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Soy flour dispersibility and performance as wood adhesive

Charles R. Frihart* and Holly Satori

US Forest Products Laboratory, Madison, WI 53726, USA

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Soy flour adhesives using polyamidoamine-epichlorohydrin (PAE) resin as the curing agent are being used commercially to make bonded wood products. The original studies on the soy-PAE adhesives used purified soy protein isolate, but the much lower cost soy flour is now used commercially. We examined the performance of commercially available soy flours that have their proteins either mainly in their native (90 protein dispersibility index (PDI)) or denatured (70 and 20 PDI) states. We expected that the more native state soy proteins with their better dispersibility would provide better adhesion to wood surfaces and enhanced reaction with PAE resin. Small-scale wood bonding tests showed that neither of these effects was observed without and with a low level of PAE. In these tests, the solids content of the soy formulations had a large influence on adhesive viscosity but little influence on bond strength. Additionally, little difference was observed in any of the adhesive or viscosity properties between the soy flours having either a 0.152 or 0.075 mm (100 or 200 mesh) particle size.

Keywords: soy flour; dispersibility; bond strength; viscosity; particle size

1. Introduction

Although soy flour was used for making interior plywood in the early to mid-twentieth century, it was generally replaced by urea-formaldehyde (UF) adhesives. Soy flour denatured with strong alkali provided good plywood bonds and allowed the commercial production of the interior plywood [1]. This flour could be used in combination with blood or casein from milk to impart a higher level of moisture resistance. These adhesives needed to be mixed in the plywood manufacturing plant because their potlife was only about 8 h [1]. UF adhesives eventually replaced most of the soy-based adhesives by providing a rapid cure under hot pressing conditions, especially when using an acid catalyst, good water resistance under ambient soaking and drying accelerated tests, low cost, and colorless bondline.

The major drawback of UF adhesives is that the polymerization process is reversible. In the presence of water, especially at elevated temperatures, UF resins will decompose to give off formaldehyde. This depolymerization is a chemical reaction with a low activation energy; thus, formaldehyde emissions increase with increased temperature and humidity [2,3] and UF adhesives do not do well in water boil tests [4].

Although there has been interest in soy protein adhesives for environmental reasons [5] and some of the products possess sufficient water resistance [6–8], none received much commercial acceptance until the discovery that using polyamidoamine-epichlorohydrin (PAE) resins enhanced wet strength [9,10]. Interaction of PAE with soy protein prior to curing has

*Corresponding author. Email: cfrihart@fs.fed.us

been reported [11], but PAE's main attribute is reacting with the wood and proteins during curing. Like most soy adhesive research, the published studies have been carried out using soy protein isolate (SPI), but not with soy flour, which is now used for the commercial adhesives for economic reasons.

Soybeans are an important crop in the USA and the most valuable component of the bean is the soy oil that is extracted from the crushed beans with a solvent. The main use for the defatted (solvent-extracted), crushed beans is as animal feed. However, this defatted material can be ground to yield soy flour (about 50% protein) that has been used in the past for wood adhesives [1]. Heat or vacuum or both can be used to remove the remaining solvent from the defatted soybean to give the commercially available soy products. The commercial soy flours are offered in different levels (20, 70, and 90) of protein dispersibility index (PDI) with 90 being the closest to the native structure and 20 the most denatured (changed from native structure). The PDI depends on the heat exposure of the soy flour, with the lowest 20 PDI involving most heat. Two forms of higher protein content commercial products also come from soybeans: concentrate (about 70% protein) and SPI (above 90% protein). The range of soy products and their properties are shown in Table 1 [12,13].

Studying the reaction of PAE with SPI provides some useful information, but SPI does not necessarily react with PAE in the same way as the protein in flour, in its more native state, does. The isolation of SPI from the flour can cause denaturation of the protein as illustrated by the reduced urease activity with SPI compared with that of the flour [14]. It is also known that carbohydrates can alter the protein structure [15]. Hunt et al. have shown that the curing ability of soy flour is different from that of concentrate in some cases [16]. In addition, PAE is known to react with carbohydrates that contain carboxylic acid functionality [17] and the carbohydrate fraction of soy flour does contain some carboxylic acids [18,19].

Although much is known about soy proteins and their behavior in general [13,20–22], little has been reported on soy flour reactions with PAE with consideration of structure–property relationship [22]. A reasonable proposal is that a more dispersible soy flour with more exposed reactive groups

- should have a greater ability to coat and penetrate into the wood surface to provide better adhesion and
- should react more readily and completely with PAE to provide a stronger adhesive.

