Formaldehyde-Free Wood Composites from Soybean Protein Adhesive

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ABSTRACT: Commercial particleboards are currently synthesized by blending wood furnish with formaldehyde-based resins and curing them under a combination of heat and pressure. Particleboards manufactured with urea-formaldehyde resin are known to liberate formaldehyde during their service lives. Formaldehyde's carcinogenicity has prompted the search for environmentally-friendly resins for wood composite manufacture. Soybean protein-based adhesives have been developed as a renewable and formaldehyde-free replacement for urea-formaldehyde resins. Particleboards processed using the soybean protein adhesive matched or exceeded performance criteria of M-2-grade commercial particleboards when evaluated as per American National Standards Institute (ANSI) specifications.

KEYWORDS: Protein, biobased, green chemistry, wood composites, adhesive, soybean, renewable

1 INTRODUCTION

Wood is the classic renewable resource but extensive harvesting of old growth forests has resulted in a significant reduction in the size of logs available for commercial use. Decreasing wood supplies and increasing demand for wood products have heightened the demand for engineered wood composites such as particleboard, plywood, medium-density fiberboard (MDF), and oriented strand board (OSB). Wood composites are manufactured by combining wood furnish with suitable polymeric adhesives under the influence of pressure and heat, which is an excellent means of maximizing useful production from limited resources. The wood furnish used in composites are obtained from relatively small trees, and include tree residues such as bark and shaving, thereby utilizing a significant portion of the tree. Recycled or urban wood can also be reused in composite board manufacturing. An estimated 366 million board feet of particleboard, plywood, MDF, and OSB were used for nonresidential construction in the United States during 2011 [1].

Presently, the vast majority of wood adhesives are formaldehyde-based products such as urea-formaldehyde (UF) resins. Particleboards based on these adhesives are known to liberate formaldehyde over their service lives [2, 3]. Although UF resins are cost-effective and enable quick cure, the toxicity and carcinogenicity of formaldehyde presents a serious health concern [4]. The EPA has classified formaldehyde as a human carcinogen [5]. Formaldehyde has a pungent, irritating odor even at very low concentrations (< 1 ppm). Low dose acute exposure to formaldehyde can result in headache, rhinitis, and dyspnea, while higher doses may cause severe mucous membrane irritation, burning, lachrymation, and lower respiratory effects such as bronchitis, pulmonary edema, or pneumonia [6]. In May 2006, a public interest group conducting indoor air testing in Federal Emergency Management Agency (FEMA)-issued trailers in Louisiana and Mississippi reported that 94% of the trailers had indoor levels of formaldehyde in excess of that identified by the Environmental Protection Agency (EPA) and Consumer Products Safety Commission (CPSC) as triggering adverse health effects in humans [7, 8]. Environmental regulations governing formaldehyde emissions are slated to become more stringent in the future. In 2010, the President signed into law a bill reducing the allowed emission levels to 0.09 ppm (US SB1660, 2009-2010, 111th Congress).

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In the early 1900s, soybean protein was employed as a binder in wood composites [9, 10]. By the 1930s, the development of inexpensive, more water-resistant, and faster-curing formaldehyde-based resins significantly reduced the use of soybean protein adhesives in wood composites [11]. Since then, several attempts have been made to reduce formaldehyde emissions from composite products. Riebel *et al.* [12] described methods of preparing a legume-based thermosetting resin for producing composites by blending soybean flour with methyl diphenyl isocyanate. Kuo *et al.* [13] developed a soybean-based adhesive resin containing 70% soybean flour and 30% phenol-formaldehyde resin. Wang and Sun [14] describe particleboards derived from wheat straw blended with methylene diphenyl diisocyanate, corn stalk pith, and sodium hydroxide-modified soybean protein isolate. Amaral-Labat *et al.* [15] produced particleboards with glyoxalated soy flour adhesive blended with tannin and a polymeric isocyanate. However, isocyanates present toxicity issues specific to handling and processing. Li and Liu [16] modified soybean protein with the key functional groups found in mussel adhesive protein, i.e., catechol, amino, and mercapto groups, to replace UF resins in wood composites for interior use, especially in plywood manufacture. Wescott and Frihat [17] proposed the use of methylolated soybean flour (prepared by reacting soybean flour with formaldehyde) along with one or more reactive petroleum-based comonomers to develop particleboard adhesives. Yet there are no commercially viable technologies that completely replace the formaldehyde-based adhesive with a formaldehyde-free resin without negatively affecting particleboard properties.

