

Shear Strength and Water Resistance of Modified Soy Protein Adhesives

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ABSTRACT: Soy protein polymers recently have been considered as alternatives to petroleum polymers to ease environmental pollution. The use of soy proteins as adhesives for plywood has been limited because of their low water resistance. The objective of this research was to test the water resistance of adhesives containing modified soy proteins in walnut, maple, poplar, and pine plywood applications. Gluing strength and water resistance of wood were tested by using two ASTM standard methods. Glues with modified soy proteins had stronger bond strength than those containing unmodified soy proteins. Plywood made with glue containing urea-modified proteins had higher water resistance than those bonded with glues containing alkali-modified and heat-treated proteins. After three 48-h cycles of water-soaking, followed by 48 h of air-drying, no delamination was observed for either walnut or pine specimens glued with the urea-modified soy protein adhesives. Gluing strength for wood species with smooth and oriented surface structure was lower than for those with rough, randomly oriented, surface structures. Wood species with greater expansion of dimensions during water-soaking had a higher delamination rate than those showing less expansion.

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About 1.2 billion pounds of thermoplastic resins are used as adhesives and coatings in the United States annually for applications with plywood, particle board, paper manufacture, book-binding, textile sizing, abrasives, gummed tape, matches, and many other packaging and labeling applications (1). Soy protein was used as an adhesive in the 1930s before it was replaced by petroleum-based adhesives (2). However, soy protein adhesives have low gluing strength and water resistance (2). Petroleum-based adhesives have many advantages, such as strength and high water resistance, but most of them contain phenol formaldehyde, a major cross-linking agent that causes environmental problems and even toxicity in both processing and product distribution. Petroleum reserves are limited, and politically controlled. In addition, petroleum-based adhesives may not be completely biodegradable, which can lead to waste accumulation. Therefore, a need exists to develop natural polymer-based adhesives and explore their potential applications.

Soy protein polymers recently have been reconsidered as alternatives to petroleum polymers in single-use items to prevent

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environmental pollution. Soy proteins are complex macromolecules that contain about 18 different amino acid monomers connected through peptide bonds to form the primary structure (polypeptide chain), which dominates their properties. A number of side chains are connected to these monomers and interact with many inorganic and organic materials and cellulosic fibers. These side chains often are modified easily by physical, chemical, or enzymatic methods to obtain desirable properties (3–5).

The principle of protein gluing is that the protein molecules disperse and unfold in solution. The unfolded molecules increase the contact area and adhesion onto other surfaces, and they become entangled with each other during the curing process to retain bonding strength (2). Selected protein modification techniques could increase the tendency to unfold and, consequently, increase the bonding strength. Protein modification also could move some hydrophobic amino acids, which are buried inside the molecule, outward to increase water resistance.

Alkali, such as sodium hydroxide, has been the most common chemical used to increase the gluing strength and water resistance of soy protein-based adhesives. Hettiarachchy *et al.* (6) prepared adhesives with alkali (NaOH)- and trypsin-modified soy proteins. They found that the bond strength and water resistance of the modified soy protein adhesives were enhanced compared with those of unmodified soy protein adhesives. The alkali-modified soy protein adhesive was stronger and more water resistant than trypsin-modified soy protein adhesive. The authors believed that alkali might increase the unfolding of protein molecules, resulting in an increased contact area and exposure of the hydrophobic bonds.

Urea is another useful denaturation chemical that unfolds the secondary helical structure of a protein (3). Urea has oxygen and hydrogen atoms that interact actively with hydroxyl groups of the soy proteins, a reaction that may break down the hydrogen bonding in the protein body and, consequently, unfold the protein complex. The objective of this research was to study the adhesion properties of urea-modified soy protein in plywood applications and compare them with those of alkali- and heat-modified soy protein.

MATERIALS AND METHODS

Acid-precipitated soy protein isolate (SPI) (PRO-Fam 970) was provided by Archer Daniels Midland (Decatur, IL) and served as the control. It contained more than 90% protein (dry basis). Urea (Mallinckrodt Chemical Works, St. Louis, MO)

and alkali (NaOH, Fisher Scientific, Fairlawn, NJ) were all analytical-grade reagents.