We also expected that a finer particle size soy flour with more surface area, especially for the less dispersible soy flours, should provide greater bond strength. Thus, to learn more about soy flour properties, we examined these hypotheses by testing the properties of commercially available soy flours. To test these hypotheses, we measured and compared the apparent viscosities and bond strengths of dispersions containing 20, 70, and 90 PDI flours of 0.152 and 0.075 mm (100 and 200 mesh) particle sizes at 20, 25, 30, and 35% soy solids with PAE levels of 0 and 5 wt.% solids to soy solids.

Table 1. Commercial soy product types.

Product	Cost ≈ ¢/lb	Protein (%)	Carbohydrate (%)	Oil (%)
Bean	15	40	35	20
Flour[a]	15	45	50	0
Concentrate	50	65	35	0
Isolate	130	90	10	0

[a]Available in high (90%) to low (20%) protein dispersibility indices.

2. Experimental

The soy flours used were the following: Prolia™ 100–90, Prolia™ 200–90, Prolia™ 100–70, Prolia™ 200–70, Prolia™ 100–20, and Prolia™ 200–20 (Cargill Inc., Cedar Rapids, IA, USA). Other chemicals were PAE CA 1920 (Ashland-Hercules Water Technologies, Wilmington, DE, USA) and sodium azide (Sigma Aldrich, Milwaukee, WI, USA).

A Horiba D-47 pH meter was used to measure the pH values. Apparent viscosities were measured using a Brookfield Digital Viscometer Model LVTD (Stoughton, MA, USA). A similar shear history for the samples was ensured by vigorously hand mixing the sample for 30 s, allowing it to stand for 10 s, inserting the spindle into the sample, switching on the viscometer motor, and then recording the viscosity value 10 s after the spindle started moving.

The soy flour dispersions were made by first measuring sufficient quantity of water for soy solids level and then adding the soy flour followed by 0.5 mL of aqueous sodium azide to reduce bacterial growth (0.1% w/v). If PAE was part of the formulation, sufficient PAE was then added to yield 5 wt.% PAE solids to soy solids. Finally, the desired amount of soy flour (20, 25, 30, or 35%) was weighed and added to the liquids. The mixture was then hand stirred for 30 min to complete the process. The pH and viscosity of the dispersions were measured.

The various soy flour and soy flour-PAE dispersions were tested for their wood bonding strength using an Automated Bond Evaluation System (ABES) Model 311c tester (Adhesive Evaluations Systems, Inc., Corvallis, OR, USA) for forming and breaking the bonds to determine strength and wood failure. The wood used for the test was hard maple and the wood samples bonded were 117 mm along the grain × 20 mm across the grain × 0.6 mm thick strips. These wood samples were equilibrated at 22 °C and 50% relative humidity for at least 24 h before testing. During processing with the ABES, a 5-mm wide strip of adhesive was applied to one wood specimen and was then immediately overlapped with another. This area was then hot pressed in the ABES unit at 0.2 MPa for 120 s at 120 °C. After this time period, the platens were retracted and the full specimen was removed from the unit. All samples (seven for dry testing and seven for wet testing of each combination of PDI, particle size and presence or absence of PAE) were allowed to reequilibrate at 22 °C and 50% relative humidity at least overnight before testing.

For testing bond strength, half of the specimens were tested dry and the other half were tested wet after a 4-h water soak at 22 °C. Each sample was placed back into the ABES unit and the grips were engaged. The grips then pulled each sample and the load at failure was recorded. The bond strength was calculated by dividing this load by the adhesive overlap area of 100 mm^2 to give the shear bond strength. The percentage of wood failure was also recorded but not reported here; the fracture was often in the wood outside the bonded area for the dry samples and the failure was in the adhesive for the wet samples. The standard deviations in strength and wood failure were calculated for each combination and differences were determined by comparing two standard deviation error bars for the different combinations.

3. Results and discussion

For the various combinations of different soy flours, percent solids, and with or without PAE, the pHs of the mixtures were similar. In general, the pH of these soy flour samples in water was about 6.3 (Table 2). The more acidic PAE dropped the pH values to around 6 (Table 3). Unpublished work has shown that the bond strength of soy-based adhesives is relatively

Table 2. Properties of soy formulations with no added PAE resin.

