Modification of Soy Proteins and Their Adhesive Properties on Woods

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ABSTRACT: Adhesive properties of trypsin-modified soy proteins (TMSP) on woods were investigated. A simple method developed in our laboratory, consisting of measuring the force required to shear the bond between glued wood pieces in the Instron universal testing machine, was used to examine adhesive strength of modified soy proteins on wood. Adhesive strength of TMSP was measured for cold-pressed (ambient temperature for 2 h) and hot-pressed (60, 80, 100, and 120°C for times varying from 0.5 to 2.5 h) woods. Of the woods examined, soft maple gave the highest strength [743 Newtons (N) at a protein glue concentration of 2 mg/cm^2]. For soft maple and cold-pressing, TMSP at 2 mg/cm^2 gave twice the adhesive strength of unmodified protein controls, 743 vs. 340 N. Also, the adhesive strength of TMSP increased from 284 to 743 N as glue concentration was increased from 1 to 2 mg/cm^2. However, hot-pressing of wood pieces beyond 1 h at 120°C and 30% relative humidity resulted in decreased adhesive strengths of TMSP compared to controls. Further, adhesive strengths of hot-pressed glued wood samples decreased when the relative humidity at which they were kept for curing increased from 30 to 60%. This negative effect of increased humidity on adhesive strengths of glued wood pieces was not observed with cold-pressed TMSP.
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Soybeans are primarily used for food applications to provide essential amino acids and nitrogen. Soy proteins also provide flavor, texture, and other functional properties (1). Soybean meal is mostly used for animal feeds (2). Soy proteins have been used in many industrial products, such as adhesives for wood and paper, binders in coatings and paints, and as emulsifiers in colloidal rubber products (3–5). The introduction of cost-effective synthetic petrochemical products with superior performance and quality resulted in declined industrial use of soy proteins. The increased demand for adhesives, the uncertainty of continuing availability of petrochemical products, and demand for environmentally safe products promoted the development of adhesives from renewable, inexpensive sources.

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Most work has been directed toward developing soy protein products with good solubility and adhesive strength for binding pigments in paper coatings and water-based paints (5). Cone and Brown (6) used alkali to obtain more desirable adhesive properties from soybean flour by controlling the denaturing process of alkali on protein. Boyer *et al.* (7) described a procedure for extracting soy protein by slow freezing and thawing of soybean protein curd to produce protein binders suitable for spinning synthetic fibers, paper coatings, and water-based paints.

The chemistry and the properties of soy proteins related to functional properties in food systems are well documented (8–11). Enzymatic and chemical modifications of soy proteins have been used to improve dispersing and emulsifying functional properties (12–15). The understanding of chemistry, selective modification, and functional properties of modified soy protein will play a major role in the development of industrial products, such as adhesives and binders from soy protein.

In this work we describe a simple method to measure adhesive strength of modified soy protein on wood and a procedure to produce modified soy protein with enhanced adhesive property.

EXPERIMENTAL PROCEDURES

Materials. Soy protein isolate (SPI) was obtained from Archer Daniels Midland Co. (Decatur, IL). Enzyme trypsin (type II from porcine pancreas, activity 1500 units/mg) was purchased from Sigma Chemical Co. (St. Louis, MO). Wood pieces (walnut, cherry, soft maple, poplar, and yellow pine with dimensions of 5 × 2 × 0.3 cm) were purchased from White River Hardwoods, Woodworks, Inc. (Fayetteville, AR).

Preparation of modified protein. SPI (10 g) was suspended in 140 mL deionized water and stirred (magnetic stirrer) for 10 min to obtain uniform dispersion. The pH of the dispersion was adjusted to 8.0 with 1N NaOH, the temperature was brought to 37°C by incubating in a shaker (Lab-Line-Environ-Shaker; Lab-Line Instrument, Inc. Melrose Park, IL) for 15 min at 180 rpm, followed by adding 2.0 mg (3000 units of activity) of trypsin (solubilized in 10 mL deionized water). The mixture was incubated at 37°C for 1 h with shaking, and

the enzyme was inactivated by heating at 90°C for 3 min. The trypsin-modified SPI was frozen and freeze-dried.

