Soy Adhesive-Moisture Interactions

Chris Hunt
U.S. Forest Service, Forest Products Laboratory

Jim Wescott
Heartland Resource Technologies

Linda Lorenz
U.S. Forest Service, Forest Products Laboratory

Abstract

One barrier to a broader use of soybean-based adhesives is their sensitivity to water. When using high levels of the dispersion aids urea and glycerin, we have observed an increase in wet bond performance with adhesives made using soy concentrate over those using soy flour when both contain a polyamidoamine-epichlorohydrin (PAE) crosslinking agent. We then investigated the effect of different soy flour components on wet bond performance in these systems. It appears that, in the quantities present in soy flour, the low molecular weight (MW) carbohydrates have a larger impact on wet performance than low-MW peptides when dispersion aids are present. The data presented here suggests that caution should be used when extrapolating results of protein studies to products made with soy flour.

Introduction

Defatted soy flour derived from soybeans was once the dominant raw material for plywood adhesives in the U.S., but was replaced by petroleum-based products that were cheaper and offered higher moisture resistance. Recently there has been a resurgence of interest in bio-based material in an effort to shift our dependence from petroleum to domestic, renewable feedstocks (Sun 2005, Li 2007, Zhong et al. 2007, Wescott and Birkeland 2008). The Forest Products Laboratory is working in cooperation with Ashland Chemical and Heartland Resource Technologies to understand and improve soy adhesives for the wood products industry. While developing soy-based adhesives for wood products, we focused on improving and understanding wet strength properties, to make them more competitive with petroleum-based systems.

In our work we observed a strong interaction between soy and the dispersion aids, glycerin and urea. The wet strength performance of soy concentrate adhesives were improved, or unaffected, by the addition of large quantities of these dispersion aids, while soy flour adhesives consistently lost a significant proportion of wet strength when dispersion aids were present. We then investigated some possible explanations for these observations.

In this study, soy flour and concentrate are compared. Soybean processing starts with defatting (removing oil) by extracting soybean flakes with hexane. The remaining material (~50% protein, 50% carbohydrate) is desolventized and dried to form defatted soy flakes or soybean meal depending on the operation. Soy flour is produced simply by grinding the defatted soy flakes to a finer particle size. Soy concentrate is formed by taking the defatted flakes and extracting them with ethanol to remove soluble sugars. More specifically, it removes ~18% of the original mass: ~15% low molecular weight (MW) carbohydrates (primarily sucrose, raffinose, and stachyose), and ~3% in small peptides. In addition, the ethanol extraction reduces the soy protein solubility in water from ~60 to 70% for 60 PDI (protein despersibility index) soy flour or flake to below 10%, suggesting that the proteins refold to expose hydrophobic groups on the outside and hide hydrophilic groups on the inside of the protein structure.

Once we observed the differences between flour and concentrate in the presence of dispersion aids, we examined the source of these differences. We developed and tested three theories: 1) Low-MW carbohydrates could be disrupting the wet bond by attracting water and possibly consuming PAE resin without contributing to wet strength. This theory was tested by adding low-MW carbohydrate to the concentrate-urea adhesive. 2) Low-MW peptides could react with and chain-terminate the PAE crosslinking agent. Primary amines and carboxylic acids are both known to react with the PAE functional group, the azetidinium ion. The effect of low-MW peptides was tested by adding glycine to the urea/concentrate

adhesive. 3) Finally, the proteins in flour could irreversibly assume a new conformation from the exposure to ethanol during the extraction process. The effect of ethanol exposure was tested by placing ethanol on flour, evaporating the ethanol, and testing the ethanol-treated flour-urea adhesive.

Methods

Three-ply, 12 × 12 inch (305 × 305 mm), #1 hard maple plywood panels were made from veneers 3.33 mm thick. Adhesive was applied by roller and each veneer weighed to record the actual adhesive applied. Assembly time consisted of a 3 to 4 min open time, 15 min closed time, 5 min cold-press at 120 psi, (827 kPa) and 4 min hot-press at 120°C, 150 psi (1047 kPa). Veneers were preconditioned at 80°C/30% RH before assembly, and stored at least three days at 70°C/50% RH between cutting and testing.

