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Comparison of protein-based adhesive resins for wood composites

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Abstract The search for new value-added uses for oilseed and animal proteins led us to develop protein-based wood adhesives. Low-fat soy and peanut flours and blood meal were hydrolyzed in an alkaline state, and PF-cross-linked protein resins were formulated by reacting the protein hydrolyzates with phenol-formaldehyde (PF) in solid-to-solid ratios ranging from 70% to 50% hydrolyzates and 30% to 50% PF. Physical properties of medium density fiberboard (MDF) bonded with protein-based phenolic resins were compared to those of boards bonded with urea-formaldehyde (UF) and PF resins, and flakeboard bonded with soy protein-based phenolic resin was compared to PF-bonded board. As MDF binders, adhesive properties of protein-based phenolic resins depended upon protein content of proteinacious materials. MDF board bonded with blood-based phenolic resin was comparable to PF-bonded board and met the requirements for exterior MDF. Boards bonded with soy-protein-based phenolic resin met requirements for interior MDF, while peanut-based phenolic failed to meet some of the requirements. Flakeboard bonded with soy-protein-based phenolic resins was inferior to PF-bonded board but outperformed PF-bonded board in accelerated aging tests. Although they exhibit a slow curing rate, the cost effectiveness and superior dimensional stability of

protein-based phenolic resins may make them attractive for some uses.

Key words Wood adhesive · Protein-based phenolic adhesives · Phenol-formaldehyde · Fiberboard · Flakeboard

Introduction

Natural glues derived from soy, blood, and casein reached their peak use in the early 1960s. They were subsequently supplanted by petroleum-based synthetic resins. Carbohydrates and protein are two groups of renewable materials suitable for use as wood adhesives. However, it is a significant challenge to develop wood adhesives from natural materials at reasonable costs to compete with synthetic thermosetting adhesives and meet stringent performance requirements. A current concept to achieve this goal is to use these natural substances as copolymers with synthetic resins to reduce dependency on petrochemicals. In this respect, proteins are more suitable than carbohydrates because various functional groups in proteins provide abundant functionality for chemical cross-linking.

Golick and Dike¹ formulated exterior phenolic plywood glues containing up to 70% dried blood. Ash and Lumbuth² prepared plywood glues containing high blood solids blended with phenol-formaldehyde (PF) resins that required a special mixing procedure to avoid high viscosity. Weakley and Mehlretter³ developed moisture-resistant plywood adhesives by cross-linking casein with dialdehyde starch. All these protein-based glues had a high viscosity problem so that they could only be used as plywood glues but not for spray applications to manufacture particleboard, fiberboard, and oriented strand board (OSB).

Research on protein-based adhesives during the past 10 years has been largely directed toward soy protein, primarily because of its availability and low cost. Steele et al.⁴ invented a cold-setting adhesive for finger-jointing lumber containing equal parts of soy protein isolate and phenol-resorcinol-formaldehyde resin. A US patent⁵

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describes the methods for preparing a soybean-based molding compound by cross-linking soy flour with polymeric 4,4-diphenylmethane diisocyanate. A PF-cross-linked soy resin comprising 70% soy flour and 30% PF was developed by Kuo et al.⁶ This light-colored soy resin can be used as a liquid resin for exterior plywood or as a powder resin for molded products, but it was not adequate for use as a spray resin. Subsequent research resulted in soy-based adhesives of the same composition that can be used as spray resins.⁷ Hse et al.⁸ also developed a similar PF-cross-linked soy resin for the production of OSB. These results suggested that the protein-based phenolic resin could be improved by increasing the amount of PF ingredient, resin content, or altering pressing conditions. Therefore, the objectives of this study were to compare adhesive properties of PF-cross-linked blood, soybean, and peanut resins as fiberboard and flakeboard binders.