ADHESIVE STRENGTH MEASUREMENT ON WOOD

Cold-pressing. Wood pieces were air-dried at ambient temperature for three days. Modified SPI (0.25 g) was dispersed in 5 mL deionized water. One hundred milligrams of this dispersion was placed on each side of a wood piece (5 × 2 × 0.3 cm) and spread on a marked area (2 × 2 cm^2) to give a protein concentration of 1.0 mg/cm^2. Two other wood pieces were superimposed on the glued portions (Fig. 1) and pressed with a load of 5 kg for 2 h. The mass was removed, and the glued wood pieces were allowed to dry overnight at ambient conditions. To investigate the effect of humidity on adhesive property of the protein glue, glued wood pieces were placed in chambers maintained at 30 and 60% relative humidities (RH) at ambient temperature for four days to attain equilibrium and were tested for adhesive strength.

Hot-pressing. The glued wood pieces, prepared as shown in Figure 1, were placed in an oven at 120°C and pressed with a 5-kg mass for times varying from 15 to 120 min to examine the effect of heat-curing time on the adhesive property. The mass was removed, and the glued wood pieces were placed in chambers maintained at 30 and 60% RH at ambient temperature (23°C) for four days to attain equilibrium and then were tested for adhesive strengths. This procedure was repeated with hot-pressing at 60, 80, and 100°C.

Adhesive strength determination. The force [in newton (N)] required to break the glued wood pieces was measured with an Instron (Model 1011; Instron Corporation, Canton, MA) by pulling them apart from the two edges (Fig. 2). The Instron loading rate was 20 mm/min. The force (N) required to shear the glued portions was expressed as adhesive strength

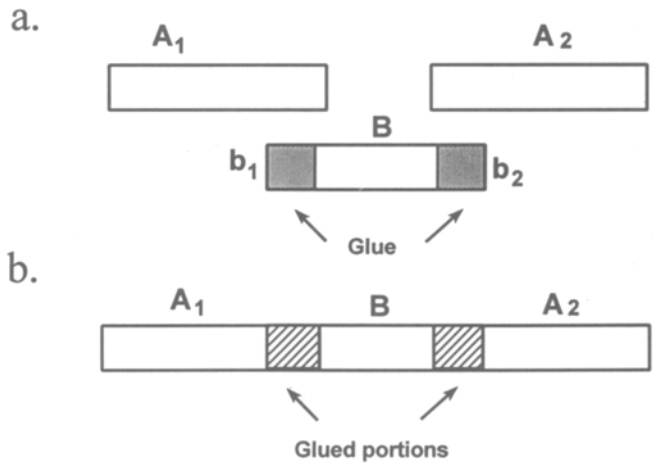

FIG. 1. Diagram illustrating the steps involved in wood gluing. (a.) Modified protein glue (100 mg of 10% solution) was applied on each side (b_1 and b_2, area 2 × 2 cm) of wood piece B. (b.) Two wood pieces, A_1 and A_2, with same dimensions as B were placed on glued areas and pressed.

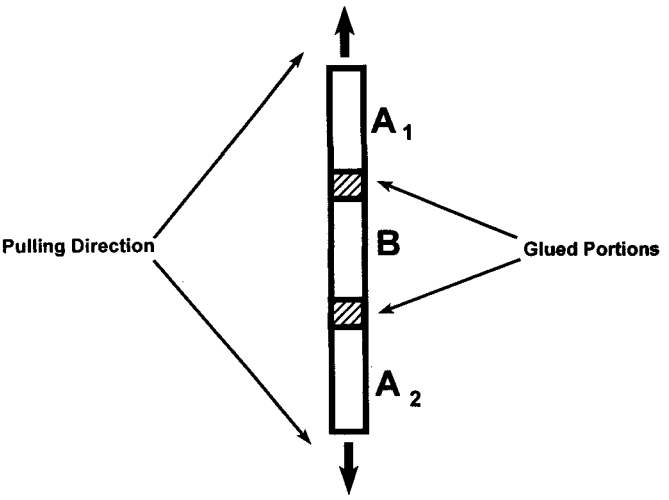

FIG. 2. Diagram showing the direction of pulling (speed 20 mm/min) to determine adhesive strength of glue with an Instron (Instron Corporation, Canton, MA). The wood pieces (A1 and A2) glued onto wood B were pulled in the direction shown by the arrows in the Instron.

of modified protein glue. All the adhesive strength data reported are means of six replications unless otherwise specified.