Enzymatic and/or chemical modification of proteins can be tailored to control peptide size and minimize side reactions, improving access to protein functional groups. Proteolytic enzymes selectively hydrolyze peptide bonds, e.g., trypsin is known to hydrolyze peptide bonds whose carbonyl function is directed by basic amino acids such as lysine or arginine, whereas chemical cleavages of peptide bonds are residue specific in their action. Hettiarachchy *et al.* [18] reported significant improvement in adhesive properties of trypsin-modified soy protein on intermediate hardwoods such as soft maple. However, lower strength was observed with softwoods such as yellow pine and poplar, and some hardwoods like walnut.

Soybeans are the largest source of protein feed and the second largest source of vegetable oil in the world. The United States is the world's leading soybean producer and exporter. Farm value of U.S. soybean production in 2008-2009 was $29.6 billion, the second-highest value among U.S.-produced crops, trailing only corn. Soybean and soybean product exports accounted for 54 percent of U.S. soybean production in 2008-2009. Soybeans are about 90 percent of U.S. total oilseed production, while other oilseeds—such as cottonseed, peanuts, sunflower seed, canola, flax, and safflower—account for the remainder [19].

Soybean seeds contain about 40% protein. Soybean protein isolate (SPI) is the most highly refined soybean protein product sold commercially, and contains > 90% protein on a moisture-free basis [20]. Due to its high water solubility and protein content, SPI is widely used in food applications such as bakery products, breakfast cereals, and as an amino acid source to substitute for casein, egg white and meat. Only a very small percentage of soybean protein is used in industrial nonfood applications, primarily in paper coatings and wood adhesives [21].

2 MATERIALS AND METHODS

2.1 Materials

Soybean protein isolate (Pro-Fam® 781) and defatted soybean flour (DSF, Kaysoy® 7B) were provided by Archer Daniels Midland Company (Decatur, IL). Wood furnish was kindly provided by Roseburg Forest Products (Taylorsville, MS). Nitric acid and calcium oxide were obtained from Fisher Scientific (Fair Lawn, NJ). Lignin (Indulin® AT) was supplied by MeadWestvaco (Covington, VA). Pine oil was donated by Hillyard, Inc. All raw materials were used as received.

2.2 Characterization

Mechanical tests were performed using the MTS 810 Material Test System. Formaldehyde emissions were determined according to ASTM D 6007. Rheology testing was performed using the Brookfield CAP 2000+ viscometer. Particleboard strength and water resistance properties were evaluated according to ASTM D 1037 guidelines and compared against ANSI specifications. Part A of ASTM D 1037 describes the general methods for evaluating the engineering and design properties of particleboard panel materials via modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond (IB) strength. The MOR and MOE (in MPa) were calculated from the load-deflection curves according to the following formula:

$$MOR = \frac{3P_b L}{2bh^2} \tag{1}$$

where P_b is the maximum load (N), L is the span (mm), b is the specimen width (mm), and h is the specimen thickness (mm).

$$MOE = \frac{P_{bp}L^3}{4bh^3Y_p} \tag{2}$$

where P_{bp} is the load at the proportional limit (N) and Y_p is the deflection corresponding to P_{bp} (mm).

IB (in MPa) was calculated from the rupture load (P_s) using the following formula:

$$IB = \frac{P_s}{bl} \tag{3}$$

where P_s is the maximum load (N), l is the length (mm), and b is the specimen width (mm).