The three-cycle soak test followed the ANSI/HPVA HP-1 2004 standard (ANSI 2004), where five specimens of 2 × 5 inch (50 × 127 mm) from each board were exposed to three cycles of soaking and drying. The maximum allowable continuous delamination on any specimen is 2 inches (50 mm). Shear testing was also done according to ASTM D 906-98 (ASTM 2004) with four dry and six wet specimens from each board, all pulled in the closed lathe check direction to better assess bond integrity.

Adhesives were made with either toasted soy flour (ADM Kaysoy) or soy concentrate (ADM Arcon AF). All soy flour was exposed to a urease heat denaturation step before urea addition. Adhesive recipes used when discovering the flour-concentrate differences are given in **Table 1**. For investigating the cause of these differences (**Fig. 1** and **2**), the following procedures were used. For flour-urea, 14.67 g flour and 29.33 g urea were added to 54.96 g water. For concentrate-urea adhesive, 20.7 g urea, 10.33 g concentrate, and 68.48 g water were mixed at 50°C for 30 min, then cooled and filtered through a 20-mesh screen. For carbohydrate replacement, a 50/50 mixture of sucrose and raffinose was added at 17.6% of soy concentrate weight to match the 15% weight loss of soy flour in the commercial processing of flour to concentrate. For peptide replacement, glycine was added at 3% to concentrate to simulate peptide losses in the conversion of flour to concentrate. For the carbohydrate and peptide replacement study, PAE crosslinking agent (CA1400 from Hercules Chemical, Passaic, NJ) was added at 6.8% of solids. The basic PAE structure is shown in **Fig. 3**. The azetidinium ion is highly reactive with electron donating groups, so is likely reacting with the rare deprotonated primary amines or with carboxylate groups in amino acids.

Unless stated otherwise, soy adhesives were applied at a spread rate of 30 g wet adhesive per square foot per glueline, at pH of 6.5 ± 0.5. Typical viscosities are ~2000 cps at 30 rpm using a Brookfield DV series viscometer (Middleboro, MA) with spindle #3. For **Table 1** and **Fig. 2**, one panel was made with each adhesive, while **Fig. 3** contains two panels per adhesive. In **Fig. 4** three separate adhesive batches were made from different lots of soy. Two panels were made from each batch, giving six boards at each condition. The term "significant" indicates $p < 0.05$ in a student t-test.

Results and Discussion

In our work on adhesive formulation, we observed that soy concentrate seemed to need a dispersion aid, such as urea or glycerin to make a functional adhesive. Without the dispersion aid our soy-concentrate adhesives behaved like sand in water and often exhibited low bond strength, likely caused by poor distribution and transfer of the adhesive because of its rheology. The poor spreading of our soy concentrate in water adhesive is likely a function of the very low solubility of the protein. With these dispersion aids added at 200 wt% to the soy, however, the concentrate adhesives were very smooth, spreadable, and had good wet strength. On the other hand, soy flour with added dispersion aids at these levels consistently had lower wet strength than soy flour

Table 1. ~ *Plywood wet shear strength and 3-cycle soak pass % as function of formulation.*

Soy	Dispersion aid	PAE/ solids	Soy	Dispersion aid	PAE	Spread rate	Protein	Dry 906	Wet 906	% Pass 3-cycle soak
			(%)	(%)	(%)	(wet g/sf)	(g/sf)	(psi)	(psi)	
Flour pH 13	-	0.0	28.1	0.0	0.0	32.4	4.6	402	37	0
Flour	-	0.0	25.0	0.0	0.0	36.7	4.6	249	0	0
Flour	-	9.8	22.2	**0.6**	2.2	32.0	3.6	395	214	0
Flour	-	19.1	20.0	**1.0**	4.0	26.3	2.6	380	235	75
Concentrate	-	0.0				Unspreadable				
Concentrate	-	9.7				Unspreadable				
Concentrate	-	19.0	18.6	0.9	3.7	28.9	3.1	362	183	100
Flour	Urea	0.0	14.7	29.3	0.0	25.6	1.9		blow	
Flour	Urea	9.8	12.0	24.9	3.6	23.7	1.4	364	112	0
Flour	Urea	19.1	10.1	21.8	6.1	20.2	1.0	401	187	0
Concentrate	Urea	0.0	12.7	20.3	0.0	30.8	2.2	266	0	0
Concentrate	Urea	9.8	10.6	25.3	3.2	24.9	1.5	439	201	100
Concentrate	Urea	19.1	9.1	22.0	5.5	21.2	1.1	435	229	100