				Dry bond strength		Wet bond strength	
Soy concentration (%)	Mesh-PDI	pH	Viscosity (Pa.s)	Value (MPa)	SD (MPa)	Value (MPa)	SD (MPa)
20	100–90	6.25	1.33	4.1	0.8	0.4	0.0
	200–90	6.27	0.66	4.0	1.0	0.4	0.2
	100–70	6.27	2.36	5.1	1.3	0.6	0.2
	200–70	6.3	1.19	4.6	0.8	0.6	0.2
	100–20	6.36	0.25	4.2	0.6	0.8	0.1
	200–20	6.32	0.92	4.7	0.9	0.9	0.1
25	100–90	6.18	13.16	4.9	1.2	0.1	0.1
	200–90	6.3	3.92	5.1	0.9	0.6	0.1
	100–70	6.33	19.34	4.7	0.7	0.7	0.2
	200–70	6.26	7.72	3.8	0.5	0.7	0.1
	100–20	6.3	2.08	4.4	1.2	0.9	0.1
	200–20	6.27	5.62	4.0	0.8	0.9	0.2
30	100–90	6.21	109.8	5.0	1.2	0.1	0.1
	200–90	6.24	111.0	5.0	1.3	0.4	0.2
	100–70	6.12	294.6	4.7	0.8	0.4	0.3
	200–70	6.17	364.2	5.2	1.2	0.7	0.2
	100–20	6.2	483.0	6.2	1.1	0.8	0.1
	200–20	6.26	230.6	5.7	0.3	0.9	0.1

Table 3. Properties of soy formulations with added PAE resin.

Soy concentration (%)	Mesh-PDI	pH	Viscosity (Pa.s)	Dry bond strength		Wet bond strength	
				Value (MPa)	SD (MPa)	Value (MPa)	SD (MPa)
20	100–90	5.97	1.86	4.7	1.7	3.0	0.4
	200–90	6.01	1.42	5.3	1.1	2.8	0.5
	100–70	5.97	1.21	5.1	1.1	3.1	0.3
	200–70	6.01	1.34	5.2	1.5	2.8	0.6
	100–20	6.00	0.39	4.2	1.1	2.8	0.4
	200–20	6.02	0.52	4.9	1.4	2.9	0.4
25	100–90	5.94	16.20	5.6	1.1	1.7	0.2
	200–90	5.97	9.72	4.5	1.3	2.1	0.3
	100–70	5.94	7.56	6.7	0.8	2.4	0.2
	200–70	5.99	7.92	5.3	1.0	2.4	0.4
	100–20	5.90	1.59	6.2	0.7	2.4	0.1
	200–20	5.97	2.82	6.4	0.7	2.3	0.2
30	100–90	5.96	2000	6.6	1.4	2.3	0.2
	200–90	5.91	>2000	6.1	1.6	2.3	0.5
	100–70	5.90	1500	6.9	0.7	2.4	0.2
	200–70	5.88	>1500	6.6	0.6	2.6	0.2
	100–20	5.91	1000	6.3	0.7	2.7	0.3
	200–20	–	>1000	5.8	1.3	2.5	0.4

insensitive to pH in the range of 5–8 both alone and with added PAE. Other factors, such as viscosity, viscosity stability, and cure rate are more sensitive to the adhesive pH [23].

Viscosity is an important property for wood adhesives in general and a particular challenge of working with soy-based wood adhesives is their non-Newtonian behavior [22]. The viscosity should be low enough to give good spreading and penetration, but not so low that overpenetration results in a starved bondline and bleed through for the thin surface veneers of decorative plywood. Viscosity increases with higher solids content; the traditional highly alkaline soy flour adhesives had low solids due to viscosity constraints [1]. These latter adhesives were acceptable for plywood because the water would generally soak into the wood during the longer press times. However, when making composites, such as particleboard or fiberboard, low solids content of the adhesive is a major problem. The excess water generates steam in the hot press that can cause internal voids called blows when the pressing pressure is released. Thus, the balance between viscosity and solids content is a very important issue.