Materials and methods

Protein sources

Mixed porcine and bovine whole blood (fibrin and red cells were not removed) meal, low-fat soybean flour, and low-fat peanut flour were used as protein sources to formulate protein-based phenolic adhesive resins. The whole blood meal was a fertilizer-grade product sold for about US \$0.44/kg, containing approximately 85% protein on a moisture-free basis. The low-fat soybean and peanut flours were by-products of oil extraction by the extrusion and expending process referred to as EE meals in the oilseeds industry. Soybean (dehulled) and peanut (with hull) flours contained 48% and 40% protein, 37% and 40% carbohydrates, 6% and 8% fat, 3% and 6% fiber, and 6% and 7% ash, respectively. Low-fat soybean and peanut meals or flours are sold for less than US \$0.22/kg as animal feeds.

Protein hydrolysis

The proteinaceous materials were first alkaline hydrolyzed to obtain water-soluble and low-viscosity hydrolyzates. Blood meal was hydrolyzed with 8% NaOH in water at 120°C for 2 h while soybean and peanut flours were hydrolyzed with 10% NaOH in water at 140°C for 2 h. The hydrolyzates obtained were non-Newtonian (thixotropic) fluids. The viscosities of blood, soybean, and peanut hydrolyzates at pH 9.5, 36% solids, and 25°C were 235, 1090, and 1380 Pa·s at 10 rpm and 170, 270, and 320 Pa·s at 100 rpm, respectively. Viscosities of each hydrolyzate and resin were measured at room temperature with a Brookfield digital viscometer, DV-II (Stoughton, MA, USA).

Resin formulation

Urea-formaldehyde (UF) resin with 65% solids and 200 Pa·s viscosity at 25°C was obtained from Hon (Muscatine,

IA, USA). The PF resin with 50% solids and viscosity of 200 Pa·s was obtained from Borden Chemical (La Grande, OR, USA). The PF resin prepared in our laboratory for the formulation of protein-based phenolic resins was formulated as follows: a mixture of 1 mol phenol, 2.4 mol formaldehyde, and 0.1 mol NaOH with a sufficient amount of water was heated at 65°C for 1.5 h, and then heated at 95°C for 1 h continuously. The characteristics of the PF resin were 55% solids, pH 9.5, and 50 Pa·s viscosity at 25°C. To formulate protein-based phenolic resins, protein hydrolyzates were heated to 50°C, followed by slowly addition of PF resin with vigorous stirring for 20 min so that the resulting resins contained 70%, 60%, or 50% hydrolyzate solids and 30%, 40%, or 50% PF resin solids. The protein-based phenolic resins had a solid content of about 42%, a pH of 9.3 to 9.5, and a viscosity range of 1000–1500 Pa·s depending on the hydrolyzate/PF composition.

Board fabrication and testing

The board dimensions were 38 × 38 × 1.27 cm, using steel stops for thickness control. The protein-based phenolic resins required for each formulation were applied to the flakes with an air-atomization nozzle (0.21 MPa air pressure). The blended fibers and flakes were hand-felted into a randomly oriented and homogeneous mat with a forming box on a caul plate. The mat was pressed at 6 MPa (pressure-gauge force) to reach a panel thickness of 1.27 cm in less than 30 s, and then decompressed the second half of the cycle. The fabrication conditions for medium density fiberboard (MDF) were as follows:

- Fiber furnish: equal mix of juvenile hybrid poplar whole tree fiber and cornstalk fiber refined with a Sprout-Bauer single disc atmospheric refiner (target dimensions: 0.3 mm in thickness, 1 mm in length)
- Resin solids: 12% based on dry weight of fiber (5% moisture content)
- Target density: 0.75 g/cm³
- Press temperature: 165°C for UF, 175°C for PF, and 200°C for protein-based phenolic resins
- Press time: 5 min for UF, 7 min for PF and protein-based phenolic resins

Flakeboard was made with the wood flakes of juvenile hybrid poplar with the following conditions:

- Hybrid poplar flakes: 7.6 cm long, approximately 1.27 cm wide, and 0.5 mm thick
- Resin solids: 5% PF and 7% protein-based resins based on dry flakes (4% moisture content)
- Flake orientation: random
- Target density: 0.65 g/cm³
- Press temperature: 175°C for PF and 200°C for soy protein-based phenolic resins
- Press time: 7 min for PF and soy protein-based phenolic resins

