Investigation of Soy Protein-Kymene®
Adhesive Systems for Wood Composites

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ABSTRACT: This study investigated a new adhesive system, consisting of soy protein isolate (SPI) and Kymene® 557H (simply called Kymene) (a commercial wet-strength agent for paper), that was prepared by mixing SPI and Kymene. Wood composites bonded with SPI-Kymene adhesive preparations had shear strengths comparable to or higher than those bonded with commercial phenol formaldehyde resins. Wood composites bonded with the new adhesive system had high water resistance and retained relatively high strength even after they had undergone a boiling-water test. The new adhesive system is formaldehyde-free, easy to use, and environmentally friendly. Kymene was proposed to serve as a curing agent in SPI-Kymene adhesives.

Paper no. J10654 in *JAOCS 81*, 487–491 (May 2004).

KEY WORDS: Adhesive, Kymene, shear strength, soy protein, wet-strength agent, water resistance, wood composites.

Soybeans, one of the major crops in the United States, consist of about 40% protein, 21% fat, 34% carbohydrate, and 4.9% ash, thereby making soy protein one of the most abundant biopolymers (1,2). Soy protein is used mainly for animal feed and food applications. However, in recent years, the existing U.S. markets for soy protein have faced very tough competition from foreign countries, especially those in South America. This international competition has led to a loss of export markets. As a result, extensive efforts are being made to find new uses for soy protein in other markets.

One market with significant volume potential for soy protein is wood adhesives. In 1999, the forest products industry in the United States and Canada spent over $7.4 billion on wood adhesives (3). Formaldehyde-based wood adhesives [e.g., urea formaldehyde (UF) resins, phenol formaldehyde (PF) resins, and melamine formaldehyde (MF) resins] predominate in the wood adhesive market (4). The UF resins, however, have a tendency to release formaldehyde during the manufacture and use of wood panels (4–7). Formaldehyde vapor is potentially carcinogenic and is hazardous to human health, causing eye and throat irritations as well as respiratory discomfort (8–10). Tightened environmental regulations on the emission of volatile organic compounds, including formaldehyde, in the production and use of wood composites have generated pressure on the forest products industry to develop more environmentally friendly wood adhesives. Moreover, most commercial wood adhesives use petrochemicals as raw materials. The high volatility of the petroleum markets has caused great economic losses in the wood composites industry (11). In addition, there is a concern about the long-term supply of global oil resources. Therefore, increasing concerns about the effects of emissive formaldehyde on human health and our heavy dependence on petrochemicals have generated a need for development of formaldehyde-free wood adhesives from renewable natural resources.

The use of soy protein as an adhesive dates back to ancient times, although its first commercial use as a wood adhesive for the production of plywood did not begin until the 1930s (12). As a wood adhesive, soy protein has many unique properties such as low cost, ease of handling, low press temperatures, and the ability to bind wood with relatively high moisture content. Because wood composites bonded with soy protein have a relatively low strength, low resistance to water, and sensitivity to biological degradation, virtually all major markets for soy protein-based adhesives have now been taken over by stronger and more water-resistant formaldehyde-based adhesives. However, soy protein represents a very practical and inexpensive material for wood adhesives. Its former use as a wood adhesive in the 1930s to 1960s and its positive public perception would make it very competitive as a wood adhesive if economical techniques to overcome its drawbacks could be developed.

In recent years soy protein has been added to PF and phenol-resorcinol-formaldehyde adhesives to lower the emission of formaldehyde (13,14). Modifications of soy protein with either alkali or the protease enzyme trypsin have significantly improved its adhesive strength and water resistance (15,16). Addition of urea, guanidine hydrochloride, and SDS has led to greater improvements in adhesive strength and water resistance than those obtained from the alkali treatment (17–19). These results greatly improve our understanding of soy protein-based adhesives. However, the overall performance of these modified soy proteins, in terms of adhesive strength and water resistance, is still not comparable with synthetic resins such as PF and resorcinol PF. In this paper, we report on an innovative way of utilizing soy protein in a formaldehyde-free wood adhesive with strength properties comparable to commercially used PF resins. The adhesion mechanisms of this new adhesive system are discussed.

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MATERIALS AND METHODS

Materials. Sugar maple veneer was a gift from State Industry (Eugene, OR). Kymene® 557H wet-strength resin was a gift from Hercules Inc. (Wilmington, DE). The solids content of Kymene 557H wet strength resin was 12.5%. Soy protein isolate (SPI) consisting of 86 wt% protein and about 14 wt% of carbohydrates was provided by Protein Technologies International (St. Louis, MO). PF resins (RPMX272A79) for production of laminated veneer lumber were provided by Georgia Pacific Resins, Inc. (Albany, OR).

