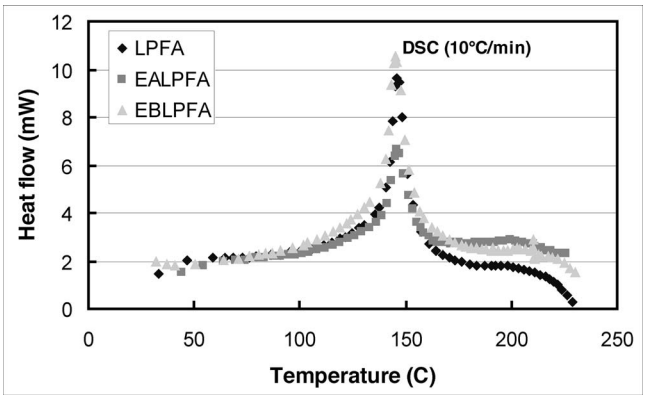


Figure 1.—Heat flow as a function of temperature for unmodified organosolv lignin and biomodified organosolv lignin–based resins with 33 percent phenol substitution. LPFA = lignin-phenol-formaldehyde (LPF) resin with 33 percent phenol replacement with lignin, in which lignin is organosolv lignin without modification; EALPFA = LPF resin with 33 percent phenol replacement with lignin, in which lignin is organosolv lignin modified by 76A (OLEA); EBLPFA = LPF resin with 33 percent phenol replacement with lignin, in which lignin is organosolv lignin modified by 332A (OLEB).

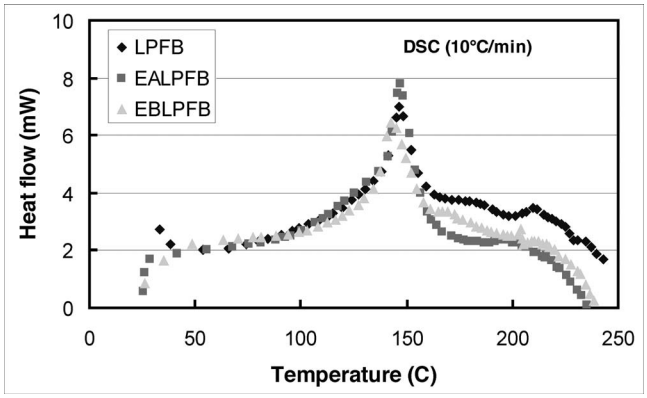


Figure 2.—Heat flow as a function of temperature for unmodified organosolv lignin and biomodified organosolv lignin–based resins with 50 percent phenol substitution. LPFB = lignin-phenol-formaldehyde (LPF) resin with 50 percent phenol replacement with lignin, in which lignin is organosolv lignin without modification; EALPFB = LPF resin with 50 percent phenol replacement with lignin, in which lignin is organosolv lignin modified by 76A (OLEA); EBLPFB = LPF resin with 50 percent phenol replacement with lignin, in which lignin is organosolv lignin modified by 332A (OLEB).

Table 5.—Peak temperature and activation energy (Ea) of lignin phenolic resins.

	Peak temperature (°C)			Ea (kJ/mol)	
Code[a]	2.5°C/min	5°C/min	10°C/min	Ozawa method	Kissinger method
LPFA	129.8	138.2	146.3	112.0	110.9
LPFB	128.5	133.3	146.5	96.1	94.2
EALPFA	131.0	136.7	146.3	119.8	119.1
EALPFB	133.1	137.6	146.9	130.2	130.0
EBLPFA	128.7	138.6	145.3	109.9	108.8
EBLPFB	123.6	131.6	143.5	90.27	88.2

[a] See Table 1 for definition of codes.

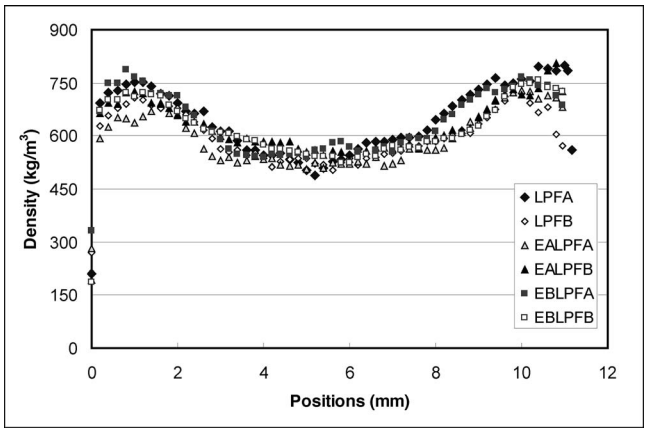


Figure 3.—Local density as a function of different positions in thickness direction. LPFA and LPFB = lignin-phenol-formaldehyde (LPF) resin with 33 and 50 percent phenol replacement with lignin, respectively, in which lignin is organosolv lignin without modification; EALPFA and EALPFB = LPF resin with 33 and 50 percent phenol replacement with lignin, respectively, in which lignin is organosolv lignin modified by 76A (OLEA); EBLPFA and EBLPFB = LPF resin with 33 and 50 percent phenol replacement with lignin, respectively, in which lignin is organosolv lignin modified by 332A (OLEB).

