IMPROVED WATER RESISTANCE OF BIO-BASED ADHESIVES FOR WOOD BONDING

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SUMMARY

Synthetic resins, such as phenol-formaldehyde (PF), are dominant in wood bonding for exterior and semi-exterior applications because of their excellent water resistance. Replacement of petroleum-based resins with ones having high biomass content would further enhance the environmental preferability of reconstituted wood-based materials. Past studies on using soybean flour in these applications have not led to viable adhesives with high biomass content. However, use of proper denaturation, stabilization, and crosslinking reactions leads to high-soybean-content adhesives that can replace PF as the face resin for strandboard. In the first step, the soybean flour is treated with hot caustic to denature the protein but with limited hydrolysis that can produce small peptide fragments. Once the denaturation has opened the protein structure, the exposed functional groups can be reacted with formaldehyde to produce a stabilized protein. This material can then be reacted with phenol and formaldehyde to produce a strong wood-bonding adhesive. The adhesive has been used to produce strandboard having strength and water-resistance values equal to those obtained using a commercial phenol-formaldehyde adhesive. The soybean-PF adhesive is 40% to 66% by weight soybean flour, thus reducing dramatically the use of petroleum-based phenol and formaldehyde.

INTRODUCTION

Proteins from various sources have been used as wood adhesives for a long time (KEIMEL 2003, LAMBUTH 2003). However, because of both performance and cost issues, synthetic adhesives have largely displaced protein adhesives. Interest in using biomass-derived adhesives has been strong for both environmental and cost considerations (KUMER et al. 2002). The cost of petroleum products has risen faster than many biomass sources, including some agricultural products. A particularly desirable source is soybean flour, the ground form of the meal, which is the residue after the more valuable oil has been removed from the soybean. Prior studies have used both flour and the more expensive protein isolates. The flour was commonly used in the early 1900s for bonding plywood by treating the flour with aqueous caustic prior to application. Although this adhesive led to the development of the plywood industry, it was displaced by easier to use, more durable, and lower cost synthetic adhesives. Recently, cost has become more favorable for soybean flour, which has been mainly used for animal feed. The water-resistance limitation and stability issues of soybean adhesives have not previously been solved for formulations high in flour content.

In addition to the durability issue, protein dissolved in caustic leads to high-viscosity solutions. For ease of application to wood, the adhesive viscosity must be lowered either
by using low solids content or by hydrolysis of the protein. The original protein adhesives used low solids content. More recent studies have concentrated on hydrolysis of the protein to create smaller fragments. The two main methods are chemical hydrolysis using hot caustic (KREIBICH et al. 1998, VIJAYENDRAN and CLAY 2001, HSE et al. 2001, KARCHER 1997, STEELE et al. 1998) and enzymatic treatment (KALAPATHY et al. 1995). Creating small fragments requires more polymerization reactions to form a strong adhesive product, and obtaining a sufficient number of reactions can be difficult because many of the fragments may not have sufficient reactive sites for forming the backbone polymer and providing crosslinking sites. The standard polymerization reactants with soybean proteins are phenol, formaldehyde, and caustic. The formaldehyde links the amino groups on the protein, and the phenol induces condensation reactions to form a polymer. The completeness of these reactions can be problematic because amines do not react well under the basic conditions employed in these formulations (PIZZI 2003). In addition, the formaldehyde reaction with some amino acids yields cyclic structures (SKRZYDLEWSKA 1994), preventing the amino acid from being incorporated into the polymer backbone. These problems have led generally to low levels of soybean proteins being used in formulations of soy and phenol-formaldehyde (PF).

If the caustic treatment is less severe, the protein can be denatured without significant hydrolysis. These larger proteins lead to a more viscous product, but they should be more polymerizable. Once denatured, the proteins need to be stabilized for storage but activated towards further polymerization. Formaldehyde has been used to crosslink proteins, but these reactions are considered reversible (BJORKSTEN 1951).

MATERIALS AND METHODS

Soybean Flour Reactions

The soybean flour used in these processes was extruded with 11% oil, 44% protein content, with 90% of the material passing through a 100-mesh screen.

Soy-F: After heating a solution of 10.1 g of sodium hydroxide in 255.3 g of water and 1.9 g of ethylene glycol to 70°C, 126 g of soybean flour was added over about 20 min with rapid mixing. Then the temperature was raised to 90°C and held for 1 h. To the rapidly stirring solution, at 90°C 48.2 g of 37% formaldehyde (Aldrich, methanol stabilized) were added dropwise over 5 min. The mixture was maintained at 90°C for an additional 55 min, followed by cooling to 30°C and filtering through a course screen (about 700 µm).