Preparation of alkaline SPI. Alkaline SPI was prepared based on the methods of Hettiarachchy and colleagues (15,16). SPI powder (30 g) was mixed with 400 mL of distilled water at room temperature and then stirred for 120 min. The pH value of the mixture was then adjusted to 10 with 1 N sodium hydroxide. The mixture was mixed in a shaker at 50°C and 180 rpm for 120 min. It was then concentrated to two-thirds of its original volume with an Amicon membrane concentrator (the membrane had a 10 kDa M.W. cutoff), freeze-dried, and used as an adhesive ingredient.

Preparation of SPI-Kymene wood adhesives. Alkaline SPI (5.0 g) was added to Kymene 557H (30 mL) and stirred at room temperature. A sample was removed from the SPI-Kymene reaction mixture at a predetermined time and used as an adhesive for bonding sugar maple veneer. SPI and Kymene at a 1.33:1 SPI/Kymene dry weight ratio were mixed for 60 min. The resulting SPI-Kymene adhesive was then used to make wood composites for the evaluation of dry strength and water resistance [the boiling-water test (BWT)]. The solution of alkaline SPI (5.0 g) in water (30 mL) served as a control.

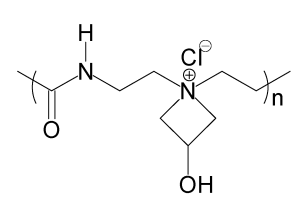
Preparation of wood composites and measurement of lap-shear strengths of the composites. Alkaline SPI-Kymene adhesive preparations, the alkaline SPI solution, the Kymene 557H solution, and the PF resins were evaluated for their abilities to bond two pieces of maple veneer. The bonding area was 1 cm^2 (1 × 1 cm). An adhesive preparation was applied to one side and one end of a maple veneer strip (1 × 10 cm). The adhesive spread rate was 10 mg/cm^2 on a dry adhesive basis. Two maple veneer strips were stacked together and hot-pressed at 120°C for 5 min at a pressing pressure of 200 psi. The lap-shear strength was measured with an Instron Testing Machine. The crosshead speed was 1 mm/min. Bond strength was reported as the maximum shear strength at breakage between two pieces of maple veneer.

Water resistance of the wood composites. A water-soaking-and-drying (WSAD) test was used to evaluate the water resistance of the wood composites for interior application (17–19). More specifically, the bonded wood composites were soaked in water at room temperature for 24 h, dried at room temperature in a fume hood for 24 h, and their shear strengths were measured. A separate BWT was performed in accordance with U.S. Voluntary Product Standard PS l-95 for Construction and Industrial Plywood (published by the U.S. Department of Commerce through APA—The Engineered Wood Association, Tacoma, WA); i.e., test specimens were boiled in water for 4 h and then dried for 20 h at 63 ± 3°C. The specimens were boiled in water again for 4 h and cooled with tap water. Some specimens were evaluated for shear strength while wet. The shear strength determined in this fashion was defined as BWT/wet strength. Some specimens were further air-dried in a fume hood for 24 h and evaluated for shear strength. This shear strength was defined as BWT/dry strength.

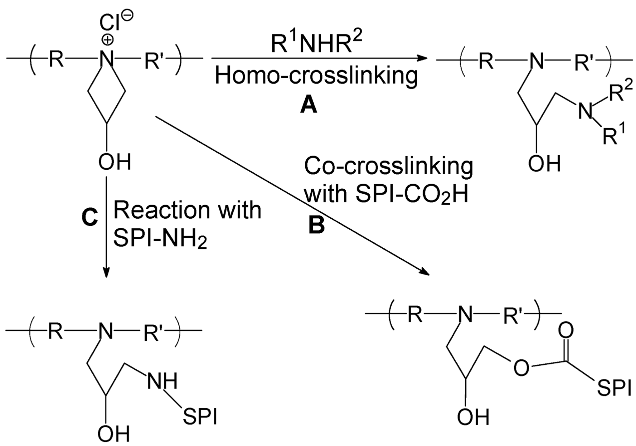
RESULTS AND DISCUSSION

Kymene 557H, a commercial product that is widely used to strengthen wet paper, is an aqueous solution of cationic polyamidoamine-epichlorohydrin (PAE) resins. A representative chemical structure of PAE resins is shown in Scheme 1 (20,21). It is well established that hydroxy-azetidium (the cationic four-membered ring structure) is the key functional group for wet-strength development in paper (22,23). According to the well-defined chemistry and wet-strength-enhancing mechanisms of PAE resins (22–29), many reactions can occur in SPI-Kymene adhesives at elevated temperatures. Major reactions in the cure of SPI-Kymene adhesives are proposed in Scheme 2. First, the azetidium group in PAE resins reacts with the remaining secondary amines in the PAE resin, thus causing homo-crosslinking (reaction **A** in Scheme 2). Second, the azetidium group may also react with carboxylic acid groups such as those of glutamic acid and aspartic acid in SPI (reaction **B** in Scheme 2). Third, various amino groups in SPI can also react with the azetidium group (reaction **C** in Scheme 2). All these reactions result in a water-insoluble 3-D network.

