

# SOY-BASED ADHESIVES WITH 1, 3-DICHLORO-2-PROPANOL AS A CURING AGENT

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## ABSTRACT

Increasing concern over the impact of formaldehyde on human health has prompted a need for a formaldehyde-free wood adhesive. In this study, we investigated a new formaldehyde-free wood adhesive system consisting of soy protein (SP) and 1, 3-dichloro-2-propanol (DCP). DCP served as a crosslinking agent for SP. The shear strength of wood composites bonded with a SP-DCP adhesive depended on the SP/DCP weight ratio and the reaction conditions such as reaction time and reaction temperature under which the SP-DCP adhesive was prepared. For a given SP/DCP weight ratio, the higher the reaction temperature, the higher the shear strength. Under the same reaction conditions, increasing the SP/DCP weight ratio, i.e., decreasing the relative amount of DCP in the adhesive, resulted in a decrease in the shear strength and water resistance of the resulting wood composites. Of all the SP/DCP weight ratios studied, 6:1 SP/DCP weight ratio at 85°C for 1.0 h gave the highest shear strength in the resulting wood composites. In terms of the shear strength, the 8:1 and 10:1 SP/DCP weight ratios were comparable to each other and were only slightly lower than with the 6:1 SP/DCP ratio. Further increasing the SP/DCP ratio to 12:1 or 15:1 greatly decreased the shear strength. The shear strength slightly increased with pressing temperature in the range of 100°C to 160°C at a press time of 5 min. Press times in the range of 1 min to 9 min had insignificant effects on the shear strength at a press temperature of 140°C. Storage of SP-DCP adhesive at room temperature for one or two days did not significantly affect the shear strength. However, a significant reduction of the shear strength was observed after the adhesive was stored at room temperature for 5 days. Wood composites bonded with a SP-DCP adhesive did not delaminate after they underwent a water-soaking-and-drying test and a boiling-water test. The crosslinking reactions between SP and DCP are discussed in detail.

*Keywords:* Adhesive, 1, 3-dichloro-2-propanol, shear strength, soy protein, water resistance, wood composites.

## INTRODUCTION

Formaldehyde-based wood adhesives such as urea-formaldehyde (UF) and phenol-formaldehyde (PF) resins currently dominate the

wood adhesive market (Sellers 2001). Formaldehyde may emit into the air during the manufacture and use of wood composites bonded with UF adhesives (Henderson 1979; Meyer and Hermans 1986; Marutzky 1989; Baumann et al. 2000). Formaldehyde is a suspected human carcinogen, and causes eye and throat irritation, and

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respiratory discomfort (Swenberg et al. 1980; Perera and Petito 1982; Heck et al. 1990). In addition, formaldehyde is on the list of chemicals that may cause Sick Building Syndrome. Therefore, the forest products industry faces ever-increasing restrictions on the use of formaldehyde and has a strong interest in developing formaldehyde-free wood adhesives.

Formaldehyde-based wood adhesives are derived from petrochemicals, but natural gas and fossil oils are naturally limited. The development of wood adhesives from renewable resources will thus be important for the sustainable growth of the forest products industry.

Soy protein (SP) is a good renewable material for making wood adhesives because it is inexpensive, abundant, easy to handle, and environmentally friendly (Lambuth 1977, 1989; Liu 1997). In fact, soy protein-based adhesives were widely used in plywood production from the 1930s to the 1960s (Lambuth 1989; Liu 1997). However, wood composites bonded with soy protein-based adhesives had relatively low strengths, low water/moisture resistance, and sensitivity to biological degradation, in comparison to UF and PF resins (Lambuth 1989). If these problems can be solved, soy-based adhesives could be used to replace formaldehyde-based adhesives for the production of some interior-type wood composites.

In an effort to develop formaldehyde-free wood adhesives from renewable materials, 1, 3-dichloro-2-propanol (DCP), a widely used solvent and reagent in various industries, was investigated as a crosslinking agent for soy protein in making SP-DCP wood adhesives.

## EXPERIMENTAL

### *Materials*

Sugar maple veneer with dimensions of 2,500 mm  $\times$  1,270 mm  $\times$  0.64 mm was contributed by State Industries (Eugene, Oregon). Soy protein, Pro-Cote® PC-150 soy polymer in powder form, was donated by Protein Technologies International (St. Louis, Missouri). The SP was a soy protein isolate with approximately 80% soy

protein content. Sodium hydroxide and 1, 3-dichloro-2-propanol (DCP) were purchased from Acros Organics (Geel, Belgium) and used as received.

