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Use of additives to enhance the properties of cottonseed protein as wood adhesives

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ABSTRACT

Soy protein is currently being used commercially as a "green" wood adhesive. Previous work in this laboratory has shown that cottonseed protein isolate, tested on maple wood veneer, produced higher adhesive strength and hot water resistance relative to soy protein. In the present study, cottonseed protein and soy protein isolates were tested on different wood types, and cottonseed protein again showed better performance relative to soy protein. Furthermore, the effects of several protein modifiers were evaluated, including amino acids, fatty acids, and other organic molecules with cationic or anionic charges. Aspartic acid, glutamic acid, acetic acid, butyric acid, and adipic acid gave improved performance when included with cottonseed protein isolate whereas no significant effect was observed on soy protein isolate. Both dry adhesive strength and hot water resistance were tested. The enhanced performance observed with these additives provides an additional incentive for the use of cottonseed protein in this application.

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1. Introduction

The global wood adhesives and binders market is valued at $13.15 billion with a volume of 16,200 kton in 2013 [1]. Most of the adhesives are based on urea–formaldehyde, melamine–urea–formaldehyde and phenol–formaldehyde resins. In order to decrease the usage of formaldehyde and petroleum-derived raw materials, there has been a partial shift in the past 15 years towards more eco-friendly bio-based wood adhesives, e.g., those based on soy and polysaccharides [2–5]. In particular, soy protein seems to be increasingly accepted in wood adhesive formulations, with several products having been commercialized [6–8].

Cottonseed protein isolate can be prepared from defatted cottonseed flour via alkaline extraction followed by acidic precipitation [9,10]. In previous work [11], we showed cottonseed protein isolate to exhibit superior adhesive strength and improved hot water resistance relative to soy protein isolate when used to bind maple wood veneer. In a follow-up work [12], we used sequential fractionation of cottonseed meal and found the adhesive properties of water and phosphate-buffer washed solid fractions to be almost as good as cottonseed protein isolate. These fractions were later tested on maple and poplar veneers with similar results [13]. Another recent publication showed that the addition of tung oil to water-washed cottonseed meal and cottonseed protein isolate improved adhesive strength and water resistance on maple veneer [14].

Adhesion of soy protein on several types of wood has been reported in the literature [15,16]. In the present study, we looked at adhesion of both cottonseed protein and soy protein isolates on different veneers, including maple, walnut, pine, and cherry. Modification of protein formulations with alkali, guanidine hydrochloride, sodium dodecyl sulfonate, and urea has also been shown to affect the adhesive properties of soy protein [11,15,17–19] and cottonseed protein [11]. Other modifiers previously studied with soy proteins included various plasticizers [20], ethylene glycol and its polymers [21], cationic polyacrylamide [22], clay [23], calcium carbonate [24], and combinations of acid, base, and salt [25]. In this work we examined several new protein modifiers, and some were found to exhibit improved adhesive strength when incorporated into cottonseed protein.

2. Experimental

2.1. Materials

Cottonseed protein isolate was prepared from defatted glandless cottonseed meal using the single-step alkaline extraction acid precipitation procedure reported in the literature [9,10]. Basically, 50 g of cottonseed meal was dispersed with moderate stirring into 750 mL of 0.027 N sodium hydroxide solution for 30 min. The slurry was partitioned into separate centrifuge bottles, and the

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solids were pelleted by centrifugation for 10 min at 10,000 g. The pH of the combined supernatants was adjusted to 5.0 with 1 N hydrochloric acid, which precipitated the protein isolate. The protein was recovered by centrifugation, washed with water, centrifuged again, and then freeze-dried. The nitrogen content of this material was 16.0%. When 3 g of the cottonseed protein product was dispersed in 25 g water, the slurry pH was 5.0.

Soy protein isolate (Pro-Fam® 781) was provided by Archer Daniels Midland Company (Decatur, Illinois, USA). The nitrogen content was 14.2%. When 3 g of this protein was dispersed in 25 g water, the pH was 6.75. Maple, walnut, pine, and cherry wood veneer were acquired from Oakwood Veneer Company (Troy, Michigan, USA). Other reagents were purchased from Sigma Aldrich (Milwaukee, Wisconsin, USA) and used without further purification.

2.2. Preparation of protein adhesives and bonded wood samples

The formulation of adhesives was adapted from those reported in the literature [15,26–28]. Adhesive preparations comprised 3 g protein and 25 mL distilled water, stirred for 2 h at room temperature. For formulations containing modifiers, the protein (3 g) and modifier (between 30 and 1500 mM final concentration) was suspended in 25 g distilled water and stirred for 1 h [26–27]. The pH for each modifier preparation was adjusted with sodium hydroxide or hydrochloric acid to the same value as that of the protein by itself.