The effects of reaction time between Kymene 557H and alkali-modified SPI on lap-shear strengths of wood composites bonded with SPI-Kymene adhesives are shown in Figure 1. Results of a statistical analysis using a Welch-modified two-sample *t*-test revealed that there was no statistical difference between any two dry strengths at a 95% confidence level, except that the dry strength at a reaction time of 30 min was significantly lower than that at a reaction time of 60 min ($P = 0.0011$). Wood composites bonded with SPI-Kymene adhesives also underwent an WSAD test. The two-sample *t*-test analysis showed that there was no statistical difference between any two WSAD strengths at a 95% confidence level. There was also no statistical difference between the dry shear strength and the WSAD shear strength at any given reaction time at a 95% confidence level, which implied that their strengths did not decrease after the specimens were subjected to an WSAD test. No delamina-



SCHEME 1



SCHEME 2

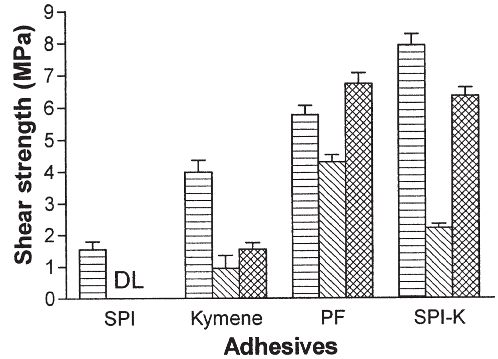


FIG. 2. Water resistance of wood composites bonded with various SPI-Kymene adhesive preparations. Shear strength of dry wood composites (horizontally lined bars); boiling-water test (BWT)/wet shear strength (diagonally lined bars); BWT/dry shear strength (cross-hatched bars). SPI: alkaline SPI only. Kymene: Kymene only. PF: phenol formaldehyde resins only. SPI-K: SPI-Kymene adhesives with 1.33:1 SPI/Kymene weight ratio, reaction time between SPI and Kymene, 60 min. DL: delamination of the wood composites. Data are the means of at least six replicates, and the error bar represents one SD. For abbreviations see Figure 1.

tion was found on any of the wood composite specimens bonded with SPI-Kymene adhesives.

Shear strengths of wood composites bonded with alkaline SPI, Kymene, PF resins, and SPI-Kymene adhesive are shown in Figure 2, and the *P*-values from the Welch-modified two-sample *t*-test of shear strengths are shown in Table 1. Wood composites bonded with alkaline SPI had the lowest dry strength when compared with other adhesives (Fig. 2). PF resins resulted in higher dry shear strength than Kymene. The dry shear strength with the SPI-Kymene adhesive was statistically higher than those with alkaline SPI, PF resins, and Kymene (Fig. 2, Table 1). The water resistance of wood composites bonded with SPI-Kymene adhesive systems was further evaluated with a BWT (Fig. 2). All wood composite specimens bonded with alkaline SPI alone completely delaminated in the BWT. After wood composite specimens underwent a BWT, BWT/dry and BWT/wet strengths of wood composites bonded with Kymene alone decreased dramatically. For PF resins, BWT/wet strengths were lower than the dry shear strength, whereas the BWT/dry strengths were higher than the dry strength at a 95% confidence level. For SPI-Kymene (SPI-K) adhesives, i.e., SPI-Kymene adhesives with the 1.33:1 SPI/Kymene weight ratio, the BWT/wet strengths were much lower than the corresponding dry strengths (Fig. 2). The BWT/wet strengths with SPI-K were lower than the corresponding BWT/wet strengths with PF resins. However, the BWT/dry strengths with SPI-K were comparable to the corresponding BWT/dry strengths with PF resins ($P = 0.3901$, Table 1). No delamination was observed for any wood composites bonded with SPI-Kymene adhesives and PF resins, whereas some delamination occurred for the wood composites bonded with Kymene alone.

