

# Protein Modifiers Generally Provide Limited Improvement in Wood Bond Strength of Soy Flour Adhesives

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## Abstract

Soy flour adhesives using a polyamidoamine-epichlorohydrin (PAE) polymeric coreactant are used increasingly as wood adhesives for interior products. Although these adhesives give good performance, higher bond strength under wet conditions is desirable. Wet strength is important for accelerated tests involving the internal forces generated by the swelling of wood and plasticization of the adhesive with increasing humidity.

Soy proteins are globular due to their hydrophobicity; thus, it was expected that adding modifiers to open the protein structure should improve protein–protein and protein–wood interactions to help withstand both internal and external forces applied to the bond. Because modifiers have been shown to improve the performance of soy protein isolate adhesives, use of these modifiers has been examined as a way to improve soy flour adhesives. Protein-disrupting chaotropic agents (urea, guanidine hydrochloride, and dicyandiamide), surfactants (sodium dodecyl sulfate or cetyltrimethylammonium bromide), and the cosolvent propylene glycol were all expected to provide increased protein–protein and protein–PAE interactions. Improved interactions would make the soy flour adhesives durable enough to better pass wet bond strength tests specified for most interior bonded wood products. However, no substantial improvement was seen in cured wood bond strengths in wet conditions for soy flour adhesives by adding any of these modifiers with or without PAE polymer addition. These results led to a proposal that carbohydrates, about 45 percent by weight of soy flour, are interfering with obtaining greater adhesive bond strengths from the protein portion of the flour.

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Although soy flour was used for making interior plywood in the early to mid-20th century, it was generally replaced by urea-formaldehyde (UF) adhesives because of their improved performance and lower cost. However, because of concerns about formaldehyde emissions from UF-bonded wood, soy flour adhesives are being used more frequently to replace UF adhesives. Soy flour denatured with alkali provides good plywood bonds with dry conditions, but this older technology is not competitive with current UF adhesives for bonds with wet conditions that are part of normal product testing. The discovery that adding polyamidoamine-epichlorohydrin (PAE) polymer to soy protein gives excellent wet strength (Li et al. 2004, Li 2007) has made soy adhesives more competitive with UF adhesives. Although the original work and a mechanistic study used soy protein isolate (SPI) (Li et al. 2004, Zhong et al. 2007), soy flour is much more economically competitive. Performance of the soy flour–PAE adhesives has been reported (Allen et al. 2010; Frihart et al. 2010a, 2010b; Wescott et al. 2010), but only a limited number of studies have been published about the factors influencing the performance of these adhesives (Frihart et al. 2010a, Frihart and Satori 2013). Prior studies have shown that soy flour

with 45 percent protein content provides less than a third of the wet bond strength provided by the SPI with over 90 percent protein content (Frihart 2011).

A key question was whether these soy flour–PAE polymer bonds can be made stronger by adding other chemicals. Soy flour adhesives under very basic conditions have been studied extensively (Lambuth 2003) because these conditions dramatically improve the wood bond strength. However, these conditions are not viable for the PAE polymer because of its rapid self-cross-linking at a basic pH that severely limits pot life and competes with its reaction with the wood and protein.

Because proteins are naturally good adhesives, as shown by the use of a wide variety of protein sources (casein, soy, blood, fish scales, and animal hides) in the early 20th

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century (Lambuth 2003, Frihart 2010), it is naturally assumed that protein in soy flour is the dominant bonding portion of soy flour and that carbohydrates present merely serve as inert diluents. However, the literature on soy flour properties is very scarce compared with the extensive literature on SPI properties. Several studies have shown that modifiers can make SPI or the main soy protein fractions of 7S and 11S into better adhesives (Sun 2005); thus, it made sense for us to evaluate with soy flour adhesives the use of modifiers that are known to alter SPI adhesives. We have used additional methods to modify soy by using the extensive literature about SPIs in food applications (Kinsella et al. 1985, Utsumi et al. 1997) where factors like moisture control and bonding to other food components are also important; these methods include the effect of salts and cosolvent on soy flour adhesives. SPI gives much better bond strength than soy flour (Frihart 2011); thus, we expected that protein modifiers could increase the bond strength of soy flour adhesives close to that observed with SPI adhesives.