Boards were wrapped in a blanket overnight immediately after pressing, followed by conditioning at 65% rela-

tive humidity (RH) and 70°C for 48h before trimming them to 35.6 × 35.6cm. The properties, such as modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding strength (IB), and percent thickness swelling (TS) of boards were evaluated. Two static bending samples and six IB samples from each board were tested according to ASTM D 1037 methods.⁹ TS was determined on four specimens that measured 10.2 × 12.7cm after a 24-h cold water soak and 2-h boiling. One sample from each of the flakeboards was also subjected to the six-cycle accelerated-aging test described in ASTM D1037. One linear expansion (LE) sample and four formaldehyde emission test (*E*-test) samples were examined according to ANSI 208.2¹⁰ and ASTM D 5582,¹¹ respectively.

Results and discussion

Table 1 shows that all MDF boards met ANSI requirements¹⁰ for interior MDF in MOR, MOE, and IB with the exception of IB for peanut/PF-bonded boards. Boards bonded with PF, blood/PF, blood/soy/PF, and blood/peanut/PF also met the ANSI requirements for exterior MDF. Boards bonded with blood/PF resin were superior in

MOE and equivalent in MOR, IB, and 2-h-boil TS to PF-bonded boards, but had a greater TS after 24-h soaking. Compared with PF-bonded boards, boards bonded with blood/soy/PF resin also performed well, in that they had better MOE, equivalent MOR and 2-h-boil TS, but had 16% lower IB and 58% greater 2-h-boil TS. Physical properties of boards bonded with peanut/blood/PF were essentially the same as those of boards bonded with soy/blood/PF. Boards bonded with UF resin were inferior to all others in the tests of dimensional stability. In addition, boards bonded with PF and soy/PF resins emitted only trace amounts of formaldehyde, 0.08ppm and 0.03ppm, respectively, while UF-bonded boards emitted 0.26ppm, just under the maximum allowed 0.3ppm set by the ANSI standard.¹⁰ Although not measured in this study, formaldehyde emission levels from all protein-based phenolic resins is expected to be similar to those boards bonded with PF and soy/PF resins measured in an earlier study.¹² In addition, protein-based phenolic resins exhibited sufficient tack for fiberboard mat integrity before pressing, and these resins did not stick to caul plates and did not require the application of release agents.

In summary, MDF boards bonded with PF and blood/PF resins performed equally well, followed in order by those bonded with blood/soy/PF, blood/peanut/PF, soy/PF, UF,

Table 1. Selected properties of medium density fiberboard (MDF) containing equal parts of juvenile hybrid poplar fiber and cornstark fiber bonded with protein-based adhesives

Resin type	Resin solids ^a (%)	Board density (g/cm ³)	MOR (MPa)	MOE (MPa)	IB (KPa)	24-h soak TS (%)	2-h boil TS (%)	<i>E</i> -value (ppm)
UF (comm)	12	0.77	29.8 (b)	2910 (d)	979 (b)	15.8 (d)	Failed	0.26
Stdev			2.8	191.7	144	0.5		
COV (%)			9.4	6.6	14.7	3.2		
PF (comm)	12	0.76	34.5 (a)	3544 (b)	1124 (a)	5.3 (a)	23.3 (a)	–
Stdev			3.6	343.4	94.5	0.6	1.7	
COV (%)			10.4	9.7	8.4	11.3	7.3	
Blood/PF	12	0.78	36.6 (a)	4151 (a)	1186 (a)	9.0 (b)	22.5 (a)	–
Stdev			2.9	194.4	104.1	2.9	2.3	
COV (%)			7.8	4.7	8.8	22.3	10.1	
Soy/PF	12	0.77	28.1 (b)	3461 (c)	648 (c)	10.9 (bc)	34.0 (c)	0.08
Stdev			2.7	248.9	16.1	5.4	4.1	
COV (%)			9.7	7.6	24.9	49.8	12.0	
Peanut/PF	12	0.76	24.8 (c)	3220 (c)	462 (d)	12.8 (c)	32.5 (c)	0.08
Stdev			3.6	480.0	10.2	5.6	5.5	
COV (%)			14.5	14.9	22.1	43.8	16.8	
Blood/soy/PF	12	0.76	34.4 (a)	3881 (b)	945 (b)	8.42 (b)	25.3 (b)	–
Stdev			3.3	309.7	9.5	1.90	2.58	
COV (%)			9.5	8.0	10.1	22.5	10.2	
Peanut/B/PF	12	0.79	35.2 (a)	3730 (b)	917 (b)	7.57 (b)	26.4 (b)	–
Stdev			2.4	190.3	4.1	0.8	4.3	
COV (%)			6.2	5.1	4.4	10.6	16.2	
ANSI A208.2 ⁷	Interior MDF		24.0	2400	550	10.0		0.30
	Exterior MDF		31.0	3100	700	10.0		0.30