To determine the useable solids level of soy flour adhesives, we increased the solids content, starting at 20% solids in 5% increments up to the point that the adhesive was too thick to mix and spread even for small scale testing. The higher viscosity adhesives could be tested under ABES conditions, even though they were too thick for laboratory plywood testing, commercial plywood production, and for composite panel production. Viscosities for soy flour formulations with no PAE are shown in Table 2 and those for formulations with PAE are shown in Table 3. For these soy flour adhesives, the viscosity slowly increased with solids content up to about 25% and then increased very rapidly beyond this point as illustrated in Figure 1. At 35% solids, the samples were too thick to obtain reliable viscosity or shear strength values. We observed that at the lower solids levels the 20 PDI flour had a lower viscosity than the 90 PDI flour, but this relationship reversed at higher solids levels. One possibility may be the differences in the hydrodynamic volume and extent of aggregation for different PDI flours [24]. In addition, the particle sizes that we used had no substantial effect on viscosity. Although higher solids content dispersions can be made, 25% solids content seems like a reasonable product for general testing.

From our prior work, we found that using an ABES unit [25] with hard maple veneer provided a good measure of both dry and wet bond strengths [26]. Although the four-hour water soak condition is shorter than that used in many other wood bond strength tests, the bond overlap is very small and the veneers are thin, allowing fast migration of the water from the bondline. Our small scale test appears to effectively test wet bond strength, nearly as well as the ASTM D905 shear test does [26,27]. We carried out both dry and wet tests, but the wet test data have historically proven to be a much better indicator of the commercial usefulness of the wood adhesive.

As stated in the Introduction, our first hypothesis was that the more dispersible (90 PDI) soy flour should provide better curing with the PAE and greater interaction with the wood, which should improve bond strength. This seems reasonable since 90 PDI means that 90% of the protein in the soy product stays dispersed in water after centrifugation. There should be more protein molecules available for interacting with the wood and the PAE resin than would be the case for the less dispersed 20 PDI flour. We examined the soy flour without added PAE resin first to determine the intrinsic adhesive properties of the soy flours (Table 2). All the soy flours had dry bond strengths similar to other wood adhesives and with no significant differences over the range of solids levels tested. However, under wet conditions the bond strengths and wood failure for the all soy flour adhesives plummeted; this effect was independent of the soy flour type and concentration. It is possible that the carbohydrates absorb a considerable amount of water that interferes with the strength of the matrix. Figure 2 shows that the more dispersible soy flours (higher PDIs) did not provide any discernible benefit to

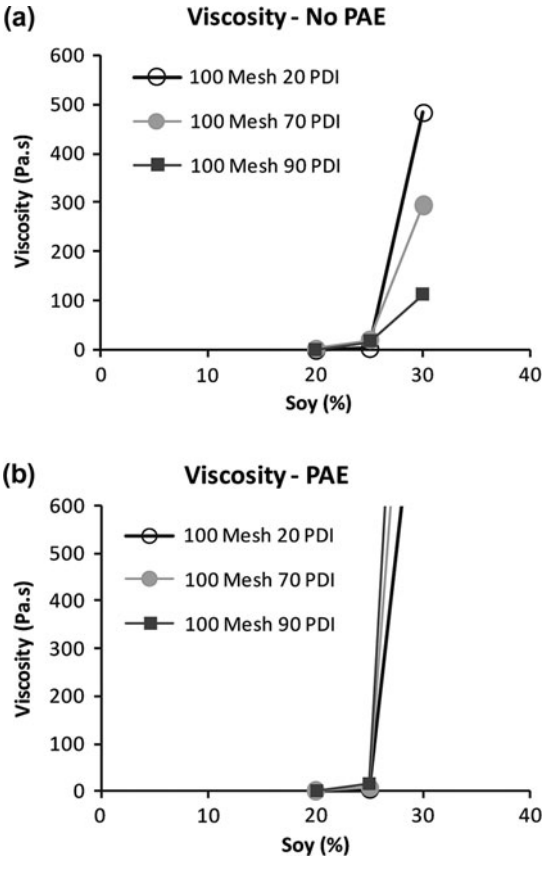

Figure 1. Effect of soy content and PDI on viscosity of adhesives made from 0.152 mm (100 mesh) soy flour without (a) and with (b) PAE.