To understand the effect of modifiers, it is important to know about protein structure and properties, which are quite different from those of most other polymers. Individual protein chains like those in soy flour fold to minimize their interaction with water because of the high hydrophobic content. These chains first fold in a specific manner based on their primary polymeric sequences into a series of  $\alpha$ -helices and  $\beta$ -sheets forming the secondary structure and then undergo a hydrophobic collapse to create a tertiary structure (Pain 2000). Although the nonpolar groups try to go to the inside of the coiled ball of the protein and the polar groups prefer the outside, the backbone sequence and the secondary structure restrict this polarity separation from being complete. Thus, many polar groups end up inside the ball and are stabilized by forming hydrogen bonds between polar groups and by forming salt bridges between acidic and basic groups. Hydrophobic groups on the outside of the ball minimize energy by interaction with hydrophobic groups on the outside of other protein balls to lead to the quaternary structure, an agglomerate of the individual protein molecules. Thus, soy protein agglomerates are dependent on a balance between attractive hydrophobic domains and repulsive electrostatic forces (Kinsella et al. 1985). The very basic conditions used for traditional soy adhesives cause the protein coils to open up because of increased electrostatic repulsion (Kinsella et al. 1985) making more viscous adhesives, but the increased availability of the functional groups leads to improved adhesive and cohesive bond strengths. The literature indicates that addition of protein-disrupting chaotropic agents, surfactants, and cosolvents change the soy protein properties (Kinsella et al. 1985, Utsumi et al. 1997, Sun 2005).

Given the large number of potentially reactive groups in soy protein (Wescott et al. 2006), we hypothesized that the addition of modifiers should improve the bonding of soy flour adhesives by exposing more of these reactive groups. Chaotropic agents, such as urea, are often used to modify proteins by loosening up the coiled structure. There is continued debate on whether the modifiers function more by making the water media less polar or by plasticizing the protein structure (Canchi et al. 2010). In either case, soy protein should be less tightly coiled for better reaction with other proteins (see Fig. 1) or the PAE polymer. Both urea

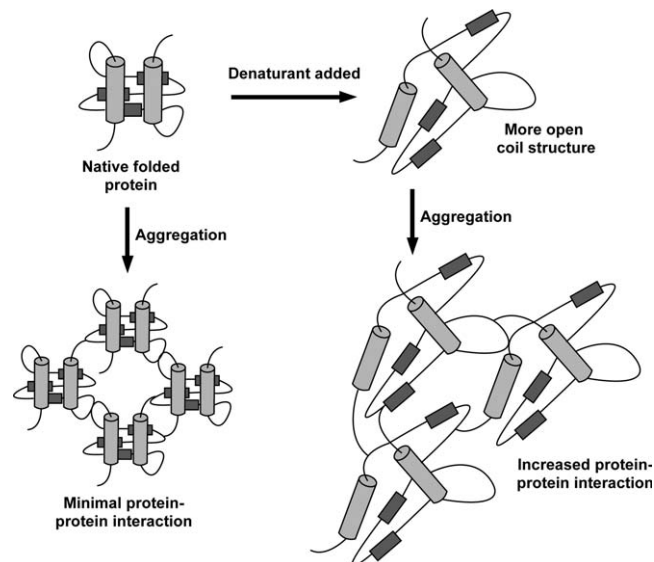


Figure 1.—Protein structures to represent the hypothesis on why chaotropic agents might provide better adhesive strength by opening the coiled structure of proteins for greater intermolecular interactions.

and guanidine hydrochloride have been shown to improve the wet bond strength of soy protein isolate wood bonds (Huang and Sun 2000a).