PF-L (laboratory-made PF solution): 94.5 g of water was combined with 23.3 g of sodium hydroxide and 274.4 g of solid phenol, and the mixture was heated to 70°C. Then 492.2 g of 37% formaldehyde was added dropwise over 60 min while maintaining the mixture at a temperature of 68°C to 72°C. The resulting clear homogeneous solution was held at 70°C for 1 h after the formaldehyde addition was completed. The temperature was then raised to 85°C and held until a Gardner-Holdt kinematic bubble viscosity of “T” was obtained (a total of 140 min), which is equivalent to a viscosity of
about 550 mPa·s. The mixture was then cooled to 40°C in a cold-water bath over 10 to 15 min. The solution was filtered through a coarse screen.

Soy-PF-A: After heating a solution of 12.0 g of sodium hydroxide in 285.9 g of water and 2.25 g of ethylene glycol to 70°C 150 g of soybean flour was added over about 20 min with rapid mixing. Then the temperature was raised to 90°C and held for 1 h. To the rapidly stirring solution, at 90°C, 48.9 g of 37% formaldehyde was added dropwise over 5 min. The mixture was maintained at 90°C for an additional 55 min. The heat source was removed from the reactor, and 44.1 g of solid phenol was then added over a period of 10 min. The addition of the cold phenol helped to cool the batch temperature to 75°C. Once a temperature of 75°C was obtained, 3.75 g of sodium hydroxide was added. After 15 min, an additional 80.4 g of 37% formaldehyde was added dropwise over 15 min, while maintaining 75°C. As soon as the formaldehyde addition was complete, 1.9 g of sodium hydroxide was added, followed 15 min later by another 1.9 g of sodium hydroxide. The entire solution was allowed to stir for an additional 90 min at 75°C. Then the mixture was cooled to 30°C and filtered through a course screen.

Soy-PF-B: A blend comprised of 65.7 parts of Soy-PF-A and 34.3 parts of PF-L was prepared in a jar with rapid shaking to assure a homogenous mixture.

Measurement of Adhesive Properties

Non-volatile solids were determined using a modified ASTM D 4426 01 method (ASTM INTERNATIONAL 2001) in that the samples were heated at 150°C for 1 h instead of 125°C for 1.75 h. Room-temperature viscosity was measured with a Brookfield LVT viscometer using a #3 spindle at 60 and 30 rpm. Gel times were measured using a Sunshine gel meter at 100°C. Extract was measured as the amount extracted from an oven-cured solids sample after 24-h Sohxlet water extraction. Free phenol was determined from high-pressure liquid chromatography (HPLC) using an Intersil ODS-3 column and an acetonitrile in water (0.05N phosphoric acid) eluting gradient from 10% to 80% solution, with 3-hydroxymethylphenol as the internal standard. The free formaldehyde was determined using a modified hydroxylamine hydrochloride back titration method (WALKER 1975). Stability was determined by measuring the viscosity with time for ambient temperature storage.

Process for Producing Random Strandboards

The adhesive was applied to wood flakes (70 by 15 by 0.8 mm, 95% southern yellow pine and blackgum, with the remainder a mixture of other species) using air atomization at 3.3% with 1.3% of a wax emulsion; these were formed into the face portion of mats. The core flakes were prepared in a similar manner using 3.9% of a PF core resin and 1.4% of a wax emulsion. These mats (55% face and 45% core) were pressed for 150 to 210 s using platens at 200°C with stainless steel caul plates. The boards were trimmed to measure density and then cut into the appropriate specimens for strength testing.
Testing of Strandboards

Testing of the strandboards was done following the guidelines in ASTM D 1037-99. In addition to the 24-h water swell, the samples were also subjected to a 2-h water boil, using the same specimen size.

