Adhesive Properties of Soy Proteins Modified by Sodium Dodecyl Sulfate and Sodium Dodecylbenzene Sulfonate

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ABSTRACT: A study was conducted on adhesive and water-resistance properties of soy protein isolates modified by sodium dodecyl sulfate (SDS) (0.5, 1, and 3%) and sodium dodecylbenzene sulfonate (SDBS) (0.5, 1, and 3%) and applied on walnut, cherry, and pine plywoods. Soy proteins modified by 0.5 and 1% SDS showed greater shear strengths than did unmodified protein. One percent SDS modification had the highest shear strength within each wood type tested. Soy proteins modified with 0.5 and 1% SDBS also showed greater shear strengths than did the unmodified protein. The 1% SDBS-modified soy protein had the highest shear strength in all wood samples tested. Compared to the unmodified protein, the modified proteins also exhibited higher shear strengths after incubation with two cycles of alternating relative humidity and zero delamination rate and higher remaining shear strengths after three cycles of water soaking and drying. These results indicate that soy proteins modified with SDS and SDBS have enhanced water resistance as well as adhesive strength. Possible mechanisms for the effects of SDS and SDBS also are discussed.

Paper no. J9429 in *JAOCS 77,* 705–708 (July 2000).

KEY WORDS: Adhesive, denaturation, DSC, protein modification, shear strength, soy protein, water resistance, wood.

Soy-based adhesives were developed in 1923 (1) but shortly after World War II were replaced by petroleum-based adhesives because of their greater gluing strength and water resistance. However, soy proteins recently have been considered as petroleum polymer alternatives in the manufacture of adhesives because they are environmentally friendly. This abundant protein resource can be obtained as a by-product from processing. Industrial utilizations of soy proteins for biodegradable resins are being promoted to increase their value (2–4). The use of soy proteins in industrial applications is based on their functional properties. Protein modification is designed to improve functional properties by altering protein molecular structure or conformation through physical, chemical, or enzymatic agents at the secondary, tertiary, and quaternary levels. Research on modified proteins has focused on functional properties for food applications such as solubility, viscosity, gelation, and emulsion stability (4–6).

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Few reports have discussed soy protein modifications to improve their adhesive properties on wood. Hettiarachchy *et al.* (7) prepared soy protein-based adhesives using alkali (NaOH)- and trypsin-modification methods. They found that the adhesive strength and water resistance of both modified soy proteins were enhanced compared to those of unmodified proteins, with the alkali-modified soy protein adhesive being stronger and more water-resistant. Sun and Bian (8) found that urea-modified soy protein was more water-resistant than that modified by alkali. Huang and Sun (9) investigated adhesive properties of soy proteins modified with different concentrations of urea and guanidine hydrochloride (GH). The results indicated that both urea and GH concentrations had significant effects on the extent of protein unfolding and, consequently, on adhesive properties. Partly unfolded protein molecules with a certain amount of secondary structure may be desirable for protein adhesion (9). As compared to urea and GH, sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) have been reported to possess unique properties in denaturing proteins (10). However, no reports were found on their effects on protein adhesive properties on wood. The objective of this research was to investigate the adhesive and water-resistance properties of soy protein isolates (SPI) modified by different concentrations of SDS and SDBS and used on walnut, cherry, and pine plywoods.

MATERIALS AND METHODS

Materials. Defatted soy flour was obtained from Cargill (Cedar Rapids, IA) and used for the separation of SPI. SDS and SDBS (Sigma Chemical Co., St. Louis, MO) were both analytical-grade reagents. Unmodified SPI was used as the control.

SPI segregation. Defatted soy flour (100 g) was mixed with 1500 mL distilled water and stirred for 30 min at room temperature. The pH of the mixture was then adjusted to 8.5 with 1 N NaOH and stirred for another 20 min. The slurry was centrifuged at 10,000 × *g* at 4°C for 20 min. The liquid supernatant was recovered, its pH adjusted to 4.2, then it was kept at 4°C for 12 h. After another centrifugation at 6500 × *g* at 4°C for 20 min, the precipitate SPI fraction was obtained. It was redissolved at pH 7.6, freeze-dried (freeze dryer, Model 6211-0495; The Virtis Company, Inc., Gardiner, NY), and

then milled (Cyclone Sample Mill, Model 3010-030; UDY Corporation, Fort Collins, CO) into a powder, with 90% passed through a U.S. #100 mesh. The freeze-dried SPI powder samples had an average protein content of 88.26% (dry basis) (LECO; Leco Corporation, St. Joseph, MI) and moisture content of 5%.