### *Adhesive preparation*

Deionized water (50 mL) in a round bottom flask equipped with a condenser and a magnetic stirrer was heated to about 40°C in a heated oil bath. SP (8.82 g) was then added to the water and stirred until well dispersed. Sodium hydroxide (0.53 g) was added to the SP suspension, and the mixture was stirred until all SP dissolved. The resulting SP solution had 15% total solids content and a pH value of approximately 11.

DCP was added dropwise to an SP solution that had been heated to a predetermined reaction temperature. After a predetermined reaction time, the reaction was stopped by removing the reaction mixture from the oil bath and allowing it to cool to room temperature. The resulting adhesive was used immediately for bonding maple veneer, except in the case of storage experiments. For the storage experiments, the resulting adhesive was stored at room temperature until used at 1–5 days.

### *Preparation of wood composites*

Maple veneer was cut into small strips (7.62 cm wide  $\times$  17.78 cm long  $\times$  0.06 cm thick) with the wide direction being parallel to the wood grains. Three maple veneer strips were bonded with various SP-DCP adhesive preparations to form two-ply composite boards with two lap-joint gluelines. Two outside strips were brushed with a SP-DCP adhesive on the surface of one of its ends, and the central strip was brushed on the surface of both its ends along the long direction with the adhesive. The adhesive-brushed areas of these three maple veneer strips were overlapped and then hot-pressed at 19.1 kg/cm<sup>2</sup> pressure with a Carver bench-top press. The press temperature and time varied with the requirements of the experiment. The resulting composite board had two gluelines, and the bonding area of each glueline was 17.78 cm<sup>2</sup> (1 cm  $\times$  17.78

cm). Test specimens with a width of 1.5 cm were cut from these boards. These test specimens had two gluelines of 1.5 cm<sup>2</sup> each. Spread rates were approximately 28 to 42 mg/cm<sup>2</sup>, which allowed for adequate squeeze-out.

#### *Measurement of lap-shear strengths*

The freshly made test specimens were stored at an ambient environment for at least 24 h before they were evaluated for shear strengths. The shear strength of each specimen was obtained with an Instron TTBML universal testing machine equipped with pneumatic grips. The crosshead speed was 1 mm/min. The maximum shear strength at breakage was recorded and the degree of cohesive or adhesive failure observed.

#### *Water resistance of the wood composites*

Water resistance of the wood composites was determined by the following three methods: water-soaking-and-drying (WSAD), boiling-water-test (BWT)/wet, and BWT/dry. The procedure for the WSAD was as follows: the test specimens were soaked in water at room temperature for 24 h, and then dried in a fume hood at room temperature for 24 h before being evaluated for shear strength. The BWT/wet was performed in accordance with U.S. Voluntary Product Standard PS1-95 for Construction and Industrial Plywood (published by the U.S. Department of Commerce through APA—The Engineered Wood Association, Tacoma, WA). Specifically, test specimens were boiled in water for 4 h, dried at 63°C ± 3°C for 20 h, and then boiled in water again for 4 h, and cooled with tap water. The shear strength was immediately evaluated while the test specimens were still wet. For BWT/dry, test specimens underwent the BWT/wet procedure and were further dried at room temperature in a fume hood for 24 h before the shear strength was evaluated.

### RESULTS

At the reaction temperature of 60°C, the reaction time had little impact on the shear strengths

of wood composites bonded with SP-DCP adhesives, and the shear strengths were lower than, or comparable to, those with SP only, i.e., the control (Fig. 1). At the reaction temperature of 80°C, the shear strengths gradually increased with an increase in reaction time (Fig. 1). However, the shear strengths were statistically higher than those of the control only at the reaction time of 3.0 h. When the SP-DCP adhesives were prepared at 85°C, the shear strengths greatly increased with the reaction time being prolonged from 0.5 h to 1.5 h (Fig. 1). However, further prolongation of the reaction time from 1.5 h to 3.0 h resulted in a decrease in the shear strengths. Shear strengths at 85°C and reaction times of 1.5 h or 3.0 h were much higher than those of the control. It appeared that the increase in the reaction temperature from 80°C to 85°C made a significant difference in the shear strengths.