RESULTS AND DISCUSSION

Past studies on soybean protein adhesives have involved either soybean flour denatured in aqueous caustic, or flour or protein isolate hydrolyzed to peptides that are then reacted with phenol and formaldehyde. The denatured protein solution has a high viscosity because of the high molecular weight of the protein fractions; therefore, it has been used at low solids content so that the adhesive can be easily applied to the substrate. The viscosity of the protein solution can be lowered by hydrolysis, but this also leads to lower final bond strengths. Thus, hydrolyzed protein normally needs to be reacted with high levels of phenolics and formaldehyde to form a strong crosslinked network from these small peptide fragments. The issue is whether the soybean protein could be denatured at higher solids to form a stable solution of reasonable viscosity. (This reaction product is referred to as a solution in this paper because when protein isolates are used solutions are produced. However, the flour does not form a complete solution due to non-proteinaceous insolubles in the flour. Thus, the main adhesive component is a solution, with the suspended solids not being essential to the process.)

Departing from the complicated normal process of solubilizing the soybean flour (LAMBUTH 2003), we found that soybean flour can be readily dispersed in a hot aqueous caustic solution (WESCOTT and FRIHART 2004). This process reduces clumping and foaming issues relative to the conventional process and can operate at higher solids contents. The foaming can be reduced further by the use of silicone antifoams. The soybean flour is added at 70°C to a sodium hydroxide solution, and after the flour is well dispersed, the temperature is raised to 90°C to complete the denaturation process.

Normally, aqueous solutions of proteins do not have good stability over time because of continued hydrolysis (LAMBUTH 2003). Moreover, addition of PF to a denatured protein solution that has not been stabilized will lead to rapid increases in viscosity, thus providing poor stability. The addition of formaldehyde stabilizes these denatured protein solutions for good storage stability. The formaldehyde serves four functions:

• Modifies the functional groups on the protein so that the protein does not reform intermolecular associations
• Stabilizes the soybean flour dispersion towards biological degradation
• Activates the protein against further reaction with the phenol
• Allows for stable blends with PF resins

The formaldehyde level is set by the amount that readily reacts with the protein; excess formaldehyde is avoided, because the product should have a low free formaldehyde level prior to any subsequent copolymerizations. To minimize the free formaldehyde in
the modified protein, a titration method involving hydroxylamine hydrochloride was used. Free formaldehyde in any product is undesirable for health reasons. The soybean flour used in these experiments readily reacted with approximately 0.4 mol of formaldehyde per 100 g of flour. Under the 75°C to 90°C reaction conditions, it is expected that the formaldehyde reacts rapidly with chain-terminating amine groups, amine groups in lysine, histidine, arginine, and tryptophan, phenol group in tyrosine, and thiol group in cysteine, as illustrated for lysine:

![Chemical Reaction Diagram]

The formaldehyde-stabilized soybean product can be an article of commerce in contrast to the unstabilized soybean proteins. This soybean protein solution can be mixed with commercial PF resins at a customer's plant.

The stabilized soybean solution was then reacted with phenol and formaldehyde to form modified soybean protein that can be reacted with a PF resin. This type of PF-activated protein is illustrated in this reaction:

![Chemical Reaction Diagram]

This product is indicated in Table 1 as Soy-PF-A. This can also be an item of commerce to be reacted with other PF resins. The stability of Soy-PF-A is illustrated in Figure 1. This product offers excellent stability compared with a commercial PF resin (PF-C).

To study the reaction of the stabilized protein solution with phenol and formaldehyde (like Soy-PF-A), a method needed to be developed to screen for the optimum conditions. Using the adhesive to make strandboard and testing its strength does not provide a full understanding of the curing process. Because the adhesive must ultimately become water resistant, its insolubility in water after curing has been found to be a good screening method. Thus, neat curing of the adhesive in an oven, followed by Sohxlet extraction with water, was found to be an important aid in the optimization process. The data in Table 1 show that just formaldehyde-modified denatured soybean flour is still very water soluble, and thus extractable, after oven drying at 150°C, suggesting that minimal irreversible copolymerization is occurring without the presence of any phenol. The formaldehyde-modified soybean flour is 90% extractable upon heat curing, as shown in Table 1. On the other hand, when the protein has the proper level of phenol and formaldehyde to crosslink the protein, the amount of extractables is less than 20% for the 40% soybean resin. In evaluating the extraction data, it is important to...
remember that the flour is not all protein. Some of the other components are water
insoluble and are not extracted. Some soluble components include carbohydrates and
other non-proteinaceous material; not all of these will react to form insoluble polymers.
Thus, along with the caustic, these components constitute the water-soluble material left
in the cured resin. The extraction method is useful for illustrating the problem with
hydrolysis versus denaturation of the soybean flour. The higher temperature of
hydrolysis leads to smaller peptide fragments that are not as effectively incorporated in
the cured adhesive, as illustrated by the higher level of extractives. This method was
useful in developing the optimum formulations for demonstrating that the soybean
protein is incorporated into the main adhesive network.