Means with the same letter in parentheses are not significantly different from each other at the 5% level

MOR, modulus of rupture; MOE, modulus of elasticity; IB, internal bonding strength; 24-h soak TS, percentage of thickness swelling after soaking in cold water for 24h; 2-h boil TS, percentage of thickness swelling after boiling in water for 2h; *E*-value, formaldehyde emission based on ASTM D 5582-94 method; UF, urea-formaldehyde resin; PF, phenol-formaldehyde resin; comm, commercial sample; Soy/PF, 70% soy hydrolyzate +30% PF; Blood/soy/PF, 35% blood hydrolyzate +35% soy hydrolyzates +30% PF; Peanut/PF, 70% peanut hydrolyzate +30% PF; Peanut/B/PF, 35% peanut hydrolyzates +35% blood hydrolyzate +30% PF; Stdev, standard deviation; COV, coefficient of variation

^aBased on oven dry weight of fiber

^bANSI A208.2, American National Standard, Medium Density Fiberboard¹⁰

Table 2. Selected properties of juvenile hybrid poplar flakeboard

Resin composition (w%/w%)	Resin solids ^a (%)	Board density (g/cm ³)	MOR (MPa)	MOE (MPa)	IB (KPa)	24-h soak TS (%)	2-h boil TS (%)	LE (%)
PF (100/0)	5	0.71	36.0 (b)	5440 (ab)	1151 (a)	6.7 (a)	17.4 (a)	0.20 (a)
Stdev			1.9	199.4	121.1	0.8	2.1	0.01
COV (%)			5.3	6.7	11.3	11.1	6.8	3.5
Soy/PF (70/30)	7	0.67	36.6 (b)	5192 (b)	641 (c)	29.0 (c)	84.1 (d)	0.40 (c)
Stdev			2.4	346.9	18.7	4.3	8.8	0.08
COV (%)			6.7	9.8	9.3	33.1	24.6	11.3
Soy/PF (60/40)	7	0.67	42.5 (a)	5826 (a)	724 (b)	12.9 (b)	35.2 (c)	0.26 (b)
Stdev			2.6	231.3	22.8	2.9	3.2	0.05
COV (%)			7.8	8.1	10.2	28.5	19.3	7.7
Soy/PF (50/50)	7	0.67	42.7 (a)	5343 (ab)	786 (b)	9.0 (b)	26.0 (b)	0.25 (b)
Stdev			2.1	309.2	24.9	32.4	1.9	0.03
COV (%)			5.1	8.8	9.9	8.9	7.5	5.9
CSA 0437 (O-2), ^b OSB parallel			29.0	5516	345	15.0		0.35

Means with the same letter in parentheses are not significantly different from each other at the 5% level

LE, linear expansion; OSB, oriented strand board

^aBased on dry weight of wood flakes

^bCanadian Standards Association, cited by National Institute of Standards and Technology, PS 2-92

and peanut/PF resins. Research before the 1960s indicated that wood products bonded with blood glues were much more moisture resistant than those bonded with soy glues, and the addition of blood protein in soy glues improved moisture resistance of the glue joints.¹³ The protein content of blood meal is higher than that of soy flour meal by 30%–40%.¹⁴ The higher protein content in blood meal than that in soy flour makes blood glues more moisture resistant because hemoglobin in blood forms complexes with metal ions, and thus the blood glue makes up complex networks upon setting.¹⁵ Consequently, blood meal is superior to soy and peanut flours for formulating protein-based phenolic resins. In our study, the peanut/PF resin did not perform well because it has the lowest protein content among the three proteinaceous materials studied. However, as shown in Table 1, peanut flour can be used as a low-cost supplement to blood/PF resins to make exterior MDF.