Because DCP served as a crosslinking agent, the SP/DCP weight ratio had a great impact on the shear strength (Fig. 2). At the 6:1 SP/DCP weight ratio, the maximum shear strengths occurred at a reaction time of 1.0 h. At the 8:1 SP/DCP weight ratio, the shear strengths increased when the reaction time increased from 0.5 h to 2 h, and then decreased when the reaction time further increased from 2 h to 3 h. In other words, the maximum shear strengths resulted at the reaction conditions of 85°C for 2 h. As described previously, the maximum shear strength for the 10:1 SP/DCP weight ratio was observed at 85°C and 1.5 h. When the SP/DCP weight ratio was raised to 12:1 or 15:1, the shear strengths of the wood composites bonded with the resulting adhesives at all reaction temperatures studied were much lower than those at other SP/DCP ratios, and the reaction time had little effect on the shear strengths. In summary, SP-DCP adhesives prepared from the 6:1 SP/DCP weight ratio at the reaction conditions of 85°C and 1 h resulted in the highest shear strengths, whereas the adhesives prepared from the 8:1 SP/DCP weight ratio at the reaction conditions of 85°C and 2.0 h were comparable to those prepared from the 10:1 SP/DCP weight ratio at the reaction conditions of 85°C and 1.5 h

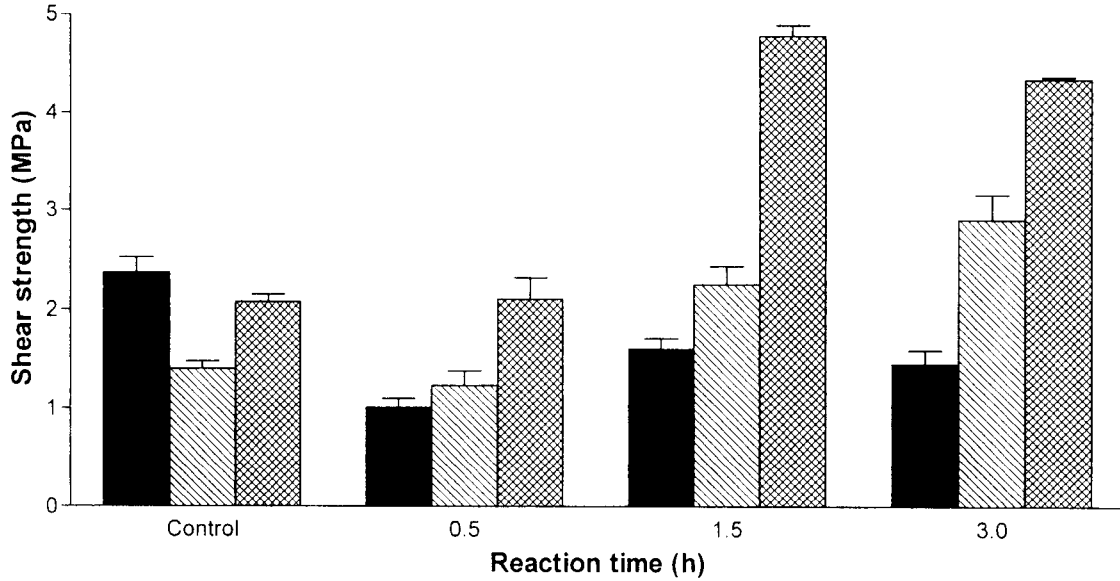


FIG. 1. Effect of reaction temperature and reaction time on the shear strength of wood composites bonded with SP-DCP adhesives (10:1 SP/DCP weight ratio). Press conditions were 5 min at 120°C. Reaction temperature: 60°C (■), 80°C (▨), 85°C (▩). Data are the means of at least six independent measurements, and the error bars show the standard error of the means. Control signifies that the adhesive consisted of dissolved SP only.