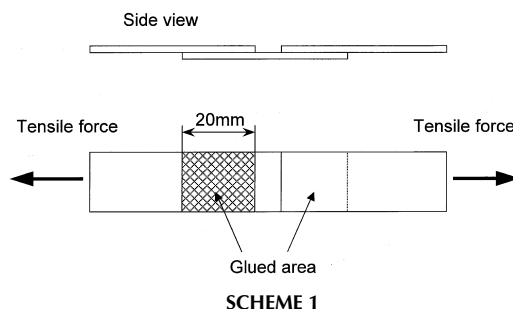
Protein modification. (i) *Urea-modified SPI (U-SPI)*. About 18% urea (3 M) was used to prepare a 3.2 N solution of urea in distilled water at room temperature. Ten grams of SPI powder was then mixed with 150 mL of the urea/distilled water solution at room temperature and stirred for about 1 h, after which the pH of the soy protein slurry was determined. The slurry mixture was freeze-dried (model 6211-0495; The Virtis Company, Inc., Gardiner, NY) and milled (Cyclone Sample Mill, model 3010-030; UDY Corporation, Fort Collins, CO) into a powder with 90% passing through U.S. #100 mesh.

(ii) *Alkali-modified SPI (A-SPI)*. The method of Hettiarachchy *et al.* (6) was followed. Thirty grams of SPI powder was mixed with 400 mL distilled water at room temperature and stirred for about 120 min. The pH of the mixture was then adjusted to 11 by using sodium hydroxide (1 N). The mixture was heated to 50°C and stirred for another 120 min to hydrolyze the SPI. The mixture was freeze-dried and milled into a powder. To compare the effects of alkali- and heat-modification on adhesive properties, heat-modified SPI (H-SPI) was prepared by mixing 30 g of SPI powder with 400 mL distilled water and heating the mixture to 50°C while stirring for about 120 min.

Viscosity of the modified proteins. The relative viscosity of the modified and unmodified soy protein was measured with a Rapid Viscosity Analyzer (RVA) (Model 3D; Foss North America, Inc., Eden Prairie, MN) by following the American Association of Cereal Chemists' method 76-21 for wheat flour slurry (7). Twenty-eight grams of the adhesive solution (about 16% solids) was used. The duration of the test was 30 min. Paddle speed was 960 rpm for the first 10 s, followed by 160 rpm for the rest of the test. Holding temperature was 95°C for 10 min.

Specimen preparation. Four woods, ranging from soft to hard, were used: pine, maple, poplar, and walnut. The dimension of each wood sample was 3 × 20 × 50 mm (thickness, width, and length). The modified SPI powder was added to distilled water at a ratio of 1:6 (SPI/water) and allowed to disperse at room temperature for about 5 min. The adhesive slurry was brushed onto the wood sample until the entire area was completely wet (about 1.5 ± 0.1 mg/cm² protein solid concentration). The amount of the slurry on each wood sample was controlled by using a consistent brushing procedure to minimize variations. The slurry-brushed wood sample was allowed to rest at room temperature for about 5 min, and then three pieces of the slurry-brushed wood samples were put together to produce one testing specimen as shown in Scheme 1, and then five specimens were pressed at a time at 104°C and 20 kg/cm² for about 15 min (model 3890; Auto "M," Carver Inc., Wabash, IN). Each pressed specimen was placed in a plastic bag and kept at room conditions until it was analyzed for shear strength and water resistance.

Shear strength and water resistance. Shear strength of wood specimens (indicator of glue strength) was tested according to American Society for Testing and Materials (ASTM) standard method D-906 by using an Instron testing machine (model 4466; Canton, MA) with a crosshead speed of 2.4 cm/min (8). The maximum shear strength at breakage was recorded.



Water resistance of the adhesive (for exterior application) was tested by using the modified method described by Hettiarachchy *et al.* (6). Specimens were soaked in tap water at room temperature for 48 h, and then dried at room temperature in a fume hood for 48 h. Soaking and drying cycles were repeated three times, and delamination of the specimen was recorded after each cycle.

Water resistance of the adhesive (for interior application) was tested by following ASTM standard method D-1183 (9). Two cycles were used. For the first cycle, the specimen was first conditioned for 60 h at 23°C in a chamber maintained at 90% relative humidity (RH), followed by conditioning for 24 h at 48°C and 25% RH. The same conditioning parameters were used for the second cycle. The shear strength of the specimen was tested after each step of the cycles.

Statistical analysis. Ten duplicates were used for each test parameter. Analysis of variance was used to analyze the data, and the means were compared by using the least significant difference method in SAS (SAS Institute, Cary, NC).

Wood expansion and surface microstructure. The dimensions of the wood species were measured before and after soaking in distilled water at room temperature for 48 h. Linear expansions (both length and thickness) and volume expansion were calculated. The microstructures of the surfaces of dry wood samples were observed by using a scanning electron microscope (AutoScan, ETEC Corporation, Hayward, CA) at an accelerated voltage of 20 kV.

