Soy Flour Adhesive Strength Compared with That of Purified Soy Proteins*

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Abstract

Although proteins are naturally good adhesives, often the most economical source has a significant carbohydrate component. Our prior studies have shown that commercial soy protein isolates (CSPI) give very good dry and wet bond strength for wood bonding, but the strengths are much lower for soy flour, especially under wet conditions. One large difference between these soy products is the percentages of carbohydrates, which generally provide poor bond strength under wet conditions. A variety of commercial isolates, concentrates, and flours were examined for their adhesive properties using a small-scale bond test that emphasizes cohesive bond strength. In studying how much the carbohydrates weaken the bond strength, we learned that the carbohydrate interference is only part of the difference between commercial soy flour and purified soy proteins (isolate and concentrate). An even larger factor is the denaturation of the isolate in the CSPI. Thus, it is important to realize that the CSPI performance may not be a good predictor of properties that can be expected from soy flours.

Except for the substitution of soy flour in phenolic resins (Frihart et al. 2013) and the use of soy flour at high pHs (Lambuth 2003), the literature on soy protein properties for adhesives has mainly focused on soy protein isolate and specific protein fractions (Sun 2005b). The assumption is that proteins are the main portion of soy flour giving bond strength and the carbohydrate portion serves as an inert diluent. Given our observed inability to greatly alter soy flour adhesion using chaotropic agents, salts, surfactants, or co-solvents (Frihart and Lorenz 2013), which is in contrast to the literature observations with soy protein isolate (Sun 2005b), we concluded that the carbohydrates were suppressing protein alteration for improved adhesion.

The approximate 2014 price and approximate compositions are shown for normal commercial soy products are given below:

- Whole soybeans

  ≈23–25¢/lb, 36% protein, 18% oil, 36% carbohydrates, 10% moisture
- Defatted meal

  ≈25¢/lb, 48% protein, 0% oil, 44% carbohydrates, <10% moisture
- Soy flour

  ≈30–35¢/lb, 50% protein, 0% oil, 40% carbohydrates, <10% moisture

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High (90%) to low (20%) PDI (protein dispersibility index)

- Soy protein concentrate

  ≥$1.00/lb, >65% protein, 0% oil, up to 35% carbohydrates

- Soy protein isolate

  ≥$1.90/lb, >90% protein, 0% oil, up to 10% carbohydrates

It is clear that the price of soy flour is attractive for commercial wood adhesives, and soy flour has about the same amount of protein as it does carbohydrate. The carbohydrate portion contains a variety of insoluble polysaccharides (containing rhamnose, arabinose, galactose, galacturonic acid, glucose, xylose, and mannose) and soluble components, such as sucrose, raffinose, and stachyose (Eldrige et al. 1979, Bainy et al. 2008). Extraction with aqueous ethanol removes many of the soluble carbohydrates along with a few of the proteins to produce soy concentrate (Sun 2005a). The purest commercial soy protein product is soy protein isolate (SPI), which has almost all of the insoluble and soluble carbohydrates removed, but also some of the proteins (Kinsella et al. 1985, Egbert 2004, Sun 2005a). Although the commercial soy protein isolate (CSPI) gives good strength, about 10 times that of soy flour (Frihart 2011), the isolate's price does not make it an attractive starting point for a wood adhesive. Thus, the initial objective was to understand if the carbohydrates in the soy flour adhesive were reducing its wet bond strength compared with the adhesive performance of the CSPI. These experiments involved examination of a carbohydrate physical interference model and understanding what other factors led to the good performance of some soy products compared with others.

Experimental

The soy flour used was Prolia 100-90 (Cargill Inc., Cedar Rapids, Iowa) along with commercial soy concentrate ARCON AF (ADM, Decatur, Illinois) and commercial soy protein isolate PRO-FAM 974 (ADM). Chemicals used were sucrose, galacturonic acid, and α-cellulose (Sigma-Aldrich, St. Louis, Missouri), pectin (Spectrum Chem. Mfg. Corp., Gardena, California), dextrin (Cargill Inc.), and stractan (Mountain Resources, Montana), an arabinogalactan polymer. The polyamidoamine-epichlorohydrin (PAE; CA 1920) was from Ashland Water Technologies (Wilmington, Delaware). Laboratory soy protein isolate was prepared using a literature method (Petruccelli and Añón 1995).