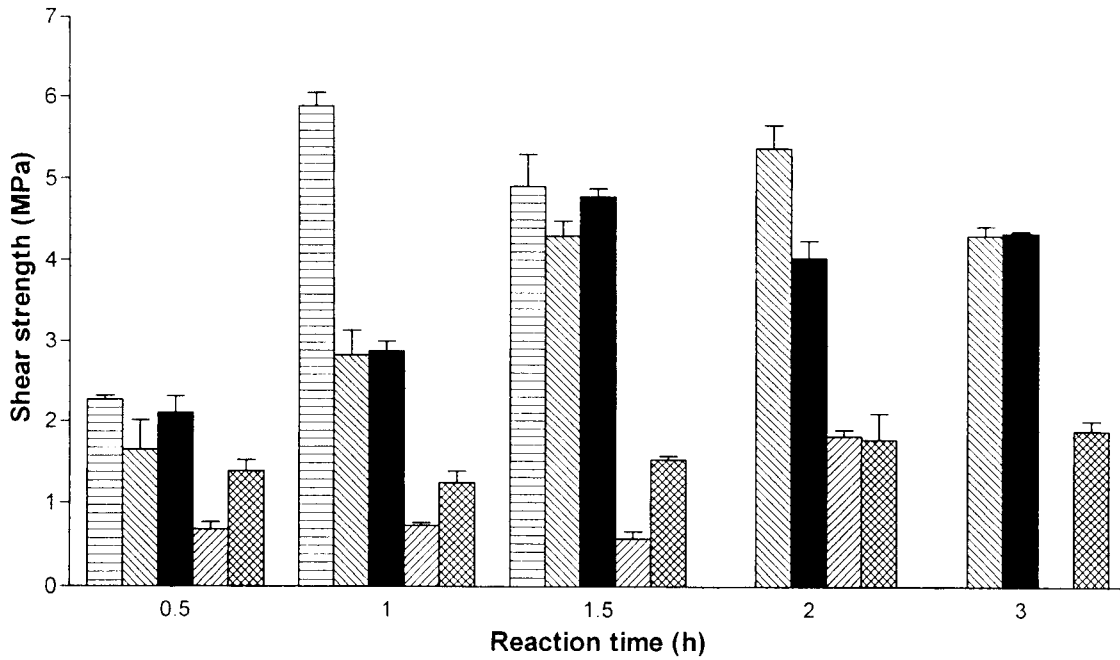


FIG. 2. Effect of the SP/DCP ratio and the reaction time on the shear strength of wood composites bonded with SP-DCP adhesives. The adhesives were prepared from the reaction of SP and DCP at 85°C for 1.5 h. Pressing conditions for wood composites bonded with SP-DCP adhesives were 5 min at 120°C. SP/DCP weight ratio: 6:1 (▨), 8:1 (▩), 10:1 (■), 12:1 (▨), 15:1 (▩). Data are the means of at least six independent measurements, and the error bars show the standard error of the means.

in terms of the shear strengths. It is desirable to use more SP than DCP in the adhesives because SP is renewable, readily available, and less expensive than DCP. Therefore, the 10:1 SP/DCP weight ratio was further studied to determine the optimum hot-press conditions for wood composite manufacture.

The shear strengths of wood composites bonded with SP-DCP adhesives slightly increased when the hot-press temperature increased from 100°C to 160°C (Fig. 3). The hot-press time in the range of 1 min to 9 min had little effect on the shear strengths (Fig. 4). In other words, 1 min is almost as good as 9 min of press time for this adhesive. Figure 5 shows the effect of storage time of SP-DCP adhesives prepared from the 10:1 SP/DCP weight ratio at the reaction conditions of 85°C and 1.5 h on the shear strengths. Storage of the adhesive for one day had little effect on shear strength. Shear strength decreased slowly with increasing storage time. After the wood composites bonded with the SP-DCP adhesives underwent a water-soaking-and-drying (WSAD) test, the shear strengths decreased by about 7% compared to

the dry composite samples (Fig. 6). After the wood composites underwent boiling-water tests (BWT), BWT/dry shear strengths decreased by about 65% and BWT/wet shear strengths decreased by about 90%. However, no delamination of the wood composites was observed after the BWT. The water resistance of wood composites bonded with the SP only is not reported because these composites specimens suffered 100% delamination under either WSAD or BWT.