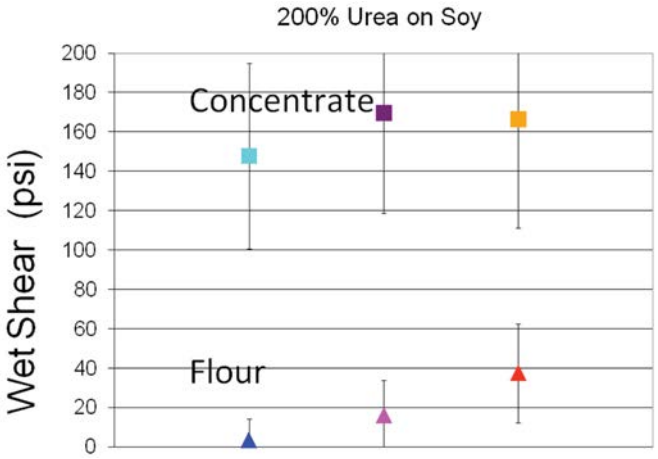

Figure 1. ~ *Wet shear strength of soy adhesive from different lots showing the difference in performance between flour and concentrate before peptides and carbohydrates were added to concentrate.*

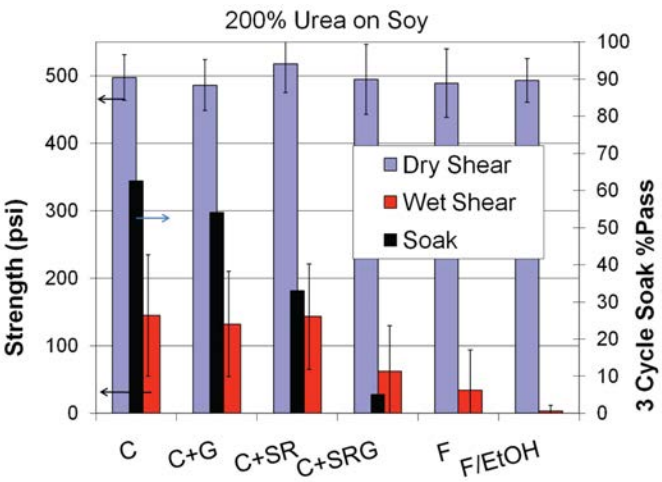

Figure 2. ~ *Change in concentrate-urea adhesive (C) with addition of peptide glycine (G), low-MW carbohydrate sucrose+raffinose (SR), and both peptide and carbohydrate (SRG). Flour-urea (F) and flour treated with ethanol (F/EtOH) shown on right.*

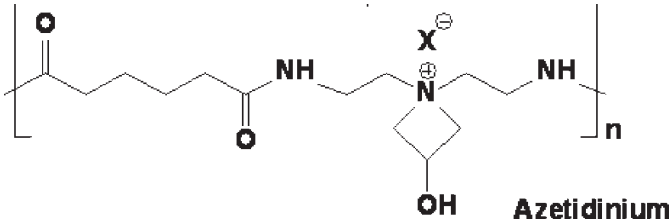

Figure 3. ~ *Azetidinium ion—the active reaction site in PAE crosslinking agent.*

without dispersion aids or concentrates with dispersion aids. The lower strength of flour + dispersion aid compared to flour alone can be rationalized by the lower protein loading when dispersion aids are present. However, flour wet strength was still inferior to concentrate, even though they had very similar protein mass/area, soy

