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Development and evaluation of new curing agents derived from glycerol for formaldehyde-free soy-based adhesives in wood composites

Abstract: Three novel curing agents (**I**, **II**, and **III**) were synthesized from epichlorohydrin and ammonium hydroxide. The combinations of soy flour (SF) with one of the curing agents (SF-**I**, SF-**II**, and SF-**III**) were investigated as adhesives for making interior plywood. Water resistance tests showed that plywood panels bonded with SF-**I** and SF-**III** adhesives met the requirements of interior plywood, whereas those bonded with SF-**II** did not. The modulus of rupture, modulus of elasticity, and internal bond strength of particleboard panels bonded with the SF-**II** adhesive all exceeded the corresponding minimum industrial requirements for M-2 grade particleboard.

Keywords: adhesion, adhesives, particleboard, plywood, polyamines, soy flour

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Introduction

Urea-formaldehyde (UF) resins are commonly used in wood-based composite panels such as plywood (PlyW), particleboard (PB), and medium-density fiberboard. Problematic is the formaldehyde (FA) emission during production and in the first periods of the lifetime of the UF-bonded panels (Myers 1983; Wiglusz et al. 2002; Nakos and Athanassiadou 2006; Roffael 2006; Salthammer et al. 2010; Ruffing et al. 2011). The development of FA-free wood adhesives has a high priority because FA was reclassified as a human carcinogen by the International Agency for Research on Cancer in 2004 (IARC 2004). Ecofriendly (FA-free) products for adhesive production are sought for, for example, based on finely milled kenaf core (Okuda and Sato 2007), technical lignins (Gosselink et al. 2010, 2011), liquefied wood (Lee et al. 2012), and hybrid adhesive systems with PF, dextrin, and fish glue (Sahaf et al. 2012), just to mention a few.

Soy-based adhesives were widely used in the commercial production of PlyW from the 1930s to the 1960s. Because the products had low strength and poor water resistance, these types of adhesives were replaced by synthetic resins. Soybean is abundant, renewable, environment friendly, and readily available. In addition, soy-based adhesives can suppress native FA emission (Birkeland et al. 2010). Therefore, soybean is one of the ideal raw materials for wood adhesives. In recent years, several FA-free, soy-based adhesives were developed, and the water resistance of the resulting PlyW panels was improved (Liu and Li 2002, 2004, 2006; Li and Liu 2004; Li et al. 2004; Li 2007; Huang and Li 2008; Jang et al. 2011; Huang et al. 2012). One of the novel products is applied for the commercial production of interior PlyW since 2004 (Li 2007). This adhesive consists of soy flour (SF) and a small amount of a petrochemical-based curing agent, namely, polyamidoamine-epichlorohydrin (PAE) resin (Li 2007).

In the present study, novel curing agents were developed from ammonium hydroxide (NH_4OH) and epichlorohydrin (ECH) for the replacement of the PAE resins in the soy-based adhesives. ECH can be derived from glycerol, which is a byproduct from biodiesel production (Schreck et al. 2006; Siano et al. 2006; Pagliaro et al. 2007). Solvay started a plant in April 2007 to produce 10,000 t y^{-1} of ECH from glycerol supplied by the biodiesel producer Diester Industrie based on their patented Epicerol process (Pagliaro et al. 2007). NH_4OH is synthesized from hydrogen and nitrogen. Accordingly, the curing agents based on ECH and NH_4OH are independent from petrochemicals.

Materials and methods

Sources of materials

SF (7% MC): Cargill, Inc. (Minneapolis, MN). ECH (99%) and NH_4OH (28–30% solution of NH_3 in water): Acros Organics (Morris Plains, NJ). NaOH: BDH (West Chester, PA). Ammonium trifluoromethane-

sulfonate ($NH_4SO_3CF_3$): Sigma-Aldrich (Milwaukee, WI). Yellow poplar, maple, white fir, and pine veneers: Columbia Forest Products (Greensboro, NC). Douglas fir wood particles for face and core PB: Flakeboard (Albany, OR). The particle distributions were determined by sieve analyses: (1) face particles, the weight of particles (%) retained on the sieves (the order of the top sieve to the bottom sieve: U.S. standard nos. 16, 35, and 60) and the bottom pan were 1%, 50%, 35%, and 14%, respectively. (2) As for the core particles, the weight of particles (%) retained on the sieves (the order of the top sieve to the bottom sieve: U.S. standard nos. 4, 10, 16, 25, and 32) and the bottom pan were 1%, 33%, 28%, 27%, 7%, and 4%, respectively.