Protein quaternary agglomerates, especially the 7S fraction of soy, are held together by hydrophobic interactions (Utsumi et al. 1997); thus, it seems reasonable that added surfactants would help separate agglomerates and open the coils to make them more accessible for forming stronger bonds either through formation of polar interactions between protein chains or through reaction with the PAE polymer in the heat curing step. Huang and Sun (2000b) and Wang et al. (2005) observed that added surfactants improved bond strength when SPI was modified with either sodium dodecyl sulfate or cetyltrimethylammonium bromide. In an extension of the surfactant approach, it might be expected that an organic cosolvent would be less polar than water and lead to a more uncoiled structure and greater reaction of the protein functional groups.

Thus, based on studies with SPI and logical analysis of protein structures, we expected the use of these modifiers to increase the exposure of functional groups to improve the bonding strength of soy flour adhesives with wood veneer both with and without added PAE polymer. Testing of these modified soy flour adhesives bonded to maple veneers was simplified by using a small-scale bonding and shear-strength testing apparatus for bonded veneer (Automated Bonding Evaluation System [ABES]) because this method is less sensitive to rheological changes in adhesive formulations (Frihart and Satori 2013) that are expected with the addition of modifiers. In addition, we have found that soaking these bonded lap shear samples in water and then testing their strength gave a good indication of how well the bonded wood would perform in the water soak delamination tests used for interior plywood (Frihart et al. 2009) and was used as the main test of adhesive performance. This test was also shown to correlate well with standard ASTM adhesives tests (Frihart et al. 2009).

## Experimental

The soy flours used were Prolia 200-90 and Prolia 200-20 (Cargill Inc., Cedar Rapids, Iowa). Chemicals used were PAE CA 1920 (Ashland Water Technologies, Wilmington, Delaware), urea, dicyandiamide, sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and 1,2-propanediol (propylene glycol; Sigma-Aldrich, St. Louis, Missouri), guanidine hydrochloride (Acros Organics, Fair Lawn, New Jersey), and lithium perchlorate (Alfa Products, Beverly, Massachusetts).

The soy flour adhesives were prepared by adding soy flour to water so that the final concentration was 20 weight percent soy flour in all cases. Modifiers, when used, were added to the water first with thorough mixing. If a PAE polymer was added, it was done last after mixing the other components and at 5 percent on a dry weight basis to the soy dry weight. Concentrations were balanced by adjusting the amount of water added. The final mixture was thoroughly mixed prior to being used as an adhesive.

ABES Model 311c (Adhesive Evaluations Systems, Inc., Corvallis, Oregon) was used for bonding and testing the shear strength of the samples. 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 a piece of uncoated veneer. The amount of adhesive used was sufficient to generate a slight squeeze-out to ensure that sufficient but not excessive adhesive was used. Using careful alignment, samples were hot pressed in the ABES at 0.2 MPa for 120 seconds at 120°C. The bonded wood samples were removed from the ABES and equilibrated at 22°C and 50 percent relative humidity at least overnight before testing dry or wet after soaking in water for 4 hours at room temperature. For each test, five bonded specimens were used, and the average and one standard deviation error bars were plotted.

## Results and Discussion

Although protein adhesives bond wood well when dry, these bonds are often insufficient under wet conditions. Testing the bond strength after water soaking or after soaking and drying cycles are typical evaluation criteria for most wood bonding applications. Thus, often the most important criterion is the strength of the bond in wet conditions. Although it is not an industrial standard test, we use the ABES equipment for screening because the uniform heating of the bond on smooth, thin, small veneer samples provides a rapid, simple, efficient, and reproducible method for measuring bonds in the dry state or wet after soaking the bonded specimen in water. ABES tests have been shown to have reasonable correlation to standard shear tests using parallel veneers as in ASTM D905 (Frihart et al. 2009, ASTM International 2012), and we have found that this bonding method was less sensitive than standard shear tests to rheological factors that occur when modifying the formulations (unpublished results). Our main objective was to keep the amount of soy flour constant in each mixture and let the total solids and viscosity vary with added modifiers, PAE polymer, or both. Tests were run on both dry and wet (water-soaked) specimens, but the wet data show the greatest effect and are considered to be more important for good ultimate performance. Although higher amounts of PAE polymer are often used in commercial applications, we added only 5 percent PAE coreactant solids based on the