2.3 Adhesive Preparation

A jacketed steel reactor was heated to 68 ± 2°C. Water (1472.8 g) was charged to the reactor and calcium oxide (85.1 g) was added under slow agitation followed by 50% of the SPI (583.5 g). Following the addition of pine oil (67.7 g), the remaining SPI (583.5 g) was added gradually while increasing the agitation speed to accommodate the increased viscosity. After the SPI had dispersed completely, the mixture was allowed to react for 90 minutes. The pH of the reaction was recorded as 11.5 ± 0.5 after 90 min at 68°C. Next, lignin (85.6 g) was added to the kettle and blended under high agitation. Upon complete dispersion of lignin, nitric acid was added to reduce the adhesive pH to 7 ± 0.5, and stirring was continued for an additional 15 minutes before discharging.

2.4 Particleboard Production

A high speed Henschel mixer was used to blend TR-SPA with the wood-furnish at a loading of 10 wt% dry adhesive on dry wood. The adhesive-furnish blend was laid on top of a stainless steel platen and formed into a mat with the help of a casting frame. A leveler was used to evenly spread the material across the platen surface and ensure optimum density distribution. The wood blend sample was slid into the hydraulic press and compressed to a gap of 1.44 cm for 360 seconds at 193°C. Upon removal from the press, the partly cured edges of the mat were cut to form a 55.88 × 50.8 cm particleboard. The particleboard was then cut to appropriate sizes for testing mechanical properties.

3 RESULTS AND DISCUSSION

3.1 Adhesive

Soybean protein is commercially available in a number of forms containing various amounts of protein and carbohydrates. Apart from SPI, commercial soybean protein is available as soybean flour and soybean concentrates. Soybean flour is obtained by grinding and screening soybean flakes either before or after removing the oil and is the least refined form of soybean protein. Soybean protein concentrates are prepared from dehulled and defatted soybeans by removing most of the water-soluble, non-protein constituents. The composition of the various soybean products is shown in Table 1 [20].

Table 1 Percent Composition of Soybean Protein Products*.

	Defatted Flour	Concentrates	Isolates
Protein	56–59	65–72	90–92
Fat	0.5–1.1	0.5–1.0	0.5–1.0
Crude fiber	2.7–3.8	3.5–5.0	0.1–0.2
Soluble fiber	2.1–2.2	2.1–5.9	< 0.2
Insoluble fiber	17.0–17.6	13.5–20.2	< 0.2
Ash	5.4–6.5	4.0–6.5	4.0–5.0
Carbohydrates	32–34	20–22	3–4

* moisture-free basis

Soybean protein isolate has a zwitterionic pH of 4.5 and contains 22% of 2S (8–22 kDa), 37% of 7S (180–210 kDa), 31% of 11S (350 kDa), and 11% of 15S (600 kDa) components [22]. Thermal treatments induce dissociation, denaturation, and aggregation of 7S and 11S, whereas acid treatments lead to denaturation and selective dissociation and unfolding of 11S with lesser effect on 7S with minimal protein aggregation. Thermal-acidic treatments induce additional modifications such as hydrolysis and deamidation [23]. Intermolecular covalent disulfide linkages involving the amino acid cysteine, and hydrophobic and hydrogen bond interactions are believed to be the main associative forces in SPI. Although SPI contains many polar amino acids such as aspartic acid, threonine, serine, and glycine, an aqueous dispersion of SPI is a poor adhesive as the majority of polar and non-polar groups are unavailable for wood particle wetting due to protein reorganization [24]. Under alkaline conditions, the SPI denatures by cleaving the disulfide linkages, unfolds, and solubilizes, exposing sulfhydryl and hydrophobic groups that associate upon drying to form disulfide and van der Waals bonding force [25]. The exposed surface area of the unfolded protein enhances its contact area, and the available functional groups interact with the wood furnish to result in increased particleboard bond strength.

3.2 Adhesive Rheological Analysis

The UF resin utilized in particleboard manufacturing is a solution supplied at 55–65% solids and has a water-like consistency. On the other hand, TR-SPA formulated with SPI appears almost solid at ambient temperature, but thins readily upon application of shear and heat (Figures 1 and 2). In fact, at shear rates > 8000 sec^{-1}, TR-SPA formulated with SPI is lower in viscosity than conventional UF adhesives. Viscosity constraints during synthesis limited the SPI adhesive solids content to 48%.