RESULTS AND DISCUSSION

Viscosity of the modified proteins. The viscosity of the unmodified soy protein decreased initially as temperature increased from room temperature to about 65°C and remained constant for about 4 min (Fig. 1). This is because the protein molecule unfolded more at higher temperature, resulting in reduced viscosity. As temperature increased to 80°C, the protein became thermally denatured, the molecules absorbed water and swelled, and the viscosity increased rapidly. However, the viscosity of the protein started to decrease immediately after reaching its maximal value at the holding temperature, presenting a shear-thinning behavior. Continued spinning of the paddle at 95°C could destroy the entangled structure, resulting in a low viscosity. During cooling, the viscosity of the protein increased again because of gelling. Compared to the unmodified proteins, the viscosities of both urea- and alkali-modified soy proteins were low and thermally stable, indicating longer work-

ing time and shelf life for these adhesives. The heat-treated soy proteins had a denaturation temperature of about 80°C with a smaller peak than the unmodified proteins, but larger than the U- and A-modified proteins.

Shear strength and water resistance. The gluing strengths of U- and A-SPI adhesives were high with walnut, maple, and poplar specimens and ranged from 58 to 65 kg/cm² (Table 1). In most samples, the wood itself was broken first in strength testing. However, the gluing strengths of all adhesives with pine were only around 30 kg/cm². Kalapathy *et al.* (10) observed similar results for trypsin-modified soy protein adhesives with five wood species. They found that gluing strength with pine was much lower than with walnut, cherry, maple, and poplar samples. Examination of surface microstructure of the pine sample showed a smooth and oriented structure compared to that of other wood samples (Fig. 2). If the surface structure is too rough, it will cause cohesive failure, and if the surface structure is too smooth, it will cause adhesive failure (11). The pine surface might be too smooth, resulting in adhesive failure, while the walnut surface might be appropriate for the SPI adhesives. Also, rough surface structure produces a random micro “finger joint” structure under pressure. A smooth surface structure, like pine wood, might have less micro random “finger joint” effects, which could be another reason for the low gluing strength. The gluing strength of all wood specimens glued with urea- and alkali-modified soy proteins, except for pine wood specimens, were higher than those glued with H-SPI, and the specimens glued with the unmodified soy proteins had the lowest gluing strength. Both U- and A-SPI slurries had lower viscosities and were thermally stable compared to the H-SPI and unmodified proteins, which indicates that the U- and A-SPI were more unfolded than the H-SPI and unmodified proteins, resulting in large contact areas, consequently high gluing strength (2).

After 60 h of incubation in a humidity chamber at 90% RH and 23°C, the gluing strength remained about the same as before incubation for the U-SPI, A-SPI, and H-SPI adhesives (Table 2). The water absorbed into the gluing interface during

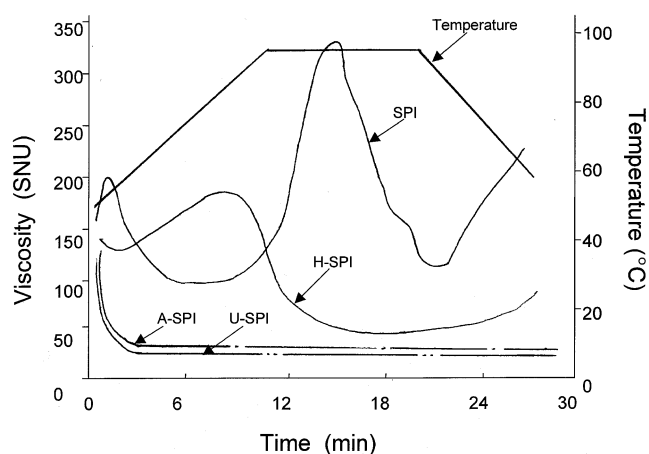


FIG. 1. Rapid Viscosity Analyzer (RVA) relative viscosity curves of modified and unmodified soy protein slurries at 16% solids content. SPI, acid-precipitated soy protein isolate (SPI); U-SPI, urea-modified SPI; A-SPI, alkali-modified SPI; H-SPI, heat-modified SPI; SNU, stirring number units.