weight of soy flour. The lower amount of coreactant allows a clearer demonstration of increased reaction with the soy. High amounts of PAE coreactant are expected to mask the soy changes because PAE resin is a good wood adhesive by itself. Adhesive spread rate is not specified because we have found that strength is not affected above a minimum spread rate that results in a slight squeeze-out of the adhesive.

Because chaotropic agents modified SPI to increase wood bond strength (Huang and Sun 2000a), probably by opening the protein structure, it seemed logical that they would also be effective with soy flour. Chaotropic agents were added to soy flour adhesives in the following concentrations: urea–soy flour (0.5:1.0 and 1.0:1.0), guanidine hydrochloride–soy flour (0.1:1.0 and 0.5:1.0), and dicyandiamide–soy flour (0.1:1.0). In addition, both salt type and concentration can have an effect on protein structure. Some salts can cause proteins to be more compact, while others cause the structure to swell by altering the electrostatic double layer around the protein coil (Boye et al. 1997). Much research has been done using salts to adjust protein properties, and their influence has been categorized by the Hofmeister series. From this information, we would expect lithium perchlorate to be an effective monovalent salt in swelling the protein structure, and therefore we used lithium perchlorate–soy flour (0.1:1.0) to allow for the greatest reaction of protein with the PAE polymer. These studies were done with Prolia 90, which is a very dispersible soy flour, having a protein dispersibility index (PDI) of 90.

Figure 2 shows the effect of chaotropic agents (urea, guanidine hydrochloride, dicyandiamide, and lithium perchlorate) on dry and wet strength without PAE polymer. With no added PAE polymer, none of the modifiers increased the dry shear strength of the soy flour adhesive. Urea at the highest concentration increased wet shear strength the most of these modifiers but not enough to make an acceptable adhesive (desired value is greater than 2.5 MPa for these ABES samples).

Figure 3 shows the effect of chaotropic agents (urea, guanidine hydrochloride, dicyandiamide, and lithium perchlorate) on dry and wet strength with 5 percent PAE polymer. With 5 percent added PAE polymer, urea (0.5) and lithium perchlorate increased dry strength of the soy flour adhesive. However, none of the modifiers significantly

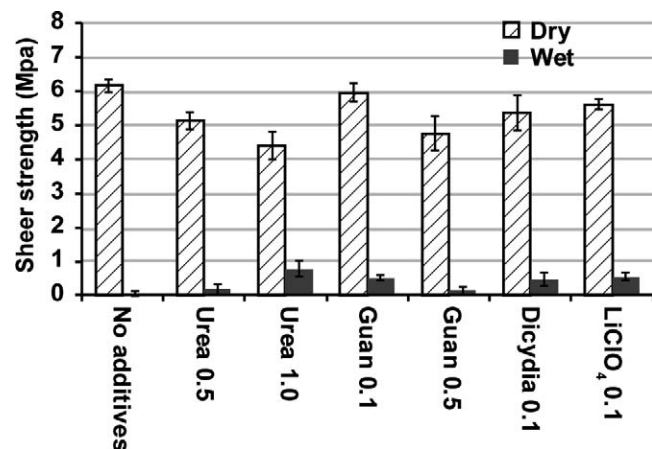


Figure 2—Effect of chaotropic agents (urea, guanidine hydrochloride [guan], dicyandiamide [dicydia], and lithium perchlorate [LiClO<sub>4</sub>]) on dry and wet shear strength of Prolia 200-90 without polyamidoamine-epichlorohydrin polymer.