Apart from SPI, adhesives were also synthesized using defatted soy flour (DSF)-grade of soybean protein that typically contains 52–54% protein and 30–32% carbohydrates. The higher carbohydrate content of DSF resulted in an adhesive with higher viscosity than the SPI-based adhesive (Figure 3). Consequently, the DSF-based adhesive could only be processed at 27.5% solids. To facilitate a direct comparison between SPI- and DSF-based adhesives, a SPI-based adhesive was also synthesized with 27.5% solids. The viscosity profiles of the two adhesives indicates that the DSF-based adhesive has approximately seven times the viscosity at any shear rate up to 8,000 sec^{-1}.

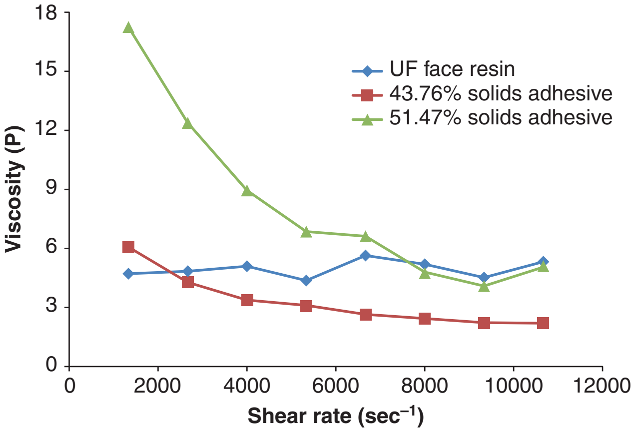

Figure 1 Rheological profile of UF resin and TR-SPA (at different solids content) at 25°C.

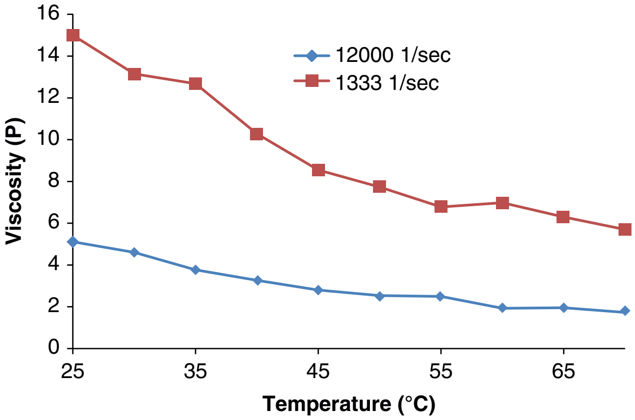

Figure 2 Forty-eight percent solids TR-SPA viscosity versus temperature.

Alkali treatment of protein results in protein denaturation, the extent of which depends on the specific alkali used and process temperature [26]. The exterior of a globular protein is denatured first, and as the protein is exposed to the alkali the proteins unfold, exposing additional surfaces to the alkali for the denaturation process to continue. Carbohydrates associated with proteins (either via *N*-glycosylation or *O*-glycosylation) typically occur on the exterior surface and form a partially protective interface around the protein [27]. Biologically, these glycoconjugates play a variety of roles in determining the function of the protein and antigenic specificity [26]. Chemically, the conjugated carbohydrates affect the process viscosity as they are liberated differentially; *N*-linked carbohydrates are liberated by alkali treatment while O-linked carbohydrates are liberated via acid treatment [27]. During the neutralization process, the carbohydrates that are no longer associated with proteins aggregate together due to their hydrophobic character having been altered by the alkali denaturation step. The carbohydrates favor a more hydrophilic environment, and are excluded from the denatured proteins upon neutralization of the reaction around pH 9.5. Below pH 9, the viscosity was reduced and the slurry became amenable to completing the neutralization process. The hyperviscosity caused by the carbohydrate phase separation from the protein slurry around pH 9.5 required that the total DSF adhesive solids be reduced as the amount of carbohydrate content increased from 25 wt% for SPI to 45 wt% solids for DSF. The final