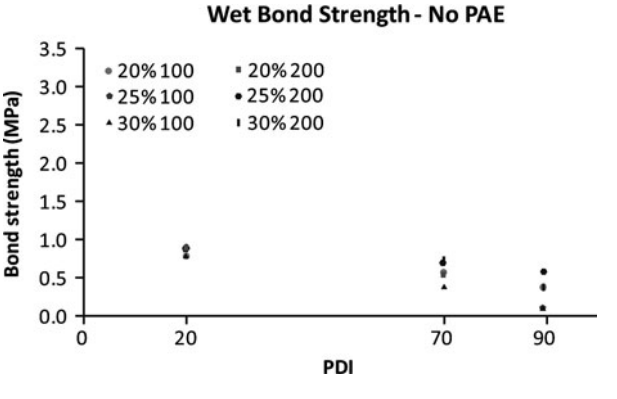

Figure 2. Wet bond strength plotted vs. percentage of solids for 20, 70, and 90 PDI flours at both 0.152 and 0.075 mm (100 or 200 mesh) particle sizes without PAE addition by testing on an ABES unit.

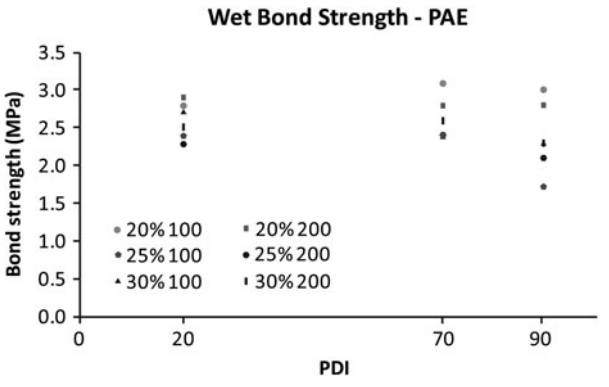

Figure 3. Wet bond strength plotted vs. percentage of solids for 20, 70, and 90 PDI flours at both 0.152 and 0.075 mm (100 or 200 mesh) particle sizes with 5% PAE addition by testing on an ABES unit.

the bond strength at these pH conditions. All these near-neutral pH soy flour adhesives had poor water resistance and provided a less water-resistant bond than the traditionally used highly alkaline soy flour formulations that can pass a three-cycle soak test for interior plywood [23].

The wet strength results underscore why the PAE resin is necessary to impart water resistance to soy-based adhesives; the wet strengths of PAE/soy combinations are much greater (Table 3) than equivalent formulations without PAE (Table 2). Although PAE levels higher than 5 wt.% are often used commercially in combination with soy flour, we used only 5 wt.% PAE to minimize the contribution caused by PAE-wood adhesion because PAE resins bond well to wood. Dry strength improved with the addition of PAE, but again, the soy flour PDI and solids content had no large effect on the shear bond strength. As shown in Figure 3, wet strengths did not benefit from the higher PDI nor was there any apparent effect of varying soy flour concentration. However, a significant improvement in wet strength clearly occurred when PAE was used (Figure 3 vs. 2). Our bond strength data do not support the concept that the more dispersible flour reacts to a greater extent with the PAE. There seems to be no improvement in the cohesive strength of the adhesive with formulations made with higher PDI soy flour. Although adding PAE provided greater bond strength under wet conditions, there was no similar improvement in wood failure, with the values being near zero for wet shear specimens.

Our second hypothesis was that the particle size should be important to the bond quality, especially for low PDI soy flours. Examples in the literature indicate that alkaline soy systems with finer particle size provided better adhesive properties [1,28]. It also seems likely that if the soy flour is not very dispersible, finer particle size would give better wetting of the wood surface and enhance the reaction with PAE. Our results (Tables 2 and 3) do not support this concept, even for the least dispersible soy. One reason may be that even the finer sized solid particles are likely to be larger than the protein aggregates in the dispersions [29].

4. Conclusion

A systematic study was done to evaluate the pH, viscosity, and bond strength properties of adhesives made from soy flours with varying levels of dispersible protein (PDI) and particle size. The viscosities of 20, 70, and 90 PDI flours increased rapidly as the solids level

increased above 25–30% in both soy flour/water systems and soy flour/PAE resin/water systems. Dry and wet shear strength test results did not support the hypothesis that more native and easily dispersible (90 PDI) soy flour would provide improved bond strength. Additionally, our findings did not validate our second hypothesis that smaller particle size soy flour should also provide improved bond strength under either dry or wet conditions. The inclusion of a low level of PAE resin resulted in a slight increase in dry shear bond strength and a significant improvement in wet shear bond strength. The formulations containing PAE curing agent exhibited no improvement in wet wood failure. Thus, soy flour PDI and particle size properties do not affect the basic bond strength of the adhesives. However, a variety of other performance issues may still influence the selection of soy flour for a particle adhesive application.

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