#### DISCUSSION

The major reactions between DCP and -OH and -NH<sub>2</sub> of SP are proposed in Scheme 1. With catalysis by NaOH, DCP would likely first form epichlorohydrin 1 that could further react with many nucleophiles, such as -NH<sub>2</sub>, -OH, -SH, and -COOH groups, in SP. For instance, the reaction of epichlorohydrin 1 with -OH and -NH<sub>2</sub> groups in SP would yield 2 and 5, respectively. The newly formed 2 and 5 could be further converted to epoxide-containing SP 3 and 6, respectively. Reaction of 3 with -OH and -NH<sub>2</sub> groups in SP

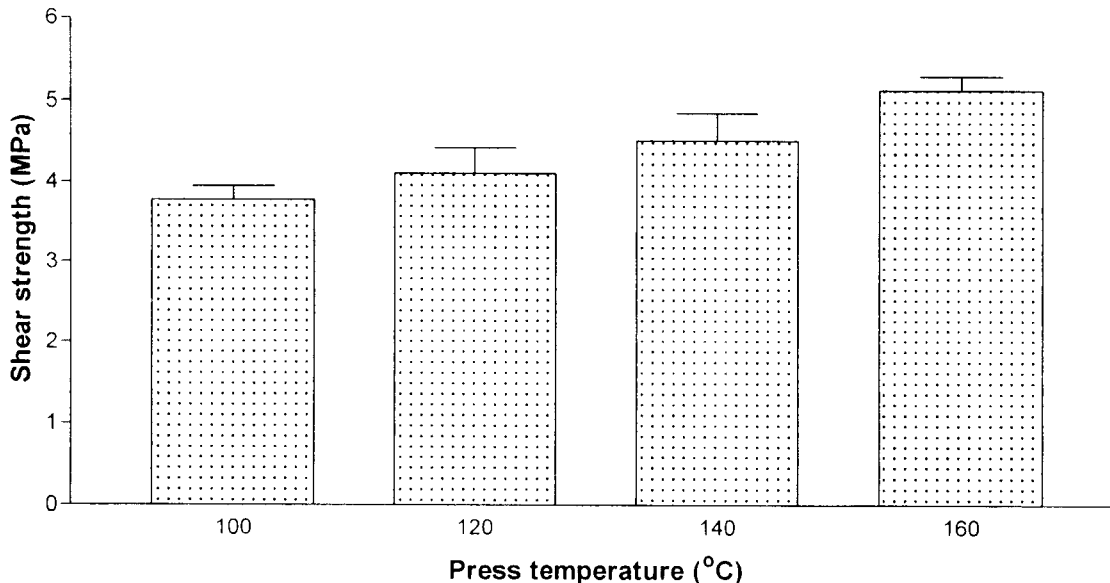


FIG. 3. Effects of press temperature on the shear strength of wood composites bonded with SP-DCP adhesives. The adhesives were prepared from the reaction of SP and DCP (10:1 SP/DCP weight ratio) at 85°C for 1.5 h. The press time was 5 min. Data are the means of at least six independent measurements, and the error bars show the standard error of the means.