In the first set of experiments, soy adhesives were prepared by adding soy flour (30%, wt/wt, of final concentration), soy concentrate (20%), or CSPI (15%) to water and mixing for 30 minutes. These three soy adhesives had about the same protein content (14%) and a manageable viscosity. If PAE polymer was used, it was then added at 5 percent on a dry weight basis to the soy solids, followed by additional mixing. In the other set of experiments, soy isolates (15% of final concentration) were added to water containing the carbohydrate to be tested and mixed for 30 minutes.

An ABES (Automatic Bonding Evaluation System), Model 311c (Adhesive Evaluations Systems Inc., Corvallis, Oregon) was used for bonding and testing shear strength of the samples (Humphrey 2010). Though the ABES does not have an associated standardized test method, it is useful for screening because it is rapid, relatively insensitive to rheological differences, produces uniform bonds on smooth veneer, and allows determination of the shear strength of bonds either dry or wet after soaking in water. Soy flour adhesive was applied to 5 mm on the end of one piece of maple veneer (117 by 20 by 0.6 mm thick), which was overlapped 5 mm with another piece of veneer. The sample was hot pressed in the ABES at 0.2 MPa for 120 seconds at 120°C. The bonded wood samples were equilibrated at 21°C and 50 percent relative humidity at least overnight before testing dry or wet after soaking in water for 4 hours at room temperature. Five specimens were tested in tensile shear for each condition and the average and 1 standard deviation are shown.

Results and Discussion

Given that our main emphasis was to understand the cohesive strength development of the soy adhesive for both dry and wet samples, we have found that the ABES test using smooth, defect-free surface veneers in a lap shear test works well and it has been correlated with the compressive shear test, ASTM D905 (Frihart et al. 2009). An additional benefit is that the ABES test is relatively insensitive to viscosity, which can vary dramatically with proteins when we change the other variables. For adhesive performance, not only are dry strength values important, but also wet strength is important for testing the durability of the bond, particularly because wood moisture contents vary considerably depending upon the exposure conditions (Frihart 2009). Our work with soy flour has shown that dry and wet adhesive bond strengths for samples made and tested using this ABES method were remarkably insensitive to the type of soy flour used (Frihart and Satori 2012) or to the addition of chaotropic agents, salts, surfactants, and co-solvents to the soy flour (Frihart and Lorenz 2013). For wet testing, we found that water soaking the bonded assembly for 4 hours was sufficient to saturate the bond given the thinness of the veneers for measuring the wet cohesive strength of the soy adhesive. Other small-scale wood bonding tests have been used (Sun 2005b, Kim and Netravali 2013), but do not allow the same control of conditions and ease of testing.

One way to better understand soy adhesives is to examine the adhesive performance of commercial soy flour, concentrate, and isolate adhesives prepared in the concentrations listed in Table 1 for dry and wet strength using our ABES standard method. Some prior work has compared similar materials for bonding ramie fibers, but the adhesives as well

Table 1.—Shear strength of soy adhesives with weights of solids in percent.[a]

	Co-reactant			
	Without PAE		With PAE	
Soy product	Dry	Wet	Dry	Wet
Flour, 30% of 90 PDI	5.0 ± 1.2	0.3 ± 0.2	6.6 ± 1.3	2.2 ± 0.2
Concentrate, 20%	6.2 ± 0.4	0.4 ± 0.1	7.2 ± 1.0	3.4 ± 0.3
Com. isolate, 15%	7.2 ± 1.3	3.0 ± 0.4	7.6 ± 0.8	5.0 ± 0.3
Lab. isolate, 30%	4.6 ± 0.4	1.1 ± 0.5	—	—

[a] PAE = polyamidoamine-epichlorohydrin; PDI = protein dispersibility index; com. = commercial; lab. = laboratory.

as bonding and testing conditions were different (Kim and Netravali 2010). These concentrations were used because they resulted in approximately the same protein concentration (approximately 14 wt%) in the final adhesive. In addition, these concentrations led to a reasonable viscosity for each material. In our bonding studies using the ABES method, we have observed similar strengths at most reasonable concentrations for soy flour (Frihart and Satori 2012), and a similar lack of concentration dependence was observed for isolate and concentrate adhesives (unpublished data). Not only did we test the commercial soy flour, concentrate, and isolate by themselves, but we also added a low level of PAE co-reactant to help tie the proteins together for wet testing, but not so high that the co-reactant dominated the strength values. The PAE polymer was used because it has been shown to be an effective co-reactant for improving the strength of both commercial soy protein isolate and flour (Li et al. 2004, Frihart and Satori 2012) and is used extensively commercially.

