Thermal and chemical treatments to improve adhesive property of rice bran

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Abstract

The development of effective biobased adhesives would benefit the particleboard manufacturing industry through reduced product costs, environmental concerns, and petroleum dependency. While most synthetic adhesives currently used are petroleum-based derivatives, desirable biobased adhesives could be developed from renewable agricultural resources. Commercial rice bran has starch and protein for making adhesive used in the production of particleboards. The objective of this study was to improve the adhesive properties of defatted rice bran by thermal and chemical treatments. Three temperature levels (80, 100, and 120 °C) and pHs (8, 10, and 12) were tested. Furthermore, the influence of sodium sulfite and sodium bisulfite on adhesive properties was also investigated. Adhesive performance was evaluated based on the maximum force required for shearing the adhesive bond between soft maple wood pieces. Modifying rice bran with heat and alkali improved adhesive strength over the unmodified bran counterpart. Adhesive strength increased from 44 N for the untreated control to 181 N for the sample treated at 100 °C and pH 12. The improved biobased adhesive can be eventually used for the production of composite panels, such as plywood, particleboards, and fiberboards.

Keywords: Rice bran; Biobased adhesive; Rice straw; Particleboard; Sulfites; Wood

1. Introduction

Rice bran, a byproduct of the rice milling industry, is obtained by the abrasive milling of brown rice to remove the outer tissues to produce polished rice (Juliano and Bechtel, 1985). The total US rice production for 2002 was projected at a record 9.6 Mt (USDA, 2002), which represents a potential to produce almost 1 Mt of this low-value byproduct. The rice bran has been mostly utilized as an animal feed ingredient, fertilizer and fuel (Juliano, 1985b; Bera, 1992; Shi et al., 1999). Although rice bran could be used as a food ingredient for human consumption, it must undergo processing before it can be used for such application. The pro-
cessing cost could make its products hard to compete with food ingredients from other sources. Thus, it is desirable to find applications that increase the value of this important byproduct.

A typical proximate composition of defatted rice bran in the United States is 15–20% protein, 0.5–1.5% fat, 10–15% crude fiber, and 9–12% ash. Rice bran also contains a significant amount of starch, which can vary from 10 to 20%, depending on the amount of rice breakage and degree of milling (Hargrove, 1994). The adhesive properties of protein and starch have long been recognized. Rice bran could be developed into adhesive with industrial applications that could increase its economic value. Because thermal and chemical modifications have been used to obtain adhesives from starch and protein, rice bran could be similarly modified to improve its binding capability. The product could potentially be used as a biobased adhesive in composite materials such as particleboard and fiberboard.

The adhesive strength of proteins depends on their ability to disperse in water and on the interactions of non-polar and polar groups of the proteins with the substrate. For native proteins, the majority of these groups are unavailable due to internal bonds. A chemical change is required to break these bonds and uncoil or “disperse” protein molecules. This change is enhanced by hydrolysis or by increasing the pH, which can be accomplished by exposure to heat, acid/alkali, organic solvents, detergents, and urea (Lambuth, 1977; Hettiarachchy et al., 1995). Zhong et al. (2002) used guanidine hydrochloride to denature soy proteins and obtained an adhesive suitable for fiberboard. Similarly, Mo et al. (2001) modified soy protein with sodium hydroxide, urea, and dodecylbenzene sulfonic acid for particleboard bonding. Kreibich (2001) hydrolyzed commercial soybean protein fractions with acid and alkaline catalysts to provide a mixture of oligomeric polypeptides and amino acids with viscosity and reactivity properties suitable for incorporation into phenolic wood adhesives.

Sulfites may also contribute to protein unfolding, and therefore, to adhesion by cleaving inter- and intra-disulfide bonds exposing molecules that can contribute to the binding capabilities of the protein. In the sodium sulfite treatment of soy protein isolates, Kalapathy et al. (1996) obtained an adhesive with satisfactory strength and viscosity at low sulfite addition. Protein solubility is also important property for obtaining homogeneous and satisfactory adhesive. Proteins from natural sources can be solubilized by a wide variety of methods, which include pH manipulation and hydrolysis. Increasing the pH of rice bran slurry with alkali has been usual approach used to solubilize rice bran proteins (Chen and Houston, 1970; Connor et al., 1976; Gnanasambandam and Hettiarachchy, 1995). Similarly, Champagne et al. (1985) were able to solubilize almost 60% of rice bran protein by adjusting the pH above 8. More recently, enzymes have been used to hydrolyze proteins to improve their solubility.