In general, the higher viscosity of the soybean flour solutions compared with standard
strandboard PF resins is not as serious of an issue as the data may indicate. The standard
method of measuring viscosity using a Brookfield viscometer is a low shear process;
however, these solutions exhibited shear thinning. The low shear viscosity must be low
enough that the non-agitated solution is pumpable. The shear thinning allows a solution
with higher apparent viscosity to be thin enough to be easily applied under high shear
conditions. The Brookfield viscosity in Figure 1 shows that the Soy PF-B is no more
unstable in viscosity over time than are the PF resins. The fact that the PF component of
the Soy-PF-B (PF-L) is much more unstable than the commercial PF resin (PF-C)
suggests that similar blends using a more stable PF resin would result in a very stable
Soy-PF-B type product.

The next step involves using the adhesives to make bonded wood products that are
commercially acceptable. These studies have involved making non-oriented (random)
strandboards (RSB) and comparing their performance in the face portion with a
commercial PF face resin; commercial PF core resin was used in all cases for the core
portion of the strandboard. The coated flakes (mainly southern yellow pine and
blackgum) were formed into mats that were then pressed into boards. Specimens from
these boards were tested for internal bond strength (IB) and thickness swell using a 24-h
soak or a 2-h boil method. The data in Table 2 show that the 40% soybean flour
adhesive Soy-PF-B has thickness swell and internal bond properties very similar to
those of the commercial PF resin at the same press times. Soy-PF-A (66% soybean) also
produced boards of equal performance but required longer press times. The PF resin
made for this study was not as good as the commercial PF resin in bond strength; the
data in Table 3 illustrate this difference (data in Tables 2 and 3 used a different batch of
chips and so were not combined).

These soy–PF adhesives can allow for a large reduction in the amount of petroleum-
based chemicals used in wood bonding. A product of equal performance and press time
to a commercial PF gave a reduction of up to 50% in phenol and 28% in formaldehyde
(Table 4). The exact savings is difficult to calculate because other chemicals are added
to commercial PF formulations at different levels, depending upon the specific
application. Because 1.5 billion kilograms of PF resin are used in wood bonding each
year (JOHNSON 2001) this research provides a route to replace significant amounts of
petroleum-based phenol with biomass.
CONCLUSIONS

Biomass protein has always provided good adhesion to wood, which led to their use in this application prior to the development of synthetic adhesives. However, except for blood proteins, they have not provided significantly water-resistant bonds. Although some proteins continue to be used in specialty applications, significant improvement in the water resistance of the proteins is necessary for their use in wood bonding to be increased.

The abundant and inexpensive soybean flour has been used as a minor component in wood adhesives and examined at greater proportions in PF adhesives. However, until this study, soybean flour formulations with water resistance equal to or greater than that of commercial phenol-formaldehyde have not been developed. By controlling the denaturation step to minimize hydrolysis, larger proteins are obtained that have sufficient exposed functional groups for reacting with formaldehyde. Formaldehyde stabilizes the protein against further hydrolysis and also activates it for reaction with PF resins. Soybean flour adhesives have been produced that give good performance at adhesive levels and press times comparable to those of commercial PF resins. A Soy-PF-B adhesive of 40% soybean was equal in performance to the PF when used under the same pressing conditions; higher percentages of soybean, as in Soy-PF-A, can be used if longer press times are utilized.

Except for blood proteins, protein adhesives have not been considered durable enough to pass water-resistance tests at high protein levels. This work has shown that through the development of the proper technology, it is possible to make soybean flour adhesives that pass the accelerated water resistance tests for strandboard products.