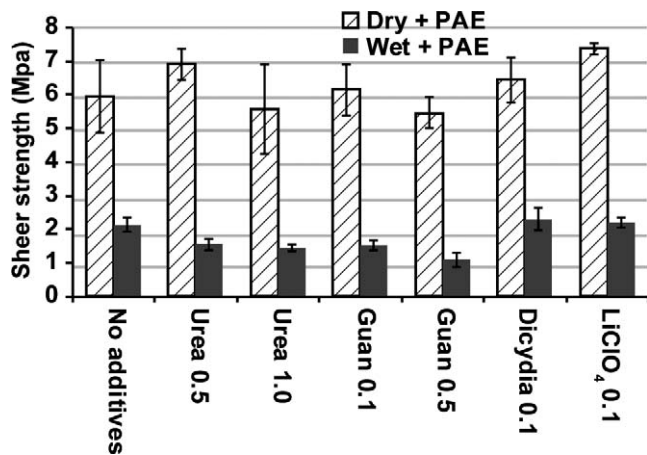


Figure 3.—The effect of chaotropic agents (urea, guanidine hydrochloride [guan], dicyandiamide [dicydia], or lithium perchlorate [LiClO<sub>4</sub>]) on dry and wet shear strength of Prolia 200-90 with 5 percent polyamidoamine-epichlorohydrin (PAE) polymer.

increased wet strength. In other work, a variety of different salts have been examined more extensively, but they have not shown any great change in the performance of soy adhesives (A. Allen, Ashland Water Technologies, personal communication, 2011).

Not having seen any great benefits by adding chaotropic agents or lithium perchlorate salt, the next step was to use surfactants to solubilize hydrophobic regions, using surfactants that had been successfully used to modify SPI (Huang and Sun 2000b, Wang et al. 2005). Figure 4a shows the effect of two surfactants on dry and wet strength of soy adhesives without PAE polymer, while Figure 4b shows the effect of surfactants on dry and wet strength with 5 percent PAE polymer. Addition of the surfactants SDS or CTAB to soy flour adhesives at 1 percent of the dry weight of the soy flour had no significant effect on the dry or wet strength of soy flour adhesive with or without the PAE polymer. Like chaotropic agents, surfactants that have been shown to significantly improve wet bond performance of SPI adhesives seemed to have no significant effect with soy flour with or without the PAE polymer.

Not having success with the addition of modifiers, the next step was adding a cosolvent to help solubilize the hydrophobic regions and not affect solubilization of hydrophilic regions. Propylene glycol (1,2-propanediol) was added as a cosolvent to soy flour adhesives, replacing 50 percent of the water, as it should be more hydrophobic than glycerin, which has been previously examined (Wescott and Birkeland 2008, Brady et al. 2012). It did not have much effect on the dry or wet strength of soy flour adhesives with or without 5 percent PAE polymer, as shown in Figure 5. Previous experiments used only the highly dispersible 90-PDI soy flour. The 20-PDI soy flour has had a more intense heat treatment and is less dispersible than 90-PDI soy flour. It was also tested because it might be more affected by propylene glycol than 90-PDI soy flour. Wet strength of 20-PDI soy flour is slightly higher than 90-PDI soy flour, but it also has a higher viscosity, which can make it harder to spread. The addition of propylene glycol gave improvement in all cases, but the improvements were small. Contrary to the literature on SPIs and the general protein literature, soy flour was not very responsive to the addition