For starch, gelatinization is needed to develop its adhesive property. Ungelatinized starch is not able to adhere to any substrate because the molecules within the ungelatinized granules are tightly bonded to one another (Kennedy, 1989). In order for starch molecules to become detached from each other, they must be hydrated, a process accomplished in a water slurry by using either thermal or chemical energy. By using this procedure, the molecules can be separated and sufficiently uncoiled so they can latch onto other particles and exert adhesive properties. Gelatinization of starch can also be accomplished by alkali hydration. Gelatinization occurs when the absorbed alkali in starch exceeds a certain critical level, which depends on the species of starch and the type of alkali (Leach et al., 1961).

The objectives of this investigation were to (a) make rice bran adhesive by controlling pH, temperature, and sulfite conditions and (b) evaluate the adhesive properties by determining the yield, viscosity, and strength of the rice bran-based adhesive.

2. Materials and methods
2.1. Materials
Defatted rice bran was obtained from RITO, Inc. (Stuttgart, AR). It contained about 3.8% fat, 16.6% protein, and 11.3% ash based on manufacturer’s specifications. Wood pieces (soft maple with dimensions 5 cm × 2 cm × 0.3 cm) were purchased from White River Hardwoods, Woodworks, Inc. (Fayetteville, AR). Wood pieces were conditioned to constant moisture content at about 11% (wb) in a Fisherbrand® Desic-
2.2. Rice bran modification

Rice bran (RB) with 11% moisture (wb) for all treatments was milled in a Stein Laboratory Mill (Model M2, The Sterlitzie Co., Atchison, KS) for 3 min and stored at 5°C prior to the thermal and chemical treatments. Milling produced 45% rice bran that passed through a US #100 mesh compared with only 10% for the original bran. A 20% milled rice bran solution was prepared in a beaker with deionized water. The pHs of the resulting slurry were adjusted to 8, 10 and 12 with 1 M NaOH solution. The slurry was then heated in a water bath shaker (Model R76, New Brunswick Scientific Co., Inc., Edison, NJ) to 80°C or in a sterilizer (Model SR-24C, Consolidated Stills and Sterilizers, Boston, MA) to 100 or 120°C. To determine the effect of sulfites on the adhesive properties of RB, 0.5 and 1 M sodium sulfite or sodium bisulfite was added into the 20% RB solution. The slurry was further adjusted to pH 12 by adding 1 M NaOH solution and then heated to 100°C as described previously. All treated slurries were oven-dried at 75°C for at least 24 h to moisture content of approximately 10% (wb). The control was not subjected to pH or temperature treatments, but was prepared similarly to the treated samples (i.e. it was made by preparing a 20% RB solution, was oven-dried, milled and sieved).

2.3. Measurement of adhesive yield, strength, and viscosity

The dried RB was milled for 3 min and sieved through a US #100 mesh screen. The sieved portion containing particles smaller than the 0.15 mm nominal sieve opening was further referred to as the rice bran adhesive (RBA). RBA yield was determined with the following equation:

\[
\text{yield} = \frac{A_t - A_r}{A_t} \times 100\% 
\]

where \(A_t\) is the total amount of oven-dried RB, and \(A_r\) is the amount retained by the 100 mesh sieve. Yield, as calculated, is not only a relative measure of the amount of RBA obtained per amount of RB, but also a measure of the hardness of the oven-dried rice bran product. The harder the product, the less likely it will break enough during milling to pass through the sieve openings. Therefore, a harder and more cohesive dried product will result in a lower RBA yield.