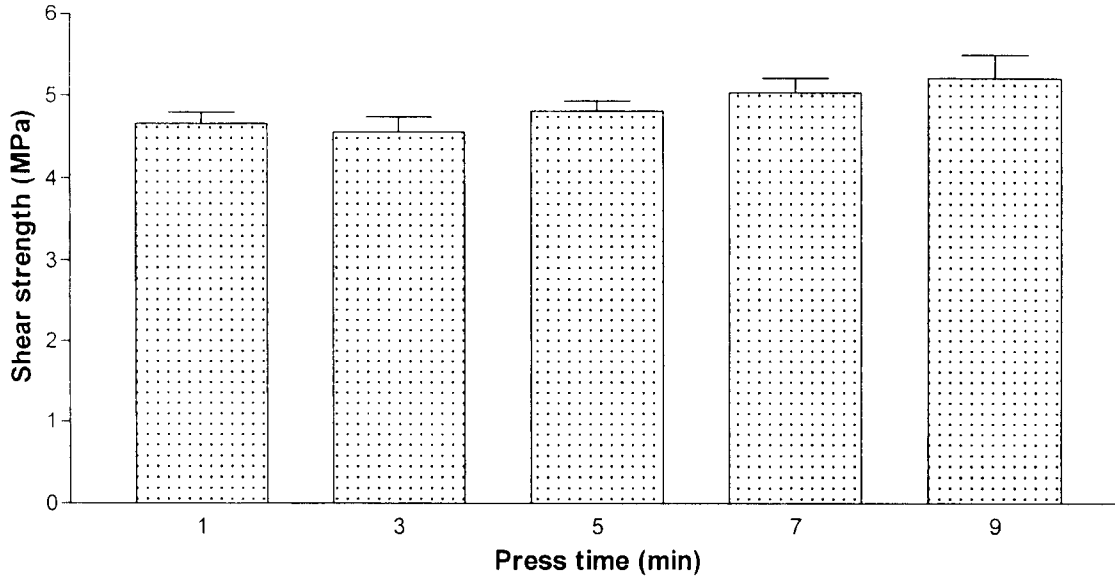


FIG. 4. Effects of press time on the shear strength of wood composites bonded with SP-DCP adhesives. The adhesives were prepared from the reaction of SP and DCP (10:1 SP/DCP weight ratio) at 85°C for 1.5 h. The press temperature was 140°C. Data are the means of at least six independent measurements, and the error bars show the standard error of the means.

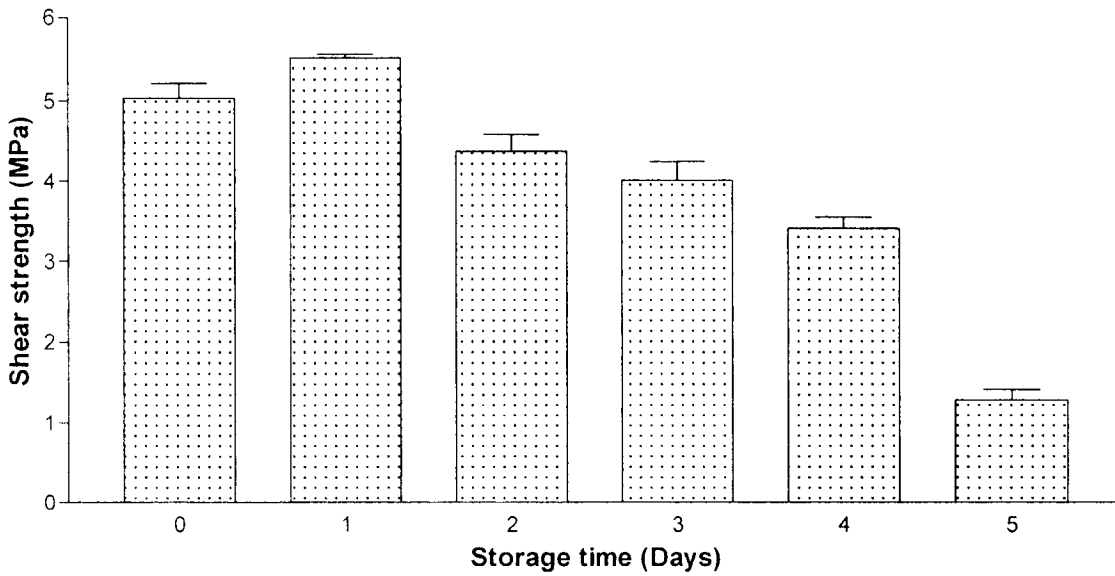


FIG. 5. Effect of storage time on the shear strength of wood composites bonded with SP-DCP adhesives. The adhesives were prepared from the reaction of SP and DCP (10:1 SP/DCP weight ratio) at 85°C for 1.5 h. The press conditions were 7 min at 140°C. Data are the means of at least six independent measurements, and the error bars show the standard error of the means.