Protein modification. Solutions of SDS (0.5, 1, and 3%) and SDBS (0.5, 1, and 3%) were prepared at room temperature. SPI powder (10 g) was suspended in each SDS and SDBS solution (100 mL), stirred, and reacted for 6 h.

Wood specimen preparation. Three wood varieties ranging from hard to soft (walnut, cherry, and pine) were used. The method described by Sun and Bian (8) was used to prepare the wood specimens for testing. Each wood piece was 3 × 20 × 50 mm (thickness, width, and length, respectively), and three pieces were glued to form a specimen. The modified protein adhesive slurry was brushed onto both ends of the middle piece and onto one end of the other two pieces. The applied area on each end was 2 × 2 cm, and the protein concentration was 1.80 mg/cm^2 with a standard deviation of 0.04 mg/cm^2. The three wood pieces with the adhesive were allowed to rest at room temperature for about 5 min before they were assembled by hand and then hot-pressed (Model 3890; Auto "M," Carver Inc., Wabash, IN) at 115°C and 20 kg/cm^2 for about 7 min. The pressed specimens were cooled and stored in polyethylene bags at ambient conditions for 4 d.

Adhesive strength test. Shear strengths of wood specimens were determined by an Instron testing machine (Model 4466; Canton, MA) operated at a crosshead speed of 2.4 cm/min. The force (kg) required to break the glued wood specimen was recorded. All adhesive strength data reported are means of eight replications.

Incubation-aging test. Water resistance (for interior application) of the adhesive was tested by ASTM standard method D-1183 (11). For the first cycle, the glued specimens were incubated in a chamber at 90% relative humidity (RH) and 23°C for 60 h and then were conditioned at 25% RH and 48°C for 24 h. For the second cycle, the aging parameters were 90% RH and 23°C for 72 h and 25% RH and 48°C for 24 h. Ten specimens were used for each treatment.

Water-soaking test. Water resistance (for exterior application) of the adhesive was tested according to the modified method described by Hettiarachchy *et al.* (7). The glued wood specimens were placed in a container and soaked in tap water for 48 h at room temperature and then air-dried at room temperature for 48 h in a fume hood. Ten specimens were used for each treatment. After three cycles of soaking and drying, the dried wood specimens were examined for delamination and shear strength.

Differential scanning calorimetry (DSC) measurement. Thermal transition properties of modified and unmodified soy protein samples were measured with a PerkinElmer DSC 7 instrument (PerkinElmer, Norwalk, CT). Each sample was analyzed in the presence of excess water (1:10). Large sample pans were used. The DSC temperature range was from 30 to 200°C, and the heating rate was 10°C/min.

RESULTS AND DISCUSSION

Shear strength. SDS modification of 0.5 and 1% gave the soy protein higher shear strength in all wood types (Table 1). Three percent SDS modification had lower shear strength, as compared to the 0.5 and 1% SDS modifications, but was still higher than the unmodified proteins in walnut and pine wood samples. For pine, the glue strength for the 3% SDS modification was not significantly less than that for 0.5 and 1% SDS modification.

The soy protein modified by SDBS at 0.5 and 1% concentrations exhibited greater shear strength than the unmodified proteins (Table 1). Modification by 3% SDBS had the least effect on adhesive strength although the glue strength for pine wood was still significantly higher than that for the unmodified proteins.

Variations in adhesive strength with type of wood were also observed (Table 1). Modified proteins had higher shear strengths with the hard wood (walnut) and intermediate hard wood (cherry). At 1% SDS modification, for example, shear strengths were greater in walnut and cherry than in the soft pine wood. The same behavior was observed with 1% SDBS-modified proteins. This was consistent with the results for urea and GH modifications as described by Huang and Sun (9) and also in agreement with the observation of Kalapathy *et al.* (12). Differences in physical properties and surface structures of the woods probably account for these variations in adhesive strength.