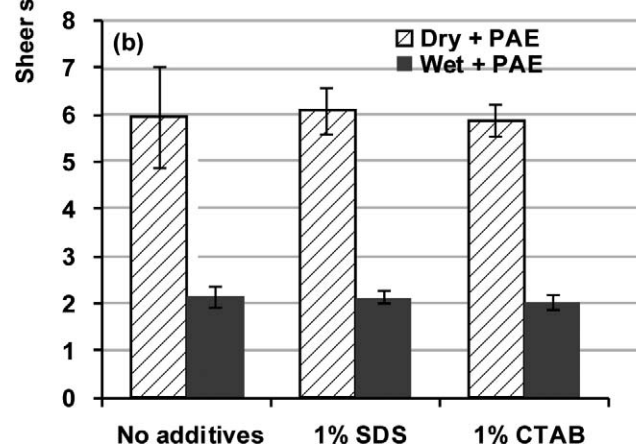
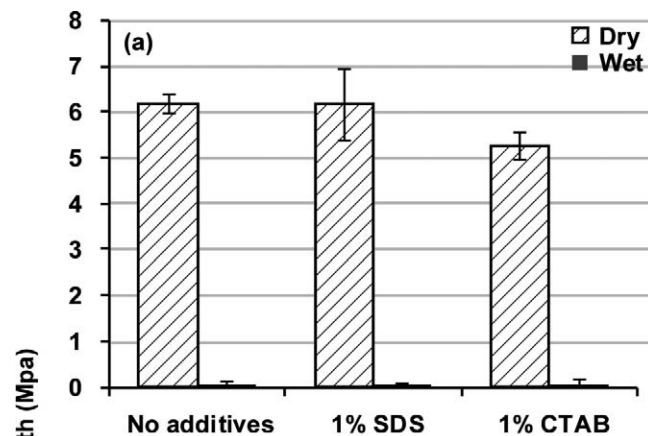


Figure 4.—The effect of surfactants on dry and wet shear strength of Prolia 200-90 without (a) or with (b) 5 percent polyamidoamine-epichlorohydrin (PAE) polymer. SDS = sodium dodecyl sulfate; CTAB = cetyltrimethylammonium bromide.

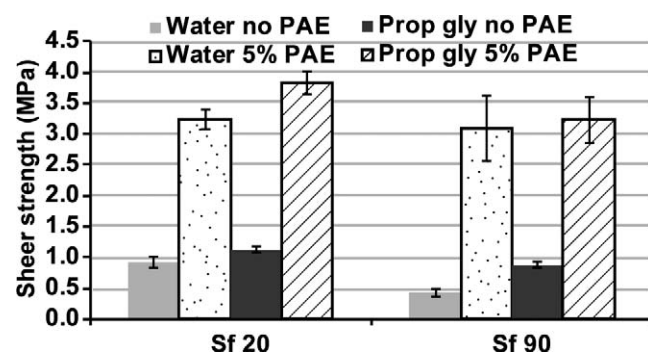


Figure 5.—Effect of propylene glycol cosolvent on dry and wet shear strength of soy flour adhesives without or with 5 percent polyamidoamine-epichlorohydrin (PAE) polymer.

of chaotropic agents, surfactants, or a less polar solvent mixture.

These experiments have led to a carbohydrate interference hypothesis to explain the performance differences between soy flour and SPI. Carbohydrates seem to be not only acting as inactive diluents but also hindering protein modification and protein-protein interactions. If carbohydrates are not removed as much as possible, soy protein is

not be available to react with denaturants or surfactants, could be prevented from achieving optimal protein–protein interactions, or both.

## Conclusions

We investigated if modifiers that improved adhesive performance of SPI were also effective in improving adhesive performance of soy flour. The chaotropic modifiers urea, guanidine hydrochloride, dicyandiamide, and lithium perchlorate and the surfactants SDS and CTAB were added to soy flour adhesives. Chaotropic agents can make proteins more accessible by disrupting hydrogen bonds or making the solvent less polar, as does a salt like lithium perchlorate, while surfactants can open the protein structure by dispersing hydrophobic regions to provide for better protein–protein interaction. However, no significant improvements in wet bond shear strength were seen when any of these modifiers were added to soy flour formulations. Also, adding a less polar solvent, such as propylene glycol, was expected to help open the protein structure for better protein coalescence, wetting of wood, and reaction with the PAE polymer, but no substantial improvement in wet bond strength was seen with the addition of propylene glycol to soy flour adhesives. Because soy flour contains about 45 percent carbohydrate and 45 percent protein compared with about 5 and 95 percent, respectively, for SPI, these experiments have led to a carbohydrate interference hypothesis to explain the performance differences between soy flour and SPI.

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