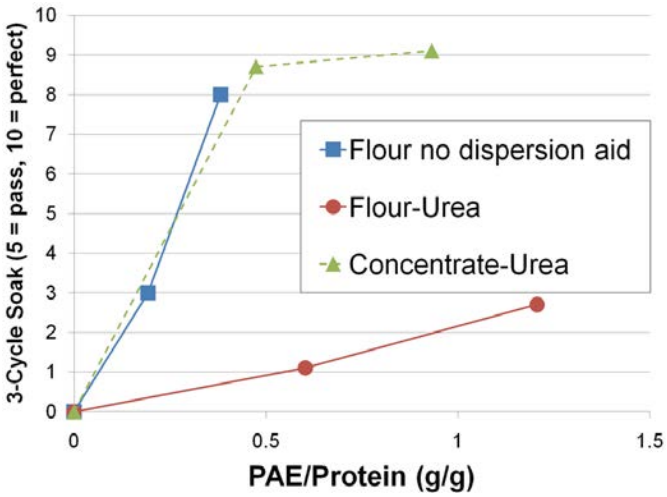

Figure 4. ~ *Three-cycle soak performance of flour and concentrate with and without urea.*

mass/area, PAE/protein, and PAE/soy. **Table 1** shows some performance results obtained with three-ply maple panels, using a PAE solution that incidentally contained urea. An alkaline denatured, pH 13, soy flour adhesive (similar to 1930s plywood formulation) is provided as a reference. This same pattern, poor performance of flour relative to concentrate in the presence of high levels of dispersion aid, was observed repeatedly on maple, pecan, and hickory substrates, and with glycerin as the dispersion aid instead of urea.

Figure 2 shows graphically the 3-cycle soak performance of panels in **Table 1**. The large drop in 3-cycle soak performance upon addition of urea could be attributed to the lower quantity of bondable material present (10–15% flour with urea vs. 20–25% without urea). Concentrate, on the other hand, had excellent performance with urea present even with protein loading very similar to flour adhesives. Therefore while the drop in wet strength of flour adhesives upon urea addition could be attributed to a lack of bondable material, the difference between flour and concentrate was still unexplained.

These data led us to question what caused the difference in wet strength between flour-urea and concentrate-urea adhesives. After considering the differences between flour and concentrate in both composition and processing, the following three hypotheses were proposed:

1. Low-MW peptides in the flour were chain-terminating the PAE crosslinking agent.
2. Low-MW carbohydrates in flour were not contributing to wet bond strength but were attracting water to the bondline.
3. The protein conformation was altered by ethanol exposure during concentrate production.

For the rest of the study, we made three master batches of concentrate-urea adhesives using different lots of concentrate to ensure that our results were not lot- or batch-specific. We first verified that the difference in wet strength between flour-urea and concentrate-urea was reproducible (**Fig. 3**). We then added low-MW carbohydrates and peptides to the three different concentrate-urea

adhesives to test our first two hypotheses and made an alcohol-treated flour-urea adhesive to test Hypothesis #3. **Fig. 4** shows the results obtained when the three hypotheses were tested.

Hypothesis #1: Low-MW Peptides

Glycine was added to the concentrate at 3% to mimic the low-MW peptides in flour. The addition of glycine alone had no statistically significant impact, though there was a slight reduction in 3-cycle soak passing percentage. As approximately 37% of soy protein amino acids contain a reactive carboxylic acid or primary amine group (UN FAO 1992), and the glycine is lower MW (75 vs. 114 Da per amino acid) and has two reactive sites per molecule, the added glycine contains approximately 35% as many sites for reaction with the PAE as the protein. With the high number of reactive sites and expected higher reactivity of glycine (high mobility, soluble, low steric hindrance, low amine pK_b) we expected a significant amount of PAE-glycine reactions and subsequent property loss from the reduction in PAE-protein reactions.