Water resistance. Water resistance is an important glue property that determines the adhesive bond durability (2). After the incubation aging test, the shear strengths of wood specimens glued with 3% SDS-modified proteins decreased significantly, as did the shear strength of specimens glued with unmodified proteins. The shear strengths of the wood specimens glued with 0.5 and 1% SDS-modified soy proteins (Table 2) remained almost the same as the initial strengths (Table 1). Both 0.5 and 1% SDS-modified proteins had better water resistance and zero delamination rate within each wood category (Table 2). The specimens glued with soy proteins modified with 1% SDS had the highest remaining shear strengths after three water-soaking cycles (Table 2).

TABLE 1
Shear Strengths (kg/cm^2) of Wood Specimens Glued with Unmodified (UnM), Sodium Dodecyl Sulfate (SDS) (0.5, 1, and 3%)-Modified, and Sodium Dodecylbenzene Sulfonate (SDBS) (0.5, 1, and 3%)-Modified Soy Proteins[a]

	SDS (%)			SDBS (%)			
Sample	0.5	1	3	0.5	1	3	UnM
Walnut	52^{a}	54^{a}	37^{c}	50^{a,b}	51^{a,b}	36^{c,d}	30^{d}
Cherry	54^{a}	55^{a}	38^{c}	55^{a}	58^{a}	33^{d}	41^{b,c}
Pine	46^{b}	45^{b}	42^{b,c}	47^{b}	49^{b}	41^{c}	31^{d}

[a]Means, based on n = 8, followed by different superscript roman letters are significantly different using least significant differences (LSD) and a probability level of α = 0.05.

TABLE 2
Shear Strengths and Delamination of Wood Specimens Glued with UnM Soy Proteins and SDS-Modified Soy Proteins After Incubation-Aging and Water-Soaking Tests[a]

	SDS-0.5%	SDS-1%	SDS-3%	UnM
Shear strength after incubation (kg/cm^2)				
Walnut	$44^{a,b}$	$46^{a,b}$	$26^{c,d}$	$25^{c,d}$
Cherry	$45^{a,b}$	50^{a}	30^{c}	38^{b}
Pine	43^{b}	43^{b}	37^{b}	21^{d}
Delamination after water soaking (%)				
Walnut	0	0	0	100
Cherry	0	0	0	100
Pine	0	0	0	90
Shear strength after water soaking (kg/cm^2)				
Walnut	26^{d}	49^{a}	24^{d}	—
Cherry	33^{c}	49^{a}	32^{c}	—
Pine	31^{c}	41^{b}	33^{c}	6^{e}

[a]Means, based on $n = 8$, followed by different superscript roman letters are significantly different using LSD and a probability level of $\alpha = 0.05$. For abbreviations see Table 1.

Specimens glued with proteins modified with SDBS at concentrations of 0.5 and 1% had higher shear strengths after the incubation-aging test and zero delamination rate after the water-soaking test compared to those glued with nonmodified proteins and 3% SDBS-modified proteins (Table 3). This indicates that soy protein adhesives modified by SDBS at concentrations of 0.5 and 1% have better water resistance. The highest remaining shear strengths after three cycles of water soaking and drying were found for the 1% SDBS modification.