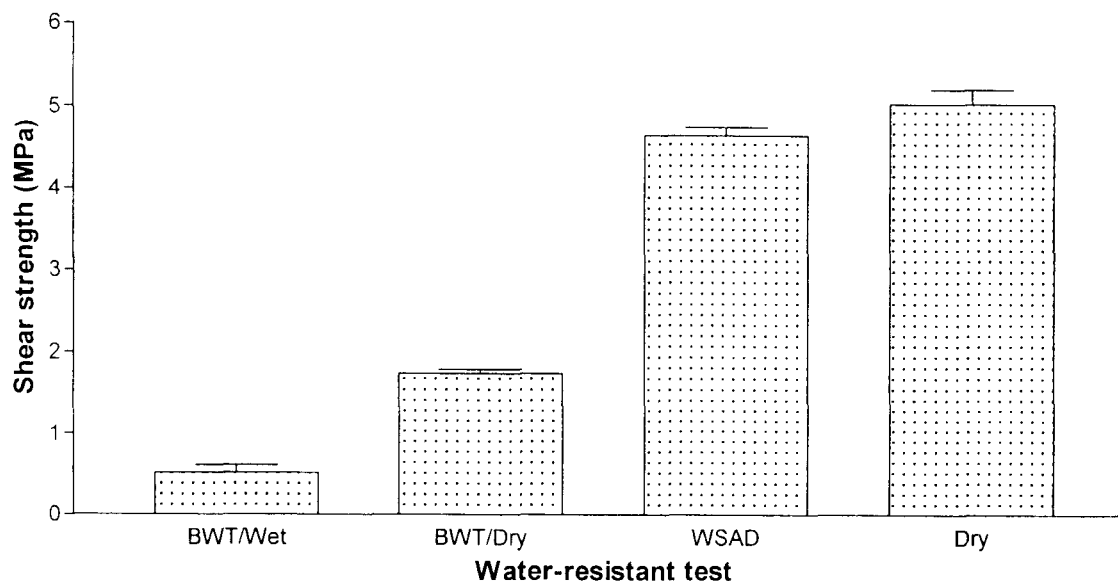


FIG. 6. Water resistance of wood composites bonded with SP-DCP adhesives. The adhesives were prepared from the reaction of SP and DCP (10:1 SP/DCP weight ratio) at 85°C for 1.5 h. The press conditions were 7 min at 140°C. Data are the means of at least six independent measurements, and the error bars show the standard error of the means.

would result in 4 and 8, respectively. Reaction of 6 with  $\text{-NH}_2$  and  $\text{-OH}$  groups in SP would afford 7 and 8, respectively. The epoxide group in 1, 3, and 6 could also react with  $\text{-SH}$  and  $\text{-COOH}$  groups in SP. Direct substitution of the  $\text{-Cl}$  group on DCP, 2, and 5 with a nucleophile such as  $\text{-NH}_2$  group is also highly possible. All the possible reactions shown in Scheme 1 are speculative, let alone specifying dominating reactions. However, the crosslinking reactions apparently occurred because the pH value of the SP-DCP reaction mixture decreased and the viscosity of the SP-DCP reaction mixture increased with reaction time. Some crosslinking reactions shown in Scheme 1 could also occur during the hot-pressing of the wood composites. The SP-DCP adhesive may form covalent linkages with wood components as well. However, we speculate that hydrogen bonds rather than covalent bonds between the adhesive and wood played the essential role in the adhesion and that reactions between SP and DCP were mainly responsible for the formation of a water-resistant three-dimensional SP network.

Results from Figs. 1 and 2 revealed that crosslinking reactions were greatly dependent

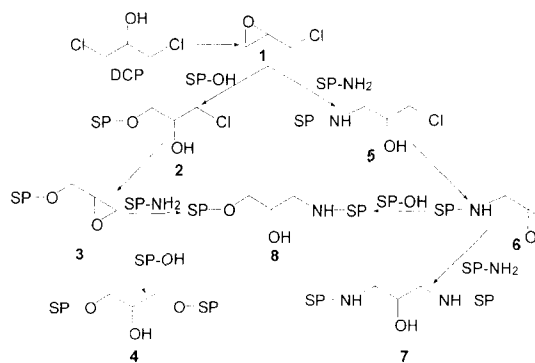
upon the reaction conditions, especially the reaction temperature. It appeared that the reaction temperature of 60°C was too low to cause significant crosslinking reactions in 3.0 h. SP-DCP adhesives prepared from 10:1 SP/DCP weight ratio at 85°C for 1.5 h could be readily applied to maple veneer, and resulted in high shear strengths and water resistance of the resulting wood composites. Therefore, reaction temperatures  $> 85^\circ\text{C}$  were not investigated.

In a certain range of SP/DCP weight ratios, the higher the DCP content, the higher the degree of crosslinking, and the higher the shear strength. The content of DCP in the SP-DCP adhesives with a 12:1 or 15:1 SP/DCP weight ratio appeared to be too low to cause sufficient crosslinking in SP, thus resulting in low shear strengths in the resulting wood composites (Fig. 2). As described previously, SP is a more desirable material than DCP for wood adhesives. Results from this study revealed that 10:1 SP/DCP weight ratio was the highest feasible ratio for production of wood composites. However, further study might lead to even higher SP/DCP weight ratio.