Hypothesis #2: Low-MW Carbohydrates

Sucrose and raffinose were added to the concentrates at 15% to mimic the low-MW carbohydrates in flour. The addition of carbohydrates alone did not significantly reduce shear strength, but again the number of specimens passing 3-cycle soak was noticeably less. When carbohydrate and glycine were both added at the same time, the wet strength values were statistically different from concentrate alone and indistinguishable from the flour-urea adhesive. The average strength decrease from carbohydrate and glycine addition was 1 and 11% respectively, but when both are added together the drop was 58%, suggesting that the accumulated bond degradation was either not linear with bond strength or else the two additives worked synergistically, suggesting a combination of Hypotheses 1 and 2 may have been responsible. Inspection of **Table 1** shows that in several cases, the increase in wet strength from 0 to 10% PAE addition was considerably higher than the change from 10 to 20% PAE. This suggests that there is a minimum threshold level of crosslinking, above which additional crosslinking agent has little impact. It may be that the combination of carbohydrates and glycine tipped the adhesive below that minimum threshold, causing wet strength to degrade sharply.

A common suggestion is that PAE, a paper wet-strength agent, might react with hydroxyl groups in the carbohydrate, resulting in chain termination. Research on PAE mechanisms has shown that PAE reacts with carboxylate groups and itself, but not significantly with hydroxyl groups (Espy 1994), so reactivity with uncharged carbohydrates is unlikely.

Hypothesis #3: Protein Conformation

Exposure of flour to ethanol clearly did not help the wet strength of the bond. On the contrary, it seems to have had a strong detrimental effect on wet strength. We originally used this evidence to rule out Hypothesis #3 that ethanol exposure produced protein conformations favorable to wet strength. One reviewer, however, questioned whether our experimental conditions, 100% ethanol for <15 min, starting with a 20 pdi flour, would mimic the extraction to produce concentrate, which commercially starts at higher pdi of ~60 and ~70% ethanol concentration. It has been claimed than 70% ethanol is optimal for denaturation of the protein (Yokohama et al. 1978). Aqueous alcohol would also be more effective at extracting soluble carbohydrate that 100% ethanol.

It is also clear that none of the variables tested had a dramatic effect on dry strength. This is not surprising as wet strength is commonly much more sensitive than dry strength at differentiating performance in soy-wood adhesives.

In summary, the extractable portions of soy flour appear to have a strong interaction with dispersion aids when these aids are present at high levels. Why this should be so is not intuitively obvious. We do not expect the dispersion aid to increase the solubility of the low-MW carbohydrates, as the carbohydrates are highly soluble in water alone. We also expect some solubility from the small peptides. What do the dispersion aids add that so severely impact wet performance? We can hypothesize that the carbohydrates degrade wet bond strength by acting as hydrophilic, swelling, nonbonding filler. It is common for excessive filler to degrade adhesive performance. Chain terminating agents that prevent crosslinking are also well known to degrade adhesive performance. However the fact that glycine alone did little to impact wet strength suggests that the crosslink density was still sufficient when the glycine was present and carbohydrate absent. We suspect that the low-MW peptides reduce crosslink density while the soluble carbohydrates and dispersion aids together increased the need for crosslinking. Soy can withstand the peptides and carbohydrates if dispersion aid is not present, and concentrate can withstand either peptide or carbohydrate when dispersion aid is present, but soy protein/PAE fails to develop sufficient wet strength when all three (peptide, carbohydrate, and dispersion aid) are present.

Conclusions

First we observed that soy concentrate requires some dispersion aid simply to make a useable wood adhesive, and that concentrates perform well with large quantities of dispersion aid in the adhesive formulation. Soy flour, on the other hand, is able to make a good adhesive with no dispersion aid at all. Large amounts of dispersion aids have a strong negative impact on wet performance of soy flour, but not soy concentrate adhesives. The fact that this interaction exists suggests that while basic work on pure proteins is very helpful, understanding how to make good adhesive from isolate is a long way from making a good adhesive from flour.

We found that on their own, neither the extracted carbohydrate nor the extracted peptides had a strong detrimental effect on bond strength with urea present, but when both were added simultaneously to a concentrate-urea adhesive the wet strength declined to a level similar to flour-urea adhesive. There is either a synergistic

effect between the carbohydrate and peptides or else the fundamental properties driving bond failure have some threshold level or are nonlinear with measure bond strength. We suspect the combination of lower crosslink density from the peptides coupled with the hydrophilicity of the carbohydrate and urea worked synergistically to degrade wet adhesive performance.

Acknowledgments

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