Dry strengths of all the adhesives were very good, but only the soy protein isolate has good wet strength without PAE polymer (Table 1). It is surprising that the Arcon AF concentrate did not give better wet strength than soy flour (Prolia 100/90) because it seemed reasonable that removal of the soluble carbohydrates and low-molecular-weight proteins in preparing the concentrate should have improved the wet bond strength. The effectiveness of even low levels of added PAE polymer in improving wet shear strength has been shown for soy flour adhesives (Frihart and Satori 2012, Frihart and Lorenz 2013), and these findings are also true for concentrate and isolate (Profam 974) adhesives (Table 1). It is informative that the low level of PAE polymer (5% dry weight/soy dry weight) was not effective in bringing the strength of soy flour with PAE polymer up to the level of the concentrate with PAE polymer or the protein isolate without PAE polymer. Our hypothesis was that the carbohydrates were interfering with good bond formation by the proteins. It is true that higher molecular weight carbohydrates can provide good bond strength under dry conditions, but these bonds are greatly weakened by the addition of water (Baumann and Conner 2002).

The data in Table 1 led to the proposal of the carbohydrate physical interference model in Figure 1. In this model, the insoluble (straight lines) and soluble (wiggly lines) carbohydrates prevent good physical contact between the proteins (circles) even when protein modifiers have been added. Most of the soluble carbohydrates are removed by extraction with aqueous ethanol to produce soy concentrate. Dry and wet ABES shear strengths of concentrate are not much better than soy flour without added PAE, but are better than soy flour with added PAE. However, almost all the soluble and most of the insoluble carbohydrates have to be removed, as is the case for the isolate, to significantly improve the ABES wet strength of the soy adhesive without added PAE polymer. In this model, PAE polymer can bridge the carbohydrates in soy flour to the PAE polymer linking protein molecules directly or through insoluble carbohydrates, which contain carboxylic acid groups that can react with the PAE polymer. In the concentrate, with removal of most of the soluble carbohydrate, it is easier for the PAE polymer to bridge across the interfering carbohydrates to connect protein molecules compared with soy flour. The isolate has few interfering carbohydrate molecules, so it is easier to join protein units without the PAE polymer, while the added PAE polymer just enhances those linkages.

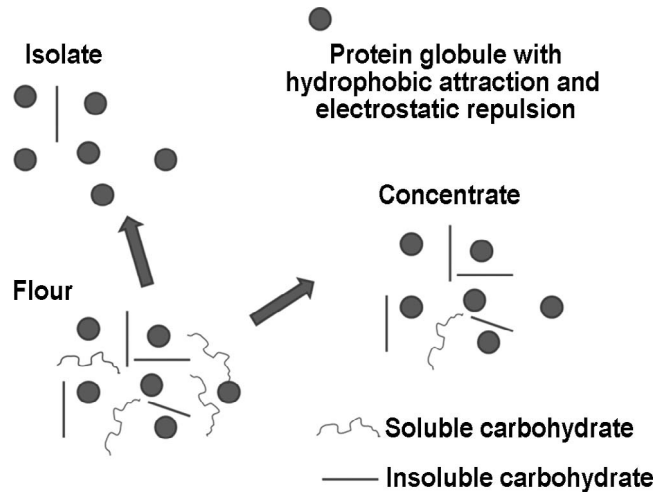

Figure 1.—Carbohydrate interference model.

Although the model in Figure 1 is reasonable based upon prior data, there was no literature information to either support or discount this hypothesis. Thus, we first tested this hypothesis by adding increasing amounts of soluble (dextrin) and insoluble (cellulose) carbohydrates to soy protein isolate and then tested the ABES wet strength of the resulting adhesives. Not as much cellulose could be added to the protein, because the viscosity became too high. As shown in Figure 2, by decreasing the protein content with the addition of carbohydrates, both dextrin and cellulose decreased the wet strength of the isolate, but not down to as low as the wet strengths for the soy flour or concentrate alone. The data show that this hypothesis may have some validity in that there was an immediate and steady reduction in strength to about 15 percent of added solids (carbohydrate/soy ratio of 0.18). However, the decrease stops at this level of carbohydrates and we observed no further reduction, which does not seem compatible with this model. A similar reduction is observed if a combination of dextrin and cellulose is used (Fig. 2). Thus, the data show that carbohydrates can cause some interference, but not enough to explain the much lower strength values for soy flour and concentrate. If interference were the key issue, then adding carbohydrates to the isolate should decrease the wet strength to the level of concentrate and flour, and as more carbohydrates are added, the strength should continue to drop instead of leveling out.