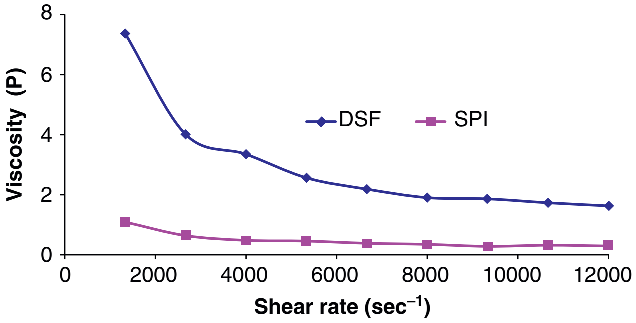

Figure 3 Viscosity profile of DSF and SPI adhesives (at 27.5% solids).

solids content of the DSF-based adhesive was reduced to compensate for the processability of the carbohydrate fraction around pH 9.5.

3.3 Mechanical Properties

The performance properties of particleboards formulated from adhesives at various solids content are shown in Table 2. Viscosity constraints limited the SPI adhesive solids content to 48%.

The MOR and MOE tests use static bending to compute the maximum fiber stress in the extreme upper and lower surface fibers of the specimen. The MOR is regarded as the product breaking strength and is also referred to as bending strength or flexural strength. The MOE refers to the material stiffness and is useful for calculating the product deflection under stress. The MOR is closely related to the board density and the amount of resin being used. The IB provides a measure of cohesion in the composite core.

Replacing SPI with DSF resulted in diminished particleboard performance but still exceeded ANSI M2 specifications (Table 3). Due to its low solids (25%), adhesive blends containing the DSF adhesive had lower adhesive solids than the SPI adhesive. This also meant that DSF adhesive-based fiber mats had proportionately higher moisture content prior to pressing, which results in higher steam pressure during pressing and the potential for delamination during the decompression cycle. The data in Table 4 indicate a gradual reduction in the board properties, particularly IB, indicating that increasing DSF content yields boards with poorer cohesion in the composite core. It is clear that the carbohydrates do not aid adhesion, but act as inert fillers and reduce SPI's adhesion potential.

3.4 Emissions

Figure 4 shows formaldehyde emissions determined via ASTM E 1333-96 of the particleboards processed at a commercial particleboard manufacturing facility. As expected, the soybean protein-based particleboards liberated significantly less formaldehyde than UF resin-based commercial-grade particleboards and UF resin-based commercial-grade boards containing a formaldehyde scavenger. Particleboards processed

Table 2 Particleboard Performance Properties.

Sample	Adhesive Solids	Density (g/cm^3)	MOR (MPa)	MOE (MPa)	IB (MPa)
ANSI M2	NA	0.64–0.80	≥ 13.00	≥ 2,000	≥ 0.45
Commercial particleboard	NA	0.81 ± 0.02	15.95 ± 1.60	2,744 ± 275	0.62 ± 0.06
TR-SPA	30%	0.81 ± 0.02	17.80 ± 1.75	3,213 ± 322	0.93 ± 0.09
	40%	0.82 ± 0.02	16.42 ± 1.62	3,040 ± 304	0.66 ± 0.07
	48%	0.81 ± 0.02	17.29 ± 1.71	3,613 ± 361	1.19 ± 0.12

Table 3 SPI-DSF Particleboard Properties.

Sample	Adhesive Solids	Density (g/cm^3)	Modulus of Rupture (MPa)	Modulus of Elasticity (MPa)	Internal Bond (MPa)
ANSI M2	NA	0.64 – 0.80	≥ 13.00	≥ 2,000	≥ 0.45
Commercial particleboard	NA	0.81 ± 0.02	15.95 ± 1.60	2,744 ± 275	0.62 ± 0.06
100% SPI : 0% DSF	45%	0.81 ± 0.02	15.98 ± 1.60	2,372 ± 237	1.08 ± 0.11
75% SPI : 25% DSF	40%	0.82 ± 0.02	17.18 ± 1.70	2,482 ± 248	0.95 ± 0.10
50% SPI : 50% DSF	35%	0.80 ± 0.02	14.58 ± 1.45	2,103 ± 210	0.73 ± 0.07
25% SPI : 75% DSF	30%	0.82 ± 0.02	14.30 ± 1.45	2,923 ± 292	0.63 ± 0.06
0% SPI : 100% DSF	25%	0.77 ± 0.02	7.62 ± 0.75	2,199 ± 220	0.63 ± 0.06