TABLE 1
Shear Strength (kg/cm²) of Wood Specimens Glued with Modified and Unmodified Soy Protein Adhesives^a

Sample	U-SPI	A-SPI	H-SPI	SPI
Walnut	60 ^a	60 ^a	54 ^a	39 ^c
Maple	58 ^a	65 ^a	56 ^a	50 ^b
Poplar	62 ^a	64 ^a	49 ^b	46 ^b
Pine	31 ^c	30 ^c	28 ^c	35 ^c

^aMeans, based on $n = 5$, followed by different superscript roman letters are significantly different using least significant differences (LSD) and a probability level of $\alpha = 0.05$. U-SPI, urea-modified soy protein isolate; A-SPI, alkali-modified soy protein isolate; H-SPI, heat-modified soy protein isolate; SPI, unmodified soy protein isolate.

incubation may have acted as a plasticizer for the adhesive, resulting in higher hydrogen bonding between protein molecules. However, after an additional 24-h incubation at 25% RH and 48°C, the gluing strengths for A-SPI, and H-SPI adhesives were reduced significantly (Table 3). The gluing strength for U-SPI remained unchanged with maple, poplar, and pine wood samples, but decreased to 38 kg/cm² with walnut. The gluing strength with the pine specimens glued with A-SPI substantially increased from 30 to 47 kg/cm². Interactions between wood surface molecular structure, wood fiber structure, the modified protein structure, and water diffusion at the interface might affect the gluing strength. The exact reasons are unknown and need further study. The gluing strengths of these specimens remained the same after the second incubation cycle.

Water-soaking and drying tests showed that the adhesives made from U-SPI had the highest water resistance, as shown by the lowest delamination rates of the glued wood specimens (Table 4). The delamination rates ranged from 40 to 80% for the A-SPI-glued specimens, 60 to 80% for the H-SPI-glued specimens, and 80 to 100% for the unmodified SPI-glued specimens. The gluing strength of the U-SPI adhesive with walnut and pine was reduced about 10% after 24 h of water-soaking and then remained the same after 72 h of water-soaking (Table 5).

Wood expansion. The expansion results of the four woods in water-soaking tests (Table 6) showed that maple had the greatest swelling, whereas poplar had zero swelling but the highest linear expansion, resulting in higher total bulk volume expansion. Maple and poplar also had higher linear expansion than walnut and pine. Woods with higher linear or bulk volume expansion would have higher shrinkage stress during drying. If the shrinkage stress is higher than the adhesive bonding strength, delamination will occur, which may explain the

TABLE 2
Shear Strength (kg/cm²) of Wood Specimens Glued with Modified and Unmodified Soy Protein Adhesives After Incubation at 23°C and 90% RH for 60 h^a

Sample	U-SPI	A-SPI	H-SPI	SPI
Walnut	64 ^a	60 ^a	58 ^a	47 ^b
Maple	54 ^a	64 ^a	55 ^a	44 ^b
Poplar	64 ^a	64 ^a	54 ^a	44 ^b
Pine	30 ^c	47 ^b	36 ^c	27 ^c

^aMeans, based on $n = 5$, followed by different superscript roman letters are significantly different using LSD and a probability level of $\alpha = 0.05$. RH, relative humidity. For other abbreviations see Table 1.

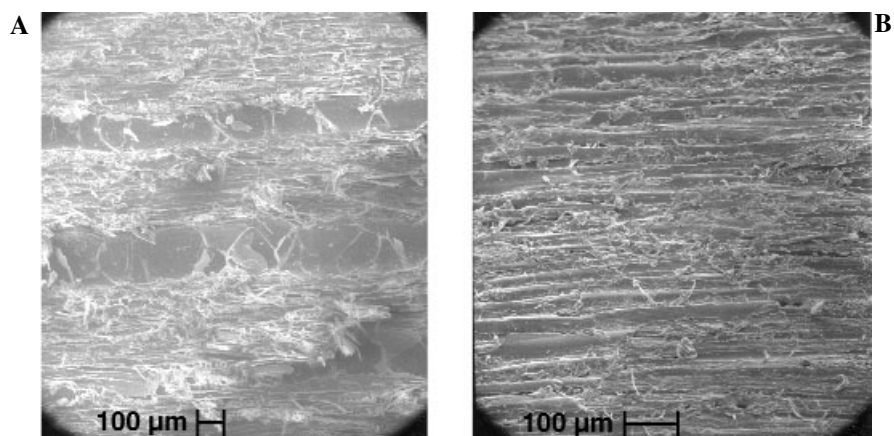


FIG. 2. Scanning electron micrograph of surface microstructure of (A) walnut and (B) pine.