To further test the assumption that carbohydrates in soy flour serve mainly as interfering molecules, several other carbohydrates were added to the soy protein isolate, at the concentration of total carbohydrates that occurs in soy flour, and tested for their effect on the ABES wet bond strength. As shown in Figure 3, adding other carbohydrates to the isolate caused only a small drop in wet strength but the results varied with type of carbohydrate. Sucrose, which can move easily into the wood, seemed to have no effect, especially compared with dextrin the other highly soluble sugar. The pectin sugars galacturonic acid and stractan (arabinogalactan) had the biggest negative effect while the cellulose had a small effect. The mixed carbohydrates representing the mixture of carbohydrates in soy flour also

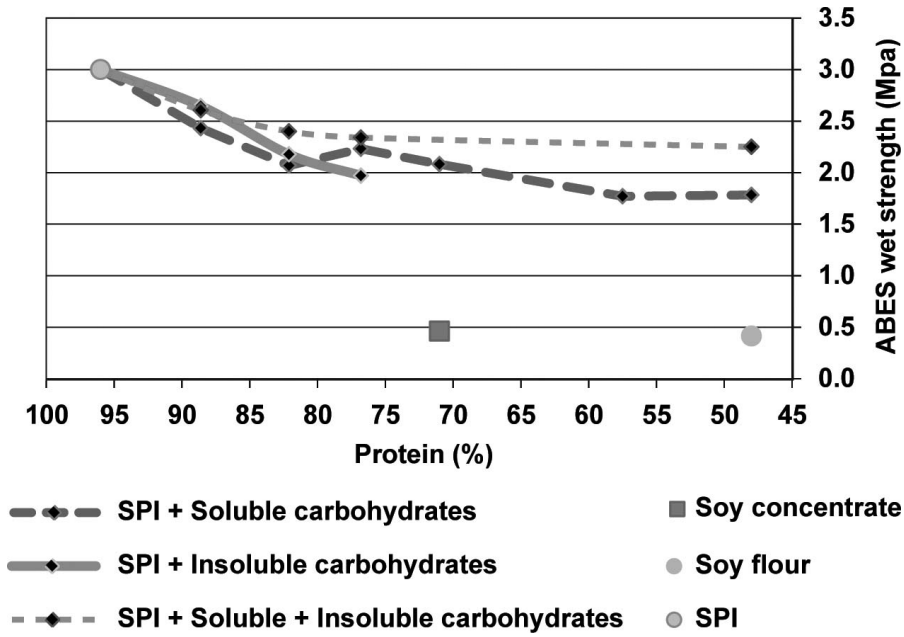

Figure 2.—Average Automatic Bonding Evaluation System wet strength comparisons of different carbohydrate additions to soy protein isolate as a percentage of total solids. SPI = soy protein isolate.

had a larger negative effect, but the reduction was not close to the strength observed for soy flour or concentrate. Thus, the carbohydrate interference model does not explain the much lower adhesive performance for soy flour compared with the CSPI.

However, the picture of the proteins becomes more complicated in that we observed very good bond strength with a commercial soy protein isolate, but poorer strength has been observed with a laboratory-prepared soy protein isolate (Sun 2005b, Wang et al. 2005) than what we observed with the CSPI. Thus, it became important to understand more about the adhesive performance of SPIs. Egbert (2004) has elaborated that the diversity of commercial SPIs on the market was mainly to provide different properties for a variety of food applications. We tested seven commercial soy protein isolates. All of these provided good wet bond strength ranging from 1.9 to 2.5 MPa despite viscosities ranging from 10 to 58,000 cps and pH values of 5.4 to 7.6 for 15 percent dispersions (detailed data not reported here). Although the specific conditions used to produce these SPI materials is not disclosed, Egbert reports that CSPI products are treated to become more ''functional,'' and thus are not in their native state. On the other hand, the work of Sun was to prepare an SPI that is in its native state. To compare adhesive properties of the native state laboratory SPI (LSPI) with the CSPI, we used the common procedure of dispersing the native flour in water at 10 percent solids and centrifuging out the insoluble carbohydrates. Acidifying this supernatant below the protein isoelectric point caused the protein to precipitate so that it could be collected by centrifugation (Petruccelli and Añón 1995). As shown in Table 1, this LSPI had less than half the wet strength of a CSPI. It is likely that the homogenization with heat and water converted the CSPI into a more functional protein (Egbert 2004) and this lead to the greater bond strength. Thus purifying the protein by removing the carbohydrates and other components in flour to obtain a greater than 95 percent protein content did make for a better adhesive. However, denaturing this protein by typical commercial functionalization (Egbert 2004) provided an even bigger increase in strength (see Table 1).