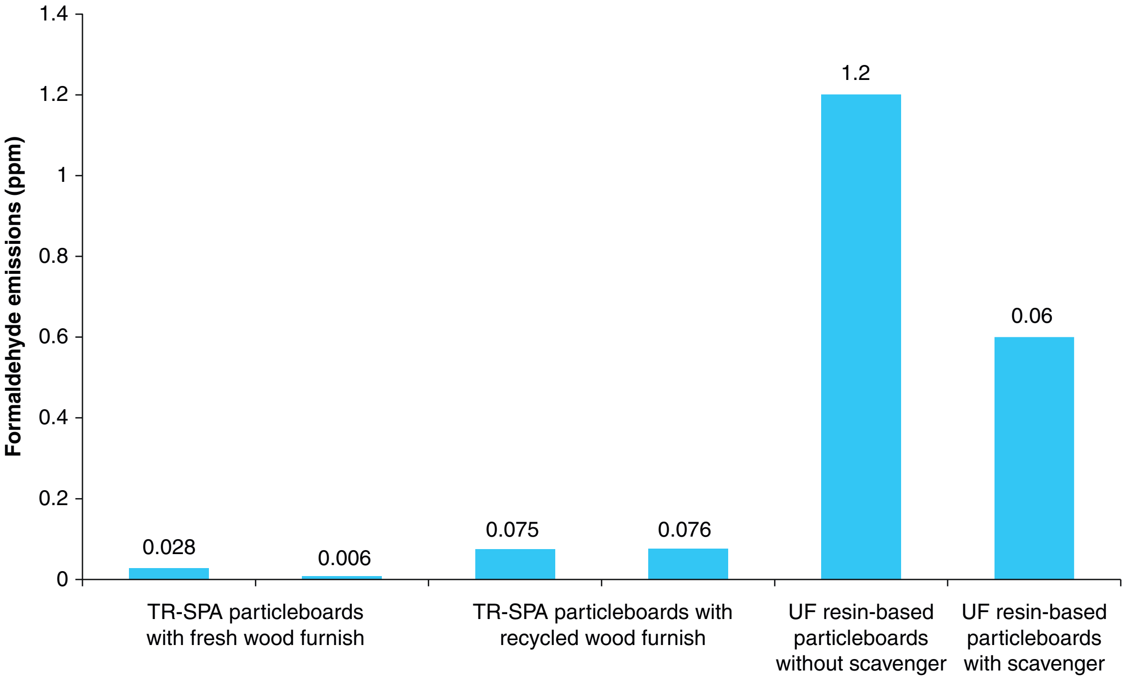

Figure 4 Formaldehyde emission from particleboards.

with soybean protein-based adhesive and wood furnish recycled from UF-resin based particleboards indicated the formaldehyde released from the UF resin associated with the recycled wood furnish. The low detectable levels of formaldehyde associated with the soybean protein-based particleboards stems from the formaldehyde liberated by wood itself under the test conditions.

4 CONCLUSION

The particleboard adhesive technology described here employs modified commercial grades of soybean protein as the sole binding resin. While the use of soybean protein as a binder is not entirely new, previous efforts to employ this natural resource were hampered by the protein's inherent hydrophilicity that was carried over to the final product, and/or the premature biodegradation of the adhesive prior to particleboard production. By selectively treating and stabilizing the protein prior to formulating the adhesive, the protein was partially denatured without sacrificing adhesion, and the resulting particleboards displayed performance properties comparable to commercial particleboards. Moreover, this adhesive formulation does not contain a wax emulsion and is totally free of all petroleum derivatives. Research efforts are underway to increase the adhesive solid content without raising the viscosity and reducing press times.

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