Viscosity. Viscosity of unmodified and modified proteins was measured in a Brookfield viscometer (Stoughton, MA). All the measurements were made at ambient temperature with spindle #2 operating at 20 rpm.

Statistical analysis. Analysis of variance (SAS Institute, Raleigh, NC) was used for data analysis, and least significant differences were computed at 5% level.

RESULTS AND DISCUSSION

A compression block shear method is widely used for screening wood glues (16). Two wood blocks (2 × 1.75 × 0.75″) glued face-to-face are used for this purpose. Shear strength is measured by clamping one block and compressing the other block with a loading device. The method developed in our laboratory is a simple one that uses an Instron to measure the shear strength of glued woods. This method allows one to determine the adhesive strength with small amounts of glue (<10 mg) in an Instron or a texture analyzer by measuring the force (N) required to shear the glued portion. Hence, this method will be useful for screening adhesive strengths of various glues on different types of wood.

Effect of enzyme hydrolysis time. Because protein glues have reasonable curing times (15–30 min for drying), the flow property that governs the penetration of glue through the wood material will significantly affect the adhesive property (17). Therefore, viscosity is an important physical property that largely governs the adhesive behavior of protein glue (18). Figure 3 shows the change in adhesive strength and viscosity of the glue with progressive enzyme hydrolysis. The adhesive strength increased sharply from 300 N to the highest value of 700 N during the first hour of hydrolysis, and then

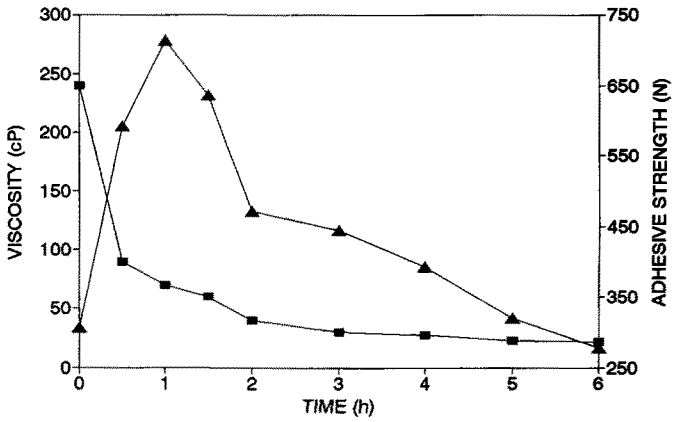

FIG. 3. Effect of trypsin hydrolysis time on viscosity and adhesive strength of modified soy protein on soft maple wood. ■, Viscosity, ▲, adhesive strength.

progressively decreased with hydrolysis time, declining to about 280 N after 6 h of hydrolysis. The viscosity, however, decreased sharply from 240 to 70 cP during the first hour of hydrolysis and decreased slowly with further hydrolysis. Highest adhesive strength with wood was obtained when the viscosity reached a fairly low value (70 cP). This low viscosity would allow easy handling of glue, smooth spreading, and sufficient penetration of glue through wood surfaces.

Adhesive strength with different types of woods. Table 1 shows the variation of adhesive strength of glue from modified soy protein with various wood types. Modified protein glue gave highest strength with soft maple wood (284 N). Modified protein gave zero or lower strengths with soft woods, such as yellow pine (0 N) and poplar (71 N), and hard wood, such as walnut (135 N). Intermediate hard woods, such as maple and cherry, had higher adhesive strengths (284 and 195 N, respectively). This variation in adhesive strength with type of wood may be due mainly to the variation in physical properties rather than chemical properties of the woods because the composition of major components of woods vary little from wood to wood (19,20). The bonding between adhesive polymers and the wood polymers is mostly caused by a combination of mechanical adhesion (interlocking by adhesive penetration through porous wood surface) and molecular attractive forces (Van der Waal forces, hydrogen bonds). Although the relative contribution of these forces is not clear, the factors influencing these forces can be attributed to the variation in adhesive strength with different types of wood. Inherent differences in physical properties of woods, such as porosity and degrees of surface roughness, can account for differences in adhesive strengths observed with the different woods (17).