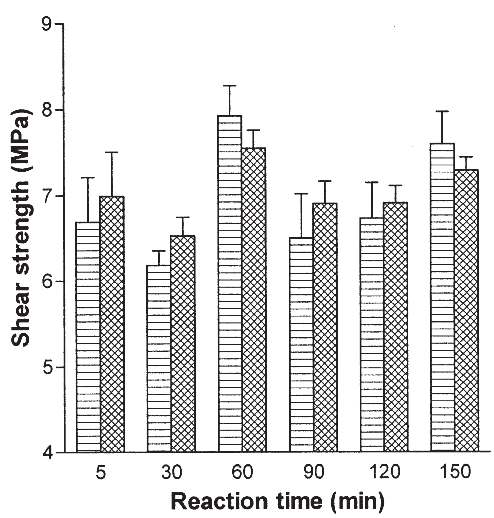


FIG. 1. Effects of reaction time between Kymene 577H (a commercial wet-strength resin; Hercules, Wilmington, DE) and soy protein isolate (SPI) on lap-shear strengths. SPI-Kymene adhesives (weight ratio of SPI vs. Kymene, 1.33) (horizontally lined bars); SPI-Kymene adhesives (weight ratio of SPI vs. Kymene, 1.33) after one water-soaking-and-drying cycle (cross-hatched bars). Data are the means of at least 10 replicates, and the error bar represents one SD.

At present, the merit of the BWT for wood composites is still controversial because wood composites are rarely exposed to such harsh conditions. However, there is a consensus that the wood adhesive can be used to make structural panels for outdoor applications if the wood composites retain reasonable strength and do not delaminate after a BWT. The BWT/wet strengths for the wood composites bonded with SPI-Kymene adhesives were still very high (*ca.* 2 MPa), a level that can even meet shear strength requirements for dry structural panels. More importantly, the wood composites regained most of their strength when they were re-dried. Soy protein has less water resistance, especially in boiling water, than PF resins because the abundant amide linkages in soy protein are hydrophilic. Therefore, it is understandable that BWT/wet strengths with SPI-Kymene adhesives were lower than those with PF resins.

The SPI-Kymene system as a wood adhesive has these unique features: (i) The key ingredient, soy protein, is abundant

TABLE 1
***P* Values of Welch Modified Two-Sample *t*-Test for Shear Strengths Shown in Figure 2[a]**

	SPI dry	Kymene dry	Kymene BWT/wet	Kymene BWT/dry	PF dry	PF BWT/wet	PF BWT/dry
SPI dry							
Kymene dry	0.0002						
Kymene BWT/wet		0.0001					
Kymene BWT/dry		0.0027	0.224				
PF dry	0.0						
PF BWT/wet			0.0001		0.0022		
PF BWT/dry				0.0	0.05	0.0002	
SPI-K dry	0.0	0.0			0.0004		
SPI-K BWT/wet			0.023			0.0001	
SPI-K BWT/dry				0.0			0.3901

[a]SPI, soy protein isolate; Kymene, a commercial wet-strength resin (Hercules, Wilmington, DE); BWT, boiling-water test; PF, phenol formaldehyde resin.

and renewable; (ii) it is formaldehyde-free; (iii) the wood composite products are attractive because of the light color of the SPI-Kymene glue line, whereas PF resins give dark glue lines. SPI-Kymene adhesives have the potential to meet strength and water-resistance requirements for exterior wood composites. However, SPI-Kymene adhesives are not cost-competitive with PF resins for making exterior wood composites because SPI is currently too expensive for use as a wood adhesive. On the other hand, soy flour is inexpensive and strength and water-resistance requirements for interior wood composites are lower than those for exterior wood composites. Soy flour-Kymene adhesives may be able to replace UF resins for making interior used wood composites.

Kymene 557H is odorless and light amber in color and is safe for use. This SPI-Kymene adhesive system was cured under commonly used conditions (press time, press temperature, and press force) for the production of wood composites. This new adhesive is an aqueous solution and is easy to apply to wood furnishes. Therefore, it should be easy to fit this new adhesive into currently used production lines for wood composites. We anticipate that the new adhesive chemistry and the results from this study will help promote research on the development of formaldehyde-free wood adhesives for commercial use.

ACKNOWLEDGMENTS

This project was supported by a grant from the National Research Initiative Competitive Grants Program of the USDA (award number: 2001-35504-10993). We thank Protein Technologies International (St. Louis, MO) for providing us with the SPI isolate. We greatly appreciate the Kymene 557H wet-strength resin from Hercules Inc. (Wilmington, DE), sugar maple veneer from State Industry (Eugene, OR), and PF resins from Georgia Pacific Resins, Inc. (Albany, OR).

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[Received May 27, 2003, accepted March 11, 2004]