A dispersion containing 10% RBA solid was prepared and stirred for 1 h to attain proper hydration before the sample was used for viscosity, pH and strength measurements. The pH and viscosity of the prepared adhesive were determined using a pH meter (Accumet® AR 20, Fisher Scientific) and Brookfield viscometer (Model RVT 200, Brookfield Engineering Laboratories, Inc., Stoughton, MA) with a #3 spindle. Viscosity was measured at 100 and 200 rpm immediately after vigorous stirring.

The strength of RBA was determined according to the method proposed by Kalapathy et al. (1995). About 0.1 g of the prepared RBA was placed on each side of a wood piece (5 cm × 2 cm × 0.3 cm) and spread on the marked areas (2 cm × 2 cm) (Fig. 1). Two other wood pieces were superimposed on the glued portions and pressed with a load of 5 kg for 2 h. The load was then removed and the glued wood pieces were allowed to dry for 24 h in a desiccating cabinet at the same temperature and relative humidity conditions noted previously. The force in Newtons (N) required to shear the adhesive bond between wood pieces was measured using an Instron testing machine (Model 1122, Instron Corporation, Canton, MA) with a crosshead speed of 0.5 mm/min. This measured force was defined as adhesive strength.

![Fig. 1. Plywood assembly for shear strength testing.](image-url)
2.4. Experiment design and data analysis

A three level split-plot design was used to determine whether the effects of temperature (main factor) and pH (sub-factor) on the properties of RBA were statistically significant both individually and through their interaction. The test with each chemical and thermal treatment was repeated three times. The results of adhesive strength measurements were averages of five repeated observations for each treatment. Statistical analyses, including ANOVA and Tukey’s Studentized Range Tests (at 95% confidence level), were performed by SAS software (SAS Institute, Raleigh, NC). The reported results of the effect of sulfites on the properties of RBA also corresponded to the average of five observations.

3. Results and discussion

3.1. Adhesive yield

In general, RBA yield decreased with the increase of treatment temperature and pH (Fig. 2). Yield decreased from approximately 60% for the control to 35% for the sample treated at pH 12 and temperature 120 °C.

Low adhesive yield that was obtained for the harder and more cohesive samples may indicate high binding capability. As treatment temperature and alkalinity increased from 80 °C and pH 8 to 120 °C and pH 12, improved adhesive cohesion was evident during oven-drying. While the dried samples treated at 80 °C and pH 8 appeared more brittle inside the drying tray and showed many cracks on the surface, the dried samples treated at 120 °C and pH 12 were much harder and had smoother surfaces than the other treatment combination. However, the samples treated at the higher temperature and pH formed a compact layer or crust at the surface that obstructed water evaporation from the inside during drying. In many cases, this resulted in an oven-dried product with an uneven moisture distribution where moistened particles at the center of the sample tended to attach to one another and further reducing the yield. Increasing the pH may result in increased protein unfolding that may also contribute to improve RBA cohesion by exposing potentially binding molecules previously buried inside the coiled protein.

The RBA yield results showed that the pH 8 treatment was similar to the pH 10 or 12 treatments, but the pH 10 and pH 12 treatments were significantly different from each other. In contrast to pH alone, temperature and pH–temperature interactions had no statistically significant effect on RBA yield. Although, the results showed that temperature was not significant, it appears from the means and standard deviation bars at pH 8 (Fig. 2) that the yield decreased as the temperature increased. This would imply that better adhesive capabilities were obtained as the temperature increased from 80 to 120 °C.

3.2. Adhesive viscosity

Viscosity is an important physical property of adhesives. In general, low viscosity is desired to facilitate handling and applying adhesives. The effect of pH and temperature treatments on the viscosity of RBA measured at 100 and 200 rpm is shown in Fig. 3a and b. The control had higher viscosity than the RBA treated with heat and alkali. Viscosity measured at 100 rpm increased from 0.014 Pa s for the control to 0.043 Pa s for the sample treated at pH 12 and 120 °C. Similarly, viscosity at 200 rpm increased from 0.019 to 0.054 Pa s.

The increased viscosity of treated RBA compared with the control is likely a result of the combined effects of starch gelatinization and protein denaturation due to pH and temperature treatments.