TABLE 1
Adhesive Strengths of TMSP[a] with Different Types of Wood After Cold-Pressing

	Adhesive strength[b] (N)				
Sample	Walnut	Cherry	Soft maple	Poplar	Yellow pine
Control	0	0	50	0	0
TMSP	135	195	284	71	0

[a]One mg/cm^2 protein concentration, cold-pressed for 2 h and cured at ambient conditions. TMSP, trypsin-modified soy protein.

[b]Values are means of three measurements. N, newton.

TABLE 2
Effect of TMSP Glue Concentration on Adhesive Strength After Cold-Pressing[a]

Protein concentration (mg/cm^2)	Adhesive strength[b] (N)		
	Cherry	Soft maple[c]	Poplar
0.5	52	30	45
1.0	195	284 (50)	72
1.5	434	738 (330)	419
2.0	440	743 (340)	454

[a]Cold-pressed for 2 h and cured at ambient conditions. Abbreviations as in Table 1.

[b]Values are means of three measurements.

[c]Value in parentheses is for unmodified protein control.

Effect of protein glue concentration. The variation of adhesive strength with protein glue concentration is shown in Table 2. As expected, there is a sharp increase in adhesive strength up to a protein concentration of 1.5 mg/cm^2. However, no significant ($P < 0.05$) further increase in adhesive strength of glue was observed above this protein concentration. Further, the glue solution became highly viscous above a protein concentration of 2 mg/cm^2, and was difficult to spread evenly over the wood surfaces.

Effect of hot-pressing. Hot-pressing is generally used with synthetic wood glues to decrease the viscosity of the glue and for fast curing. Hot-pressing of glued wood pieces at high temperature (120°C) did not improve the adhesive strength of modified proteins (Table 3). Furthermore, the data show that the control gave similar glue strength up to a heating time of 1 h. Thereafter (1–2.5 h), a progressive increase in glue strength in comparison to modified protein was observed. No improvement in adhesive strength of modified protein was observed with hot-pressing. The decreased adhesive strength

TABLE 3
Effect of Heat-Curing on Adhesive Strength of TMSP[a] on Soft Maple Wood After Hot-Pressing

Heating[b] time (h)	Adhesive strength[c] (N)	
	Modified protein	Control[d]
0.25	476	263
0.50	482	344
0.75	493	388
1.0	617	614
1.5	578	656
2.0	475	697
2.5	495	736

[a]Two mg/cm^2 protein concentration. Abbreviations as in Table 1.

[b]At 120°C.

[c]Cured at 30% relative humidity.

[d]Beyond 1 h heating, adhesive strengths of controls are significantly higher ($P < 0.05$) than those of modified protein.

TABLE 4
The Effect of Relative Humidity on Adhesive Strength of TMSP[a] on Soft Maple Wood After Hot-Pressing

	Adhesive strength (N)	
Heating[b]-time (h)	30% RH	60% RH
0.25	476	244
0.50	482	434
0.75	493	414
1.0	617	579
1.5	578	466
2.0	475	444
2.5	495	445

[a]Two mg/cm^2 protein concentration. Abbreviations as in Table 1. RH, relative humidity.
[b]At 120°C.

of modified protein with longer heating time (>1 h) could be due to structural damage caused by heating. The increase in adhesive strength of unmodified protein could be due to the exposure of more polar groups as a result of heat denaturation of soy proteins. Similar behavior was observed with unmodified and modified protein when hot-pressed at 60, 80, and 100°C (data not shown). Cold-pressing of wood is preferred over hot-pressing for modified soy protein glue applications because long heating times may cause deformation of the wood structure. Cold-pressing would be more economical because it eliminates the heating step.

Effect of humidity. One important requirement of an adhesive is the ability to retain its bonding quality under a variety of environmental conditions. Water resistance determines the durability of a glue (21). All polymer-based adhesives are permeable to water; water in the atmosphere diffuses into adhesive bond lines and weakens the joints by attacking the interface (21). The adhesive strength of the hot-pressed glue decreased slightly when stored at 60% RH in comparison to 30% RH (Table 4). However, no change in adhesive strength was observed for the cold-pressed glue when the glued wood pieces were stored at 60 and 30% RH (data not shown). This suggests that trypsin-modified soy proteins (TMSP) glue has improved water resistance.

The results show that TMSP can be used to glue selected woods, such as maple, and has the advantage of being more water-resistant.

ACKNOWLEDGMENT

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