Table 6.—Mechanical properties of oriented strandboard (OSB) made with lignin phenolic resin.[a]

Code[b]	IB (MPa)	TS (%)	WA (%wt)	MOE (MPa)	MOR (MPa)
LPFA	0.46 ± 0.08	31.58 ± 3.41	57.29 ± 4.78	4054 ± 536	37.31 ± 5.13
LPFB	0.35 ± 0.07	32.01 ± 2.84	53.92 ± 7.24	4124 ± 328	32.80 ± 5.13
EALPFA	0.41 ± 0.07	20.52 ± 2.23	31.90 ± 1.79	3711 ± 544	33.85 ± 3.30
EALPFB	0.46 ± 0.08	18.17 ± 1.33	29.83 ± 1.73	3510 ± 276	28.93 ± 6.23
EBLPFA	0.43 ± 0.08	19.12 ± 1.44	31.06 ± 1.74	3854 ± 585	34.61 ± 6.60
EBLPFB	0.48 ± 0.05	29.84 ± 4.22	52.95 ± 2.96	3651 ± 620	31.64 ± 4.53
Commercial PF	0.42 ± 0.08	25.64 ± 0.86	45.17 ± 4.33	3535 ± 419	27.44 ± 4.66

[a] IB = internal bond; TS = thickness swelling; WA = water absorption; MOE = modulus of elasticity; MOR = modulus of rupture.
[b] See Table 1 for definition of codes.

Mechanical properties of OSB panels

The density profiles of OSB panels made with lignin-based phenolic resins are depicted in Figure 3. As one can see, all density profiles look very similar and consist of three distinct zones: two high-density zones, Zone 1 (from 0 to 2 mm) and Zone 3 (from 10 to 12 mm), respectively, and the middle zone located between 2 and 8 mm. The higher pressure observed in Zone 1 and Zone 3, which corresponds to surface densities, is not necessarily a result of the resin type. It could be a result of the pressing strategy or the speed of press closure or press opening, and it can be observed within replicates for any given resin. If, however, pressing conditions are not the only factors responsible for the differences observed between the surface densities, one can conclude that increasing the unmodified fungi lignin loading ratio seems to decrease the board surface densities and that the fungi encoded 332A used to modify the lignin increased the surface densities with the increase of its loading in opposition to what is observed with the fungi encoded 76A. However, more work needs to be performed before drawing any definite conclusions, with future investigations ensuring that all pressing parameters are kept similar during the investigation.

The mechanical properties of OSB panels are listed in Table 6. As can be seen, the integrity of the OSB panels (IB) decreased with the increase of the unmodified lignin loading ratio, as it has been observed with the resin's gel time. The results shown in Table 6 indicate that an increase of the IB of the panels was observed with the increase of the loading ratios of the fungi-modified lignins.

The presence of the unmodified lignin negatively affected the TS and the WA of the OSB panels compared with those made with the modified lignin's phenolic resin. The most interesting results were obtained when the fungi-modified lignins were used to replace some parts of the phenol in the resin formulation. Decreases in both TS and WA were observed compared with those of the PF control. The lignin modified with the fungi encoded 76A performed the best, and a decrease of both TS and WA was observed with the increase of its loading ratio from 33 to 50 percent phenol replacement.

The replacement of some parts of phenol with the unmodified lignins resulted in comparable MOR and MOE panels even at 50 percent phenol replacement. However, with the fungi-modified lignins, a slight decrease of the MOE was observed, with the MOR being less affected, suggesting that more work needs to be conducted to support these results for any technology transfer to the industry. The best performing lignin-based resins in terms of MOR and MOE were not those that performed the best in terms of TS and WA, and this situation supports the argument for additional work to optimize overall mechanical performance.

Conclusions

Lignins have been fungi modified and used to manufacture OSB and plywood resins. Four fungi, encoded as 76A, 122B, 332A, and 329A, were selected to modify the lignins, and they did change the structure of lignin. Two fungi, encoded as 76A and 332A, were selected to modify the organosolv lignin for OSB resin formulation.

Gel time and DSC curing results for OSB-derived resins were not very conclusive in terms of estimating the real impact of the modified or unmodified lignins on resin curing. The physical and mechanical properties, however, did show very clearly some very interesting and positive impacts.

The OSB IB increased with the increase of the fungi-modified organosolv lignin by up to 20 percent compared with the commercial phenolic resin. The flexural MOR and MOE properties of the OSB samples were positively comparable to those obtained with the commercial phenolic resin, suggesting that these new resins could be more attractive for the industry because they are renewable and less expensive than the petroleum-based PF resin. This is particularly important because some of these OSB samples made with the modified resins showed better stability in terms of TS and WA than the OSB control samples.

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