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Soy and cottonseed protein blends as wood adhesives☆

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ABSTRACT

As an environmentally friendlier alternative to adhesives from petroleum feedstock, soy proteins are currently being formulated as wood adhesives. Cottonseed proteins have also been found to provide good adhesive properties. In at least some cases, cottonseed proteins appear to form greater shear strength and improved hot water resistance compared with soy proteins. In the present study, blends of soy and cottonseed proteins were prepared, and their adhesive properties were found to decrease steadily with increased levels of soy protein in the formulations. In addition, cottonseed- and soy-protein based adhesives were also formulated with xylan, starch, or celluloses to determine the influence of polysaccharide fillers on protein-based adhesive properties. In some cases, adhesive shear strength was retained even when the cottonseed or soy protein was mixed with up to 75% polysaccharide. For cottonseed protein/polysaccharide formulations, hot water adhesive resistance was retained when the blend contains about 50% polysaccharides. Soy protein formulations and its polysaccharide blends generally exhibited somewhat lower hot water resistance. In view of the ability of cottonseed protein/polysaccharide blends to retain shear strength and hot water resistance properties, these blends may provide an opportunity to decrease the amount of protein used in adhesive formulations, thereby decreasing cost.

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1. Introduction

In 2009 the forest products industry spent about $1.6 billion on wood adhesives globally (Kusumgar, 2011). Most commercial wood adhesives incorporate non-renewable petrochemicals, primarily urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-formaldehyde (MF) resins. Because of environmental regulations regarding emission of organic compounds, including formaldehyde, wood adhesives based on natural renewable sources have re-gained attention and been researched over the past 15 years. Various proteins have attracted research interest, including proteins from soybean (Liu and Li 2007; Sun and Bian, 1999), cottonseed (Cheng et al., 2013; He et al., 2014a; He et al., 2014b), canola (Li et al., 2012), wheat gluten (Nordqvist et al., 2012), as well as proteins from distillers dry grains (Bandara et al., 2013) and spent hen protein (Wang and Wu, 2012). Most publications have focused on soy proteins, and commercial adhesive products involving soy proteins are now available (Allen et al., 2010; Orr, 2007).

In order to advance the use of proteins as adhesives, lower cost, increased adhesive strength, and improved water resistance are all desirable. Chemical modifiers (Huang and Sun, 2000a,b; Zhong et al., 2001; Zhong et al., 2002; Liu and Li, 2002) and polyamide–epichlorohydrin resins (Li et al., 2004; Zhong et al., 2007; Allen et al., 2010) have been used to improve protein adhesive strength. We have shown that cottonseed protein exhibits better adhesive strength and water resistance relative to soy protein (Cheng et al., 2013), and are also looking into ways to further improve strength and decrease cost. For instance, one approach used is to fractionate cottonseed meal with water or buffer (He et al., 2014a). In order to reduce the cost, different procedures for the isolation of protein involving water and buffer wash (He et al., 2014b) and vigorous extraction (He et al., 2013) have also been attempted with considerable success.

Chen et al. (2013) added sucrose and glucose to soybean flour and found that increasing carbohydrate content decreased bonding strength and hydrophobicity; glucose as an additive gave higher bonding strengths than sucrose. Recently, the addition of several carbohydrates to soy protein isolate was reported to cause a small decrease in the water resistance of the formulations (Lorenz et al., 2015). In addition, blends of soy protein with phenol formaldehyde resins (Zhong and Sun, 2007; Wescott and Frihart, 2008) poly(vinyl acetate) (Zeng et al., 2012) and latex (Liu et al., 2012) have been reported. More recently nano-scale montmorillonite

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added to polyisocyanate-modified soy protein adhesive was found to decrease the bond strength but increase its water resistance (Zhang et al., 2013; Zhang et al., 2014).

Blending of different proteins as adhesives has been studied, e.g., casein and soy proteins and blood and soy proteins (Cone and Galber, 1934; Bradshaw and Dunham, 1931). However, recent work on protein blends, such as the blends of soy and cottonseed protein, have been lacking.

The purpose of the present study is two-fold. First, blends of soy and cottonseed proteins were studied to look for synergistic effects between these materials, and secondly blends of the two protein sources with different forms of inexpensive polysaccharide filler were studied. Xylan, starch, and cellulose were considered. Both adhesive strength and hot water resistance were tested. Properties depended on both the protein type and the type and weight ratio of polysaccharide in the blend.

2. Materials and methods

2.1. Materials

Soy protein isolate (Pro-Fam 781) was obtained from Archer Daniels Midland Company (Decatur, IL,USA). It had a nitrogen content of 14.2%, and a solution of the isolate (3 g) dispersed in water (25 mL) had a pH of 6.75.