The adhesive preparations were applied to pieces of wood veneer [6,28]. Wood veneer with a thickness of 0.6 mm was cut into strips 0.5 in. wide by 3.5 in. long with the wood grain parallel to the long dimension. The adhesive preparation was applied to one side and one end of the wood veneer strip, covering an area of 0.5 in. × 1 in. After 10 min of air drying, a second layer of adhesive was applied over the first layer. Two wood veneer strips were then stacked with the adhesive sections overlapping to generate a bonded area of 0.5 in × 1 in. The two strips were then hot-pressed for 20 min at 80 °C and 13.8 MPa. Ten bonded composites were prepared and tested for each adhesive preparation.

2.3. Measurement of adhesive strength

Adhesive strength was measured with a Zwick stress tester (Zwick GmbH & Co., Ulm, Germany). The crosshead speed was 1 mm/min. Bond strength was reported as maximum shear strength at breakage (in MPa) and as maximum elongation at break (%). Ten bonded strips were tested for each formulation studied, and the mean and the standard deviations were calculated. Analysis of variance was used to compare differences in adhesive performance (SAS Institute, Cary, North Carolina, USA).

2.4. Water resistance of the wood composites

The procedure was similar to that used before [11] as adapted from previous work [29–30] and ASTM D1151-00 [31]. For this test, the wood veneers were cut into strips with the dimensions of 1.0 in × 3.5 in. Each adhesive preparation was applied twice to the 1 in. end of the wood side of each veneer strip. Pairs of maple strips were overlapped and hot-pressed for 10 min at 100 °C for 10 min and 13.8 MPa.

After cooling, the bonded wood strips were heated in water for 4 h at 63 ± 3 °C and dried at room temperature for 24 h. The bonded pairs were heated again in water for 4 h at 63 ± 3 °C and then cooled with tap water. They were then air-dried for 24 h and evaluated on the Zwick stress tester for maximum tensile strength and maximum elongation at break. Ten bonded composites were tested for each adhesive preparation.

3. Results and discussion

3.1. Different wood types

In an earlier work we showed that cottonseed protein isolate gave better performance on maple veneer than soy protein isolate [11]. Later, we studied the adhesive behavior on poplar veneers [13]. It would be useful to see if the favorable performance of cottonseed protein can be observed on pine, walnut and cherry wood veneers. It appears that under the testing conditions, the results are similar irrespective of wood type (Table 1). For all these wood veneer types, cottonseed protein shows better adhesive strength than soy protein.

The hot water resistance data for these proteins and wood veneers are shown in Table 2. Cottonseed protein isolate gives greater adhesive strength than soy protein after hot water treatment for all wood types. Some wood types (e.g., walnut) appeared to give slightly better adhesive strength after hot water treatment than the other tested wood types. In the literature different adhesion values on soy proteins for several wood types were reported, and the differences were attributed to roughness or smoothness of the wood surfaces [15,16].

3.2. Modifiers for proteins

Several modifiers were tested to see if they affect the adhesive properties of both types of protein isolate. In view of the current trend toward the use of “green” and environmentally friendly agri-based materials, amino acids and fatty acids were tried initially. Several amino acids were tested including charge neutral amino acids (glycine, leucine, and tyrosine), potentially cationically charged amino acids (arginine, histidine and lysine), potentially anionically charged amino acids (aspartic and glutamic acids); these included amino acids having an aliphatic (leucine) and aromatic side chain (tyrosine). Three fatty acids were included: oleic acid, palmitic acid, and stearic acid. In order to further evaluate the effect of cationic and anionic compounds, choline chloride, acetic acid, butyric acid, and adipic acid were also included. For consistency, the formula names of the modifiers are given even though at the pH involved the amino acids are mostly in the zwitterionic form and the acids are mostly in the form of acid salts.

In an initial experiment, each modifier was added at 0.5 M concentration, and the pH was adjusted to be the same as the protein by itself using NaOH or HCl. From the data for the cottonseed protein with modifiers (Table 3), it appeared that the amino acids without ionic charges (glycine, tyrosine, and leucine), amino acids with ionizable cationic charges (histidine, lysine) and

Table 1
Adhesive properties of cottonseed protein (CSP) and soy protein (SP) isolates on different wood veneers*.

Protein	Wood	Tensile strength** (MPa)	Elongation at break** (%)
CSP	Pine	$2.40 \pm 0.18^{a,b}$	$2.0 \pm 0.1^{b,c}$
	Walnut	2.62 ± 0.25^{a}	$2.1 \pm 0.1^{a,b}$
	Cherry	2.34 ± 0.12^{b}	2.1 ± 0.1^{a}
	Maple	$2.37 \pm 0.17^{a,b}$	$2.0 \pm 0.1^{b,c}$
SP	Pine	1.82 ± 0.28^{c}	1.6 ± 0.2^{d}
	Walnut	1.78 ± 0.14^{c}	1.5 ± 0.1^{d}
	Cherry	1.91 ± 0.10^{c}	1.8 ± 0.1^{c}
	Maple	1.71 ± 0.11^{c}	1.5 ± 0.1^{d}

* Testing done on bonded wood composite strips 0.5 in. × 3.5 in. with a glued 0.5 in. × 1 in. overlap between two strips.
** n (number of wood composites) = 10 for each treatment. Data in each column with the same superscript letter indicates that the treatments are not significantly different at $p = 0.05$.