Figure 1: Viscosity stability of adhesives with respect to time for ambient storage
Table 1: Properties of resins from soybean flour and phenol-formaldehyde

<table>
<thead>
<tr>
<th>Example</th>
<th>Soy content (%)</th>
<th>pH</th>
<th>Solids (%)</th>
<th>Viscosity (mPa·s) at 60/30 rpm</th>
<th>Extract (%)</th>
<th>Free phenol (%</th>
<th>Free formaldehyde (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial phenol-formaldehyde</td>
<td>0</td>
<td>11.00</td>
<td>53.8</td>
<td>184/184</td>
<td>24.6</td>
<td>29.1</td>
<td>0.23</td>
</tr>
<tr>
<td>(Phenol-formaldehyde, no protein)</td>
<td>0</td>
<td>10.30</td>
<td>44.9</td>
<td>760/760</td>
<td>23.0</td>
<td>2.8</td>
<td>0.52</td>
</tr>
<tr>
<td>Soy-F</td>
<td>86</td>
<td>10.30</td>
<td>325</td>
<td>None</td>
<td>90</td>
<td>NA</td>
<td>—</td>
</tr>
<tr>
<td>Soy-PF-A</td>
<td>66</td>
<td>10.32</td>
<td>36.3</td>
<td>1080/11372</td>
<td>58.9</td>
<td>31.4</td>
<td>0.17</td>
</tr>
<tr>
<td>Soy-PF-B</td>
<td>40</td>
<td>10.18</td>
<td>39.1</td>
<td>1150/1256</td>
<td>28.3</td>
<td>16.6</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2: Properties of strandboards made from soybean flour and phenol-formaldehyde resins

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Face resin</th>
<th>Soy content (%)</th>
<th>Press soak time (s)</th>
<th>Density (g/cm²)</th>
<th>Thickness swell (%)</th>
<th>Internal bond (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2-h boil at 100°C (one SD)</td>
<td>24-h room temperature (one SD)</td>
</tr>
<tr>
<td>1</td>
<td>Commercial phenol-formaldehyde</td>
<td>0</td>
<td>150</td>
<td>0.644</td>
<td>56.6 (9.3)</td>
<td>33.5 (4.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>210</td>
<td>0.649</td>
<td>53.7 (8.1)</td>
<td>31.0 (2.9)</td>
<td>652 (184)</td>
</tr>
<tr>
<td>2</td>
<td>Soy-PF-A</td>
<td>66</td>
<td>210</td>
<td>0.655</td>
<td>71.5 (10.7)</td>
<td>38.9 (3.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>330</td>
<td>0.654</td>
<td>58.4 (11.5)</td>
<td>36.3 (2.8)</td>
<td>490 (79)</td>
</tr>
<tr>
<td>3</td>
<td>Soy-PF-B</td>
<td>40</td>
<td>150</td>
<td>0.649</td>
<td>62.0 (4.8)</td>
<td>34.1 (3.7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>210</td>
<td>0.665</td>
<td>55.0 (8.0)</td>
<td>36.7 (3.3)</td>
<td>691 (111)</td>
</tr>
</tbody>
</table>

SD, standard deviation
Table 3: Properties of strandboards made from soybean flour and phenol-formaldehyde resins

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Face Resin</th>
<th>Press soak (s)</th>
<th>Density (g/cm³)</th>
<th>2-h boil 24-h room (one SD)</th>
<th>Internal bond (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Commercial phenol-formaldehyde</td>
<td>210</td>
<td>0.671</td>
<td>54.2 (2.5) 41.9 (1.9)</td>
<td>600 (99) 106 (10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>330</td>
<td>0.666</td>
<td>48.3 (18) 37.3 (1.2)</td>
<td>605 (105) 97 (37)</td>
</tr>
<tr>
<td>2</td>
<td>Phenol-formaldehyde, no protein</td>
<td>210</td>
<td>0.676</td>
<td>60.2 (1.8) 42.7 (3.3)</td>
<td>636 (123) 99 (14)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>330</td>
<td>0.658</td>
<td>54.2 (3.0) 39.4 (1.4)</td>
<td>710 (66) 106 (17)</td>
</tr>
</tbody>
</table>

Table 4: Cost savings associated with the reduction of phenol in soybean–PF Resins

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Soy/phenol</th>
<th>Phenol $</th>
<th>Soy $</th>
<th>Total $</th>
<th>Savings (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF Control</td>
<td>0.0</td>
<td>0.370</td>
<td>0.000</td>
<td>0.370</td>
<td></td>
</tr>
<tr>
<td>Soy-PF-B</td>
<td>1.0</td>
<td>0.185</td>
<td>0.045</td>
<td>0.230</td>
<td>37.8</td>
</tr>
<tr>
<td>Soy-PF-A</td>
<td>3.4</td>
<td>0.081</td>
<td>0.070</td>
<td>0.151</td>
<td>58.5</td>
</tr>
</tbody>
</table>

Cost calculations based on $0.82/kg for phenol, and $0.20/kg for soybean flour (solids)

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