Table 2 shows the physical properties of flakeboard bonded with PF resin and protein-based phenolic resins. Boards bonded with protein-based phenolic resins had significantly lower IB and dimensional stability than boards bonded with PF resin. Although made with random flake orientation, all boards met the CSA requirements¹⁶ for MOR and IB, and reached over 90% of MOE parallel for OSB. With the exception of boards bonded with the soy/PF (70/30) resin, all boards also met CSA requirements for TS and LE. Figure 1 shows results of the ASTM six-cycle accelerated aging test of flakeboards bonded with PF and soy protein-based phenolic resins. In general, most physical properties and dimensional stability of board are increased with increasing board density. As shown in Table 2, the IB and dimensional stability of flakeboard bonded with PF resin were significantly higher than those of flakeboard bonded with soy protein-based phenolic resins. These results might be due to the high density (0.71 g/cm³) of flakeboard prepared with PF resin compared with that of flakeboard bonded with soy/PF resins (0.67 g/cm³). There-

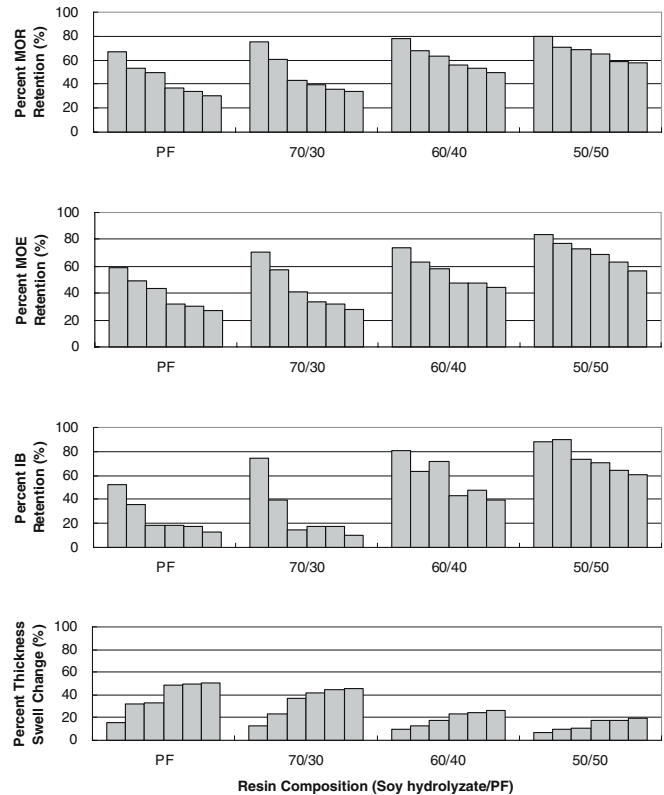
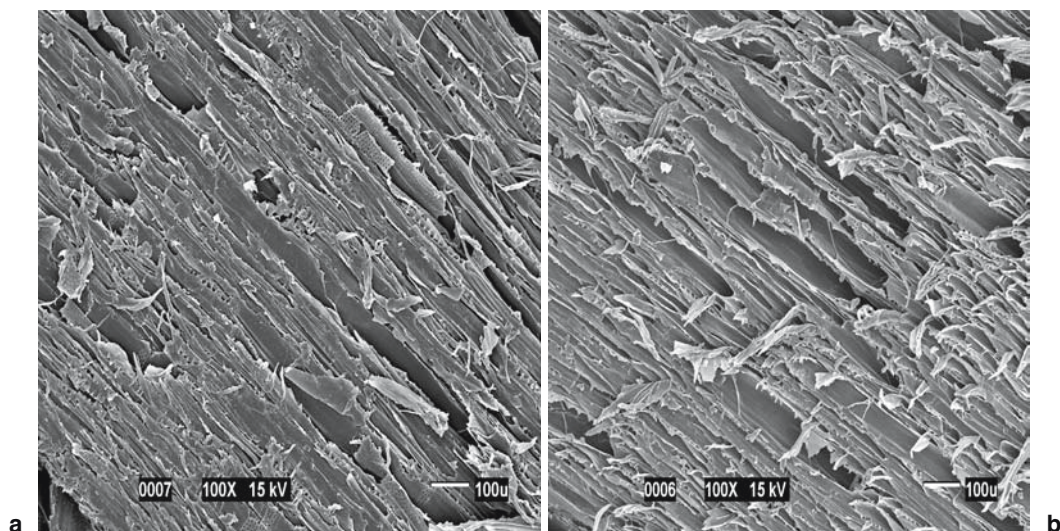