TABLE 3
Shear Strength (kg/cm²) of Glued Wood Specimens After the First Cycle of Incubation (90% RH, 23°C, 60 h; and 25% RH, 48°C, 24 h)^a

Sample	U-SPI	A-SPI	H-SPI	SPI
Walnut	38 ^c	41 ^c	50 ^b	41 ^c
Maple	57 ^a	48 ^b	41 ^c	40 ^c
Poplar	63 ^a	50 ^b	43 ^c	47 ^b
Pine	32 ^d	43 ^c	25 ^d	29 ^d

^aMeans, based on $n = 5$, followed by different superscript roman letters are significantly different using LSD and a probability level of $\alpha = 0.05$. For abbreviations see Tables 1 and 2.

TABLE 4
Delamination (%) of Wood Specimens Glued with Soy Protein Adhesives After Three Cycles of 48-h Water-Soaking Tests at Room Temperature^a

Sample	U-SPI	A-SPI	H-SPI	SPI
Walnut	0	40	60	100
Maple	20	60	80	80
Poplar	40	80	80	100
Pine	0	60	60	80

^aBased on $n = 5$ for each adhesive. For abbreviations see Table 1.

higher delamination rates achieved by maple and poplar in the water-soaking test (Table 4). This explanation is only speculation at this stage.

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REFERENCES

- Narayan, R., Polymeric Materials from Agricultural Feedstocks, in *Polymers from Agricultural Coproducts*, edited by M.L. Fishman, R.B. Fredman, and S.J. Huang, ACS Symposium Series 575, American Chemical Society, Washington, DC, 1993, pp. 2–28.
- Lambuth, A.L., Protein Adhesives for Wood, in *Handbook of Adhesive Technology*, edited by A. Pizzi and K.L. Mittal, Marcel Dekker, Inc., New York, 1994, pp. 259–281.
- Tanford, C., Protein Denaturation, in *Advances in Protein Chemistry*, edited by C.B. Anfinsen, M.L. Anson, J.T. Edsall,

TABLE 5
Shear Strength (kg/cm²) of Walnut and Pine Specimens Glued with Urea-Modified Soy Proteins After Water-Soaking for 24, 48, and 72 h^a

Sample	0 h	24 h	48 h	72 h
Walnut	60 ^a	55 ^b	49 ^b	54 ^b
Pine	31 ^c	22 ^d	22 ^d	20 ^d

^aMeans, based on $n = 5$, followed by different superscript roman letters are significantly different using LSD and a probability level of $\alpha = 0.05$.

TABLE 6
Dimension Expansion (%) Properties of the Wood Species After 48 h of Water-Soaking at Room Temperature^a

Sample	Linear (±1%)	Swelling (±0.1%)	Bulk volume (±1%)
Walnut	4.7 ^b	0.0 ^c	14.3 ^b
Maple	6.3 ^a	0.4 ^a	16.0 ^a
Poplar	7.6 ^a	0.0 ^c	16.0 ^a
Pine	5.1 ^b	0.1 ^b	13.9 ^b

^aMeans, based on $n = 5$, followed by different superscript roman letters are significantly different using LSD and a probability level of $\alpha = 0.05$. For abbreviation see Table 1.

and F.M. Richards, Academic Press, Inc., New York, 1968, pp. 121–281.

- Wolf, W.J., Soybean Proteins: Their Functional, Chemical, and Physical Properties, *J. Agr. Food Chem.* 18:969–976 (1970).
- Kinsella, J.E., Functional Properties of Soy Proteins for Food Applications, *J. Am. Oil Chem. Soc.* 56:242–258 (1979).
- Hettiarachchy, N.S., U. Kalapathy, and D.J. Myers, Alkali-Modified Soy Protein with Improved Adhesive and Hydrophobic Properties, *Ibid.* 72:1461–1464 (1995).
- AACC Methods for Rapid Visco Analyser (RVA) for Wheat Flour (76-21) approved on 10-15-97, American Association of Cereal Chemists, St. Paul, Minnesota.
- ASTM Standards for Wood and Adhesives (D-906), *Annual Book*, American Society of Testing and Materials, Philadelphia, pp. 243–246.
- ASTM Standards for Wood and Adhesives (D-1183), *Annual Book*, American Society of Testing and Materials, Philadelphia, pp. 407–409.
- Kalapathy, U., N.S. Hettiarachchy, D. Myers, and M.A. Hanna, Modification of Soy Protein and Their Adhesive Properties on Woods, *J. Am. Oil Chem. Soc.* 72:507–510 (1995).
- Mackay, C.D., Good Adhesive Bonding Starts with Surface Preparation, *Adhesive Age* 41:30–32 (1998).

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