SP-DCP adhesives are formaldehyde-free; the key ingredient, soy protein, is abundant and renewable. Wood composites bonded with a SP-DCP adhesive were strong and water-resistant. The glue line of this adhesive was very light in color. This SP-DCP adhesive could be cured under hot-press conditions (press time, press temperature, and press force) that are commonly used in the wood composites industry. Therefore, SP-DCP adhesives could potentially be used as a replacement for interior UF resins. However, DCP is not an environmentally friendly chemical although it is widely used in several industries, e.g., it is used as a solvent for hard resins and nitrocellulose, used to manufacture photographic lacquer, and used as a binder for water colors. Emission of unreacted DCP from the wood composites may not be an issue because of its high boiling point (174.3°C). Determining whether the use of SP-DCP adhesives would result in environmental pollution or harm to human health requires further investigation. According to the crosslinking chemistry suggested in this study, a polymer with multiple chlorohydrin groups could also serve as an effective curing agent for soy protein or other renewable materials. Such a polymer would theoretically be more environmentally friendly than low molecular weight DCP. We hope that the results from this study will stimulate research on the development of environmentally friendly wood adhesives using the same curing chemistry as demonstrated in this study.

#### CONCLUSIONS

This study revealed that DCP was able to serve as a crosslinking agent for soy protein. The most desirable reaction conditions in terms of shear strengths were 10:1 SP/DCP weight ratio, 85°C and 1.5 h. The optimum press temperature was 160°C, and press times ranging from 1 to 9 min had little effect on shear strengths. Storage of the SP-DCP adhesive for up to 4 days still gave dry shear strengths within the range of commercial PF adhesives (shear strengths of two-ply wood composites bonded with commercial PF adhesives ranged from 3 MPa to 7 MPa



Scheme 1. Proposed reactions between SP and DCP.

in the study, depending on the source and the targeted application of the PF resins). Wood composites bonded with SP-DCP adhesives were water resistant. About 93% of the original shear strength remained after a WSAD test. The wood composites did not delaminate after a BWT. The remaining BWT/dry shear strength was about 35% and the remaining BWT/wet shear strength was about 10% of the dry value respectively (Fig. 7). SP-DCP adhesives can be used to replace UF resins for the production of interior grade wood composites.

#### ACKNOWLEDGMENT

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#### REFERENCES

- BAUMANN, M. G. D., L. F. LORENZ, S. A. BATTERMAN, AND G.-Z. ZHANG. 2000. Aldehyde emission from particleboard and medium density fiberboard products. *Forest Prod. J.* 50(9):75–82.
- HECK, H. D., M. CASANOVA, AND T. B. STARR. 1990. Formaldehyde toxicity—new understanding. *Crit. Rev. Toxicol.* 20(6):397–426.
- HENDERSON, J. T. 1979. Volatile emissions from the curing of phenolic resins. *Tappi J.* 62:9396.
- LAMBUTH, A. L. 1977. Soybean glues: Pages 172–180 in I. S. Kiest, ed. *Handbook of adhesives*, Van Nostrand Reinhold, New York, NY.
- . 1989. Protein adhesives for wood. Vol. 2: 1–30 in A. Pizzi, ed. *Wood adhesives—chemistry and technology*, Marcel Dekker, Inc., New York.



- LIU, K. 1997. Soybeans—chemistry, technology, and utilization. International Thomson Publishing, New York, NY.
- MARUTZKY, R. 1989. Release of formaldehyde by wood products. Vol. 2:307–387, in A. Pizzi, ed. Wood adhesives—chemistry and technology, Marcel Dekker, Inc., New York, NY.
- MEYER, B., AND K. HERMANS. 1986. Formaldehyde release from wood products: An overview: Pages 1–16 in B. Meyer, B. A. K. Andrews, and R. M. Reinhardt, eds. ACS symposium series 316—Formaldehyde release from wood products, American Chemical Society, Washington, DC.
- PERERA, F., AND C. PETITO. 1982. Formaldehyde: A question of cancer policy? *Science* 216(4552):1285–1291.
- SELLERS, T., JR. 2001. Wood adhesive innovations and applications in North America. *Forest. Prod. J.* 51(6):12–22.
- SWENBERG, J. A., W. D. KERNS, R. I. MITCHELL, E. J. GRALLA, AND K. L. PAVKOV. 1980. Induction of squamous cell carcinomas of the rat nasal cavity by inhalation exposure to formaldehyde vapor. *Cancer Res.* 40(9):3398–3402.