Cottonseed protein isolate was prepared from defatted glandless cottonseed meal by the single-step procedure of Berardi et al. (1969) and Martinez et al. (1970). Briefly, 50 g of cottonseed meal was dispersed in 750 mL of 0.027 N NaOH for 30 min. The mixture was partitioned into several bottles and centrifuged for 10 min at 10,000 × *g*. The supernatants were collected, and the pH adjusted to 5.0 by adding 1N HCl dropwise to induce precipitation of the protein. The protein was separated from the liquids by centrifugation and was then water washed and centrifuged twice and then freeze-dried. A solution of three grams of protein in 25 g water had a pH of 5.0, and the nitrogen content was around 16.0%.

The amino acid profiles of soy protein and cottonseed protein isolates were previously published (He et al., 2015). From nitrogen analysis and the conversion factor of 5.7 for soy protein (Morr, 1982) and 5.3 for cottonseed protein (Rhee, 2001), the protein content for soy protein isolate can be estimated to be about 81% and for cottonseed protein about 85%. The rest of the protein samples consisted mostly of carbohydrates (He et al., 2015).

The maple wood veneers were purchased from Oakwood Veneer Company (Troy, MI, USA). Soluble starch was from Difco Laboratories (Detroit, MI, USA). Beechwood xylan, cellulose powder (20 μm size) and other chemical compounds were purchased from Sigma–Aldrich (Milwaukee, WI, USA) and used without further purification.

2.2. Preparation of protein adhesives and bonded wood samples

The procedure was adapted from those reported in the literature (Zhong et al., 2002; Sun et al., 2002; Sun and Bian, 1999; Liu and Li, 2002). Adhesive preparations were composed of 3 g of protein dispersed into 25 mL of distilled water at room temperature, which was stirred for 2 h. For the first series of the experiments cottonseed or soy protein isolate was used individually and a series of blends was made from the two proteins mixed in 20% increments. In the second series of experiments cottonseed or soy protein isolate was used individually, and each was mixed with a polysaccharide in varying weight ratios. In these experiments, again 3 g of each mixture (protein plus filler) was dispersed into 25 mL of water.

The adhesive formulations were used to bond pieces of maple veneer. Wood veneer with a thickness of 0.6 mm was cut into strips

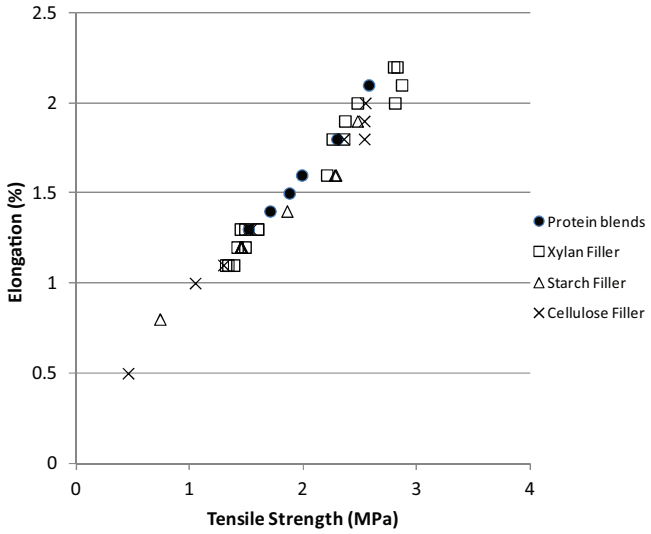

Fig. 1. Correlation between elongation at break and tensile strength for cottonseed/soy protein blends and for proteins with different amounts of xylan, starch and cellulose fillers.

3.5 in. long and 0.5 in. wide, with the wood grain parallel to the long dimension. With a brush, adhesive was applied to one end of the wood side of both strips covering a 0.5 in. by 1 in. area. After 10 min of air drying, a second layer was applied over the first layer. Pairs of the treated strips were overlapped by 1 in. with the adhesives surfaces facing each other, and the pairs were hot-pressed at 80 °C for 20 min with a pressure of 2000 psi. Ten bonded composites were prepared and tested for each formulation.

2.3. Measurement of adhesive strength

The 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 tensile strength at breakage (MPa) and as maximum elongation at break (%). Ten bonded strips were tested for each formulation and the average and standard deviations were calculated. Analysis of variance was used to test for adhesive formulation differences (SAS Institute, Cary, NC).

A plot of the maximum tensile strength versus the elongation at break data given in this work is shown in Fig. 1. These two quantities are highly correlated ($R^2 = 0.97$). A similar finding was made earlier for data on cottonseed meal fractions (He et al., 2014a). Thus, the elongation at break provides an alternative measure of the adhesive bond strength.

2.4. Water resistance of the wood composites

The procedure was similar to that used by Cheng et al. (2013) as adapted from Liu and Li (2007) and ASTM D1151-00 (2013). Maple veneer with a thickness of 0.6 mm was cut into strips with the dimension of 1.0 in. × 3.5 in. Each adhesive preparation was applied twice to the end (1 in.) of the wood side of each veneer strip. Pairs of maple strips were overlapped and hot-pressed at 100 °C for 10 min with a pressure of 13.79 MPa. 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 then 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 shear strength and maximum elongation at break. Ten bonded composites were tested for each formulation tested. In a few cases when the tensile strength exceeded about 3 MPa, the adhesive was stronger