DSC analysis. Modifications that change the secondary, tertiary, or quaternary structure of protein molecules have been referred to as denaturation (7). Detergents occupy a unique position among protein denaturants in that they are able to produce a cooperative conformational change at low reagent concentrations (10). It has been reported that proteins are partly unfolded after denaturation by the binding of detergents (10). The DSC data for soy proteins treated with SDS at concentrations of 0, 0.5, 1, and 3% (Table 4) showed that as the SDS concentration increased, the total enthalpy decreased; that is, the heat capacity of the modified soy proteins decreased. This indicates that the higher the SDS concentration, the greater the degree of protein unfolding. The lower shear strength of soy proteins modified at higher SDS concentration (3%, Table 1) might have resulted from the greater extent of unfolding. Narhi *et al.* (13) investigated the effect of SDS concentration (0.25, 0.5, 1, 2, and 4%) on the structure of aprA-subtilisin and determined the rate of SDS-induced unfolding. The amount of protein existing in the unfolded form was increased by increasing the concentration of SDS. A certain amount of secondary structure might be desirable for protein adhesion. The soy proteins modified at relatively low SDS concentration (0.5 and 1%) might have been partly unfolded and had a certain amount of secondary structure, resulting in higher shear strengths (Table 1). As protein molecules disperse and unfold in solution, the partly unfolded molecules with a certain amount of secondary structure increase the contact area and adhesion force onto other surfaces, such as wood materials, and interact with each other during the curing process to achieve bonding strength. SDS ($C_{12}H_{25}NaO_4S$) is an anionic detergent. The driving force for any degree of unfolding brought about by anion binding may be one or a combination of the following: (i) electrostatic repulsion between the charges of bound species, including the net charge of the protein; (ii) penetration of the hydrocarbon tail into the apolar regions of the protein; (iii) binding-induced changes in the protein–hydrogen ion equilibrium, resulting in an increase in electrostatic repulsion between charged species; and (iv) a favorable ratio of the number of binding sites and protein association constants in the native form to those in the unfolded form (14). Protein modification

TABLE 3
Shear Strengths and Delamination of Wood Specimens Glued with UnM Soy Proteins and SDBS-Modified Soy Proteins After Incubation-Aging and Water-Soaking Tests[a]

	SDBS-0.5%	SDBS-1%	SDBS-3%	UnM
Shear strength after incubation (kg/cm^2)				
Walnut	44^{b}	48^{a}	27^{d}	25^{d}
Cherry	48^{a}	53^{a}	$31^{c,d}$	$38^{b,c}$
Pine	44^{b}	45^{b}	42^{b}	$21^{d,e}$
Delamination after water soaking (%)				
Walnut	0	0	0	100
Cherry	0	0	0	100
Pine	0	0	0	90
Shear strength after water soaking (kg/cm^2)				
Walnut	23^{d}	48^{a}	23^{d}	—
Cherry	35^{c}	49^{a}	30^{c}	—
Pine	32^{c}	45^{b}	42^{b}	6^{e}

[a]Means, based on $n = 8$, followed by different superscript roman letters, are significantly different using LSD and a probability level of $\alpha = 0.05$. For abbreviations see Table 1.

TABLE 4
Differential Scanning Calorimetry Data Presenting Thermal Behavior for Soy Protein Isolates with Unmodification (UnM) and Sodium Dodecyl Sulfate (SDS) Modification, and Sodium Dodecylbenzene Sulfonate (SDBS) Modification

Sample	T1[a] (°C)	T2[b] (°C)	Enthalpy[c] (J/g)
UnM	74.84	91.19	9.54
SDS (%)			
0.5	74.82	89.84	5.95
1	72.81	90.17	3.39
3	—	83.52	2.57
SDBS (%)			
0.5	72.84	91.86	6.54
1	72.99	91.51	3.56
3	—	83.50	2.68

[a]T1 (°C): peak temperature for 7S soy protein fraction.
[b]T2 (°C): peak temperature for 11S soy protein fraction.
[c]Enthalpy (J/g): sum of the enthalpy for both 7S and 11S peaks.

through anion binding could move some inside hydrophobic side chains outward, where they could interact with the hydrophobic moieties of detergent molecules and form micelle-like regions (10) to increase hydrophobicity and thus increase water resistance. This was supported by the experimental data at 1% SDS modification (Table 2). Similar results were obtained with SDBS ($C_{18}H_{29}NaO_3S$), which is also an anionic detergent and very similar to SDS in structure except that it has a more hydrophobic side chain (Tables 1, 3, and 4).

ACKNOWLEDGMENTS

Contribution No. 99-463-J from the Kansas Agricultural Experiment Station, Manhattan, Kansas. This work was supported in part by research grants from the Kansas Soybean Commission and the Kansas Agricultural Experimental Station. We thank Xiaoquan Mo for her assistance in DSC analysis.

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[Received October 18, 1999; accepted April 18, 2000]