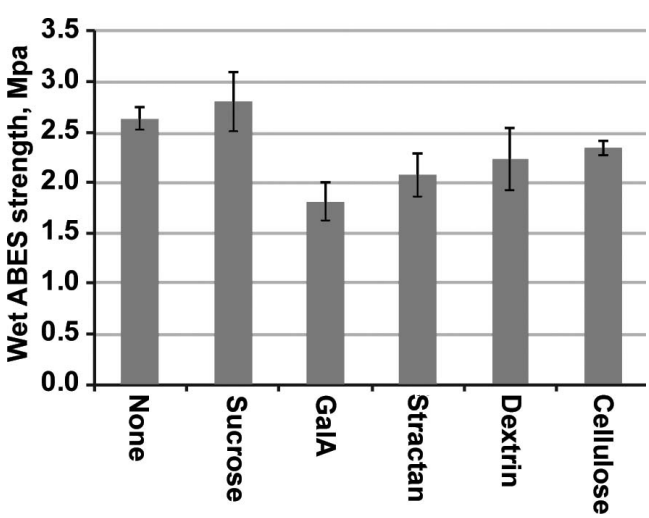

Figure 3.—Effect of added carbohydrates to 15 percent soy protein isolate with 23 percent carbohydrate based on soy by weight. ABES = Automatic Bonding Evaluation System; GalA = galacturonic acid.

An obvious question was whether adding carbohydrates to the LSPI has the same effect as it does for the CSPI. Added equal weights of dextrin and cellulose to yield 47 percent protein content also decreased the wet strength of the LSPI to the same extent that they decreased the wet strength of the commercial isolate (22.5% vs. 25% decrease), but not down to the wet strength of soy flour (0.81 vs. 0.3 MPa for soy flour; see Table 2).

The data collected show that carbohydrates play some role in interfering with protein bond strength with wood when tested under wet conditions, but it does not explain all

Table 2.—ABES wet strength of soy protein isolates plus carbohydrates compared with soy flour.[a]

	Wet strength (MPa)	Wet strength + dextrin and cellulose (MPa)
Com. isolate, 15%	3.0	2.25
Lab. isolate, 30%	1.1	0.81
Soy flour, 30%	0.3	Not applicable

[a] ABES = Automatic Bonding Evaluation System; com. = commercial; lab. = laboratory.

the difference between soy flour and soy protein isolates. Another possibility is that the carbohydrates are stabilizing the protein and do not separate well from the protein under any of the conditions that we have tested. If the carbohydrates form a strong complex with the protein that can only be disrupted by adjusting the pH at low solids content, as in the process for preparing protein isolate, this hypothesis would explain why adding chaotropic agents, denaturants, or surfactants fails to make soy flour more reactive (Frihart and Lorenz 2013), but does help the adhesion with LSPI (Sun 2005b). A newer carbohydrate interference model is that proteins in soy isolates assume conformations not possible in soy flour because they are not separated from the carbohydrates. A high level of association between some proteins and carbohydrates has been shown (Schmitt et al. 1998). This could explain the fact that the initial carbohydrate addition associates with the protein and interferes with bond strength, but once these sites are saturated, further addition has very little effect.

Conclusions

Studies on the use of soy solids for adhesives have focused on evaluating soy protein isolate and assume that carbohydrates in the flour just serve as diluents. However, our prior studies and data presented here on the adhesive strength of soy flour-, concentrate-, and isolate-bonded wood led to a carbohydrate physical interference model. Although this model allowed rationalization of the comparison of soy isolate, concentrate, and flour, testing of this model was needed. If interference were the key issue, then adding carbohydrates at high levels to the isolate should decrease the wet bond strength to the level of concentrate and flour. However, the addition of a variety of carbohydrates to the isolate caused only a small decrease. Thus, the carbohydrate interference model does not predict soy adhesive performance well. A newer model is that the proteins in soy isolates, because they are separated from the carbohydrates, are altered into conformations that do not naturally occur in soy flour.

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