The pH, temperature, and pH–temperature interactions had significant effects on RBA viscosity at both 100 and 200 rpm. Viscosity was similar for all samples treated at pH 8 and 10. However, viscosity significantly increased at pH 12 when treatment temperatures were
increased from 80 to 120 °C. The increase in viscosity at low pH values compared with the control sample may be largely due to starch gelatinization. However, at the high pH values, the increase in viscosity may be due to protein unfolding in accordance with Angleimer and Montgomery (1976) who stated that an increase in intrinsic viscosity is one of the effects of protein denaturation. Despite the increase in viscosity of pH and temperature treated samples over the control, the viscosity remained acceptably low considering, for example, the viscosity of the currently used synthetic rice straw particleboard adhesive, polymeric methylene diphenyl diisocyanate, which is 0.2 Pa s at 25 °C.

3.3. Adhesive pH

The pH value of an adhesive is an important factor for determining whether the adhesive is suitable to be used in multicomponent systems, such as particleboard, where pH may play an important role in defining the stability and characteristics of the final product. The RBA pH was measured to examine how this value compared with the pH of the RB solution prior to heat and other modification treatments. Although it is obvious that RB adjusted to higher pH will result in a RBA with a higher pH compared with that adjusted to lower pH, it is important to determine how treatment and adhesive preparation affect the pH of RBA.

The pH to which RB was adjusted prior to drying was slightly higher than the pH of RBA (Fig. 4a). This is probably due to the higher overall NaOH concentration of the undried solution than dried product. The pH and temperature had significant effects on the pH of RBA at the 95% confidence level, whereas pH–temperature interaction did not. At a given pH, 8, 10, or 12, and temperature increased, the pH of the prepared RBA slightly decreased. It is possible that at the pH, an increase in temperature may favor a chemical reaction that involves the generation of hydrogen ions, which in turn results in a slightly lower pH. The 100 °C treatment was not significantly different from the 80 or 120 °C treatments whereas the 80 and 120 °C treatments were different from each other. As expected, the pH 8, 10, and 12 treatments, were all significantly different from each other with respect to the pH of the prepared RBA.
3.4. Adhesive strength

The effect of pH and temperature on the strength of RBA is shown in Fig. 4b. The pH and temperature treatments significantly improved the adhesive performance of RBA over the control. Adhesive strength increased from 44 N for the control to 181 N for the sample treated at pH 12 and 100 °C. Except for the 120 °C treatment, adhesive strength increased with the increase of pH. The pH had a significant effect on adhesive strength, whereas temperature and pH–temperature interaction did not. At a given pH and as temperature increased from 80 to 100 °C, the adhesive strength increased with this improvement being more significant at pH 10 and 12 than at pH 8. However, as the temperature increased further to 120 °C, the adhesive strength became lower for all pH values.

In the presence of water and when the gelatinization temperature is reached, starch fully develops its adhesive properties. Above this temperature, an increase in adhesive strength may be due to the contribution of protein. Juliano (1985a) reported a final rice starch gelatinization temperature of 55–79 °C depending upon cultivar and environment. Similarly, Ju et al. (2001) reported a gelatinization temperature of 84.7 °C. Therefore, it is possible that the increase in adhesive strength above 80 °C may be due mainly to the contribution of protein.

Protein contribution to RBA strength is likely to increase with pH and temperature by an increase in dispersion and possibly solubility. Champagne et al. (1985) studied the solubility behaviors of proteins in rice bran with time, temperature, and pH and found that nitrogen solubility was highest (approximately 60% soluble at 20 °C) at pH 8 and above. Nitrogen solubility is a good estimate of protein solubility because the largest part of rice bran nitrogen is protein nitrogen (Barber and Benedito, 1980). The apparent decrease in adhesive strength at all pH levels as the temperature increased from 100 to 120 °C was not statistically significant at the 95% confidence level.