Fig. 1. Retention of flakeboard properties in six-cycle accelerated aging tests. Each bar within resin type represents one aging cycle. PF, phenol-formaldehyde; MOR, modulus of rupture; MOE, modulus of elasticity; IB, internal bonding strength

fore, all properties of flakeboard bonded with PF resins were adjusted in terms of the density of flakeboard bonded with soy/PF resins. Based on the adjusted data, boards bonded with soy/PF resins outperformed PF-bonded boards. In addition, boards bonded with PF resin and soy/PF (70/30) had very similar aging characteristics with the

Fig. 2. Scanning electron microscopy images of flakeboard bonded with soy hydrolyzates and PF in weight ratios of **a** 70/30 and **b** 50/50. The images were obtained from the fracture surfaces of IB test specimens. Fibers in **a** were partially pulled out probably due to incomplete curing of resin, and more fiber breakages were observed in **b** than in **a**. This might be due to strong interface bonding between wood components



retention of MOR, MOE, and IB. However, the corresponding values for boards bonded with soy/PF (60/40) and soy/PF (50/50) resins were higher than those for boards bonded with PF resin after each cycle of aging treatments. Figure 1 also shows that boards bonded with soy/PF (60/40) and soy/PF (50/50) resins exhibited lower TS than boards bonded with PF and soy/PF (70/30) after each cycle of aging treatments.

At 1.27 cm thickness, fiberboard and flakeboard bonded with protein-based phenolic resins needed at least 7 min pressing at 200°C to prevent hairline-blow in the core. Also, boards bonded with protein-based phenolic resins had lower IB and greater TS than boards bonded with PF resin, probably due to the fact that the protein–PF adhesive bond is not as rigid as PF bonds (Fig. 2). Once cured, however, protein-based phenolic resins showed satisfactory adhesive bonds as indicated by good results in the 2-h boil and accelerated aging tests. Excellent durability of flakeboard bonded with protein-based phenolic resins also may be explained by the physical characteristics of the cured resins. Rigid and brittle PF bonds may be subjected to gradual degradation or fragmentation because of inability to absorb stresses during the six-cycle aging treatments. Cured protein-based phenolic resin is probably more flexible due to the presence of protein, and therefore is able to absorb stresses during aging.

The results of this study showed that fiberboard and flakeboard bonded with protein-based phenolic resins with less than 50% PF showed little compromise in board properties. Therefore, protein-based phenolic resins may be cost-effective binders. Although protein-based resins require higher press temperatures and longer press times for proper curing than petroleum-based resins, they may find some suitable uses. For example, protein-based resins may be used as surface resins for flakeboard production.

Conclusions

Protein-based resins containing up to 70% protein and cross-linked with PF resins performed well in laboratory production of MDF and flakeboard. MDF bonded with protein-based phenolic resins met the requirements for exterior or interior grades, depending on the quality and quantity of protein and amounts of cross-linking PF. Resins formulated with blood meal performed almost equally well as neat PF resins. MDF prepared with soybean-based and peanut-based phenolic resins only met the requirements for interior grade. However, the protein-based resins could be upgraded by incorporation of blood protein in the formulations. Flakeboard prepared with soy protein-based phenolic resins met the CSA requirement for OSB, and showed superior aging durability to that of boards bonded with neat PF resin. It is concluded that these potentially cost-effective resins may have use in composite panel production. Excellent results of 2-h boil and six-cycle aging tests of board bonded with soy protein-based phenolic resins suggest co-polymerization of phenol–formaldehyde and protein in the resins. The exact mechanisms of protein-based phenolic resins need to be studied.

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