3.5. Effect of sulfites on rice bran adhesive

The effects of sulfites on the properties of RBA treated at 100 °C and pH 12 are listed in Table 1. Except for the sample treated with sodium sulfite (1 M), adhesive yield was not radically affected by the presence of sulfites. The yield increase for all but one treatment may be caused by a decrease in RBA cohesiveness due to disulfide bond cleavage that in turn may decrease the hardness of the oven-dried rice bran product and increase yield.

Contrary to expectation, the addition of sulfites significantly reduced the strength of RBA. This effect probably resulted from an excessive disulfide bond cleavage. Kalapathy et al. (1996) observed a similar effect of sodium sulfite on the adhesive properties of soy protein isolate. They suggested that the decrease in adhesive strength could be caused by a decrease in effective wood–protein interfacial area due to the presence of ions.

The effect of adding sulfites on the viscosity of RBA was unclear. The viscosity obtained for samples treated with sodium bisulfite or 1 M sodium sulfite did not vary significantly from the sample treated at similar pH and temperature without sulfites. The higher viscosity obtained for the sample containing sodium sulfite (0.5 M) over the control may be explained by a decrease in protein solubility due to disulfide bond breakage. Kella et al. (1989) observed a similar effect on whey proteins where solubility decreased with disulfide bond cleavage increasing viscosity. They suggested protein solubility depends not only on the surface charge, but also

<table>
<thead>
<tr>
<th>Property</th>
<th>Sodium sulfite</th>
<th>Sodium bisulfite</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 M</td>
<td>1 M</td>
<td>0.5 M</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>44.9</td>
<td>54.0</td>
<td>46.0</td>
</tr>
<tr>
<td>Strength (N)</td>
<td>27.5</td>
<td>16.5</td>
<td>26.0</td>
</tr>
<tr>
<td>PH</td>
<td>9.0</td>
<td>9.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Viscosity at 100 rpm (Pa s)</td>
<td>0.058</td>
<td>0.036</td>
<td>0.034</td>
</tr>
<tr>
<td>Viscosity at 200 rpm (Pa s)</td>
<td>0.071</td>
<td>0.048</td>
<td>0.042</td>
</tr>
</tbody>
</table>

*Control here refers to the sample modified by NaOH at pH 12 and 100 °C but without sulfites addition.
on the ratio of surface charge to surface hydrophobicity. The cleavage of disulfide bonds brings about structural changes that expose the non-polar groups previously buried inside the protein interior, thereby increasing the surface hydrophobicity. This probably decreases the surface polarity to hydrophobicity ratio, facilitating the protein–protein association and ultimately resulting in a lower solubility which in turn would increase viscosity. However, Kalapathy et al. (1996) observed the opposite, a sharp decrease in viscosity of the soy protein isolate adhesive when sodium sulfite was added. They attributed this phenomenon of the high viscosity of modified soy proteins was caused by increased intermolecular interactions due to unfolded protein molecules. Sulfites cleave the inter- and intradisulfide bonds in protein molecules minimizing intermolecular interaction, and thus, reducing viscosity. The effect of sodium sulfite on the pH of RBA appears to be negligible compared with sodium bisulfite. The pH of RBA treated with sodium bisulfite was significantly lower than the pHs of the control and the samples treated with sodium sulfite. In the presence of water, sodium bisulfite, a weak acid, neutralized the sodium hydroxide and contributed to lowering the pH. Overall, it is difficult to explain the behavior of RBA solely based on the behavior of its individual components. Interactions among rice bran constituents must play an important role in the overall behavior of the RBA.

4. Conclusion

High pH and temperature treatments proved to be effective in developing the adhesive properties of rice bran to obtain a rice bran adhesive (RBA) with improved adhesive strength compared with the untreated control. The RBA yield decreased with the increase of treatment temperature and pH. Although the RBA had higher viscosity than the control, the viscosity of RBA was still acceptable. Sulfites, on the other hand, were detrimental to the strength of RBA. Therefore, the optimal treatment conditions were 100 °C and pH 12 for obtaining the RBA with high adhesive strength. Because the RBA had a relatively low viscosity and high adhesive strength, it could be eventually used as an adhesive for particleboard manufacturing.

References