Synthesis of curing agent I

According to Alferiev and Levy (2005) and Connolly et al. (2005), ECH (99%, 4.04 mol, 316 ml), isopropanol (300 ml), and $NH_4SO_3CF_3$ (1.68 g, 10 mmol) were added to a three-neck 1 l flask in a water bath. NH_4OH (28–30%, 0.84 mol, 55 ml) was then added to the flask. The mixture was stirred at 20°C to 24°C for 48 h. The reaction solution was then stirred at 30°C to 35°C for 3 h. The solution was dried in a rotary evaporator at 40°C and 15 to 25 mm Hg to remove isopropanol. The resulting solution was dissolved in toluene (250 ml) and tert-butanol (70 ml) and then concentrated with a rotary evaporator at 40°C to 45°C and 15 to 25 mm Hg for the removal of residual ECH. The resulting thick syrup was dissolved in toluene (250 ml) and tert-butanol (70 ml) and concentrated with a rotary evaporator under the same conditions to give crude **I** (258 g). Crude **I** was dried under high vacuum (0.05 mm Hg) for 24 h before **I** (254 g) was obtained. Theoretical elementary composition from **I** ($C_9H_{18}Cl_3NO_3$): C 36.67%; N 4.75%; C1 36.16%. Found: C 35.4%; N 4.47%; Cl 37.06%, including organic and inorganic chlorine contents of 32.26% and 4.8%, respectively.

Synthesis of curing agent II

Crude **I** (28 g, with organic and inorganic chlorine contents of 0.25 and 0.04 mol, respectively) and NH_4OH (28–30% as NH_3, 0.84 mol, 56 ml) were added to a three-neck 500 ml flask equipped with a rubber stopper, a thermocouple, and a condenser. A balloon was installed on the top of the condenser for preventing the loss of NH_3 during the reaction. The mixture was stirred at 60°C for 2 h and then vacuum dried in a rotary evaporator at 70°C and 70 mm Hg for the removal of excess NH_3. White solids (**II-a**, 32 g) were obtained after drying and were then dissolved in a NaOH solution (10 g NaOH in 70 ml deionized H_2O). The resulting solution was vacuum dried in the rotary evaporator at 70°C and 70 mm Hg for further removal of NH_3. The resulting product was dried under high vacuum (0.05 mm Hg) for 48 h before the elemental analysis. Approximately 20.4 g of **II** and 14.6 g NaCl were obtained. The product was dissolved in 40 ml deionized H_2O to make a **II** solution. Elemental analysis of **II**: C 47.7%; N 17.3%.

Synthesis of curing agent III

II-a prepared in the previous procedure without the subsequent vacuum drying was reacted with ECH for synthesizing **III**. **II-a** (7 g, dry weight; NH_2 0.035 mol; residual NH_3 0.022 mol) was dissolved in water (40 g) and then ECH (18.16 g, 0.194 mol) was added and stirred at room temperature for 24 h. The reaction temperature was raised to and maintained at 35°C for another 24 h. A clear solution was obtained. The solids content of the **III** solution was 38%.

Preparation of SF-I adhesives

Crude **I** (114 g), water (1500 ml), and a 20% NaOH solution (137 g) were sequentially added to a KitchenAid mixer and mixed for 5 min at room temperature. SF (798 g, dry weight) was added to the solution and further mixed for 5 min. The total solids content of the resulting adhesive was 36%.

Preparation of SF-II adhesives

The **II** solution (58 g, including 11.3 g NaCl, 31 g water, and 16 g **II**), water (178 ml), and a 20% NaOH solution (19.2 g) were sequentially added to a KitchenAid mixer and mixed for 5 min at room temperature to form a solution. SF (112 g, dry weight) was added and further mixed for 5 min. The total solids content of the resulting adhesive was 38%.

Preparation of SF-III adhesives

The **III** solution (65 g, including 40 g water and 25 g **III** product), water (290 ml), and a 20% NaOH solution (30 g) were sequentially added to a KitchenAid mixer and mixed for 5 min at room temperature to form a solution. SF (175 g, dry weight) was added to the solution and further mixed for 5 min. The total solids content of the resulting adhesive was 36%.

Preparation of PlyW

An adhesive was applied to two sides of a veneer (60.96×60.96 cm^2; MC 12%) by an adhesive roller coater. The usage of the adhesive was 8 mg cm^{-2} on a dry-weight basis. The adhesive-coated veneer was stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. When five- or seven-ply PlyW ($PlyW_5$ or $PlyW_7$) was made, another coated veneer was put on the stacked panel and covered with an uncoated veneer. Previous steps were repeated until a PlyW panel with expected plies was made. The structure of $PlyW_5$ is uncoated/coated/uncoated/coated/uncoated. The structure of $PlyW_7$ is uncoated maple/coated white fir/uncoated pine/coated white fir/uncoated pine/coated white fir/uncoated maple. The stacked veneers were put on a table at ambient environment for 5 min, cold pressed at 0.69 MPa and room temperature for 5 min, put on a table at ambient environment again for 5 min, and hot pressed with 1.03 MPa at 120°C for 5 min (three-ply) or 6 min (five- or seven-ply). After the hot pressing, the panel was stored at ambient environment for at least 24 h before being evaluated for its water resistance.

Water resistance of PlyW

A three-cycle soak test in accordance with the American National Standard for Hardwood and Decorative Plywood/Hardwood Plywood

and Veneer Association (ANSI/HPVA HP-1-2000) was applied. Twenty PlyW specimens (5×12.7 cm^2) cut from each PlyW panel were soaked in water at 24±3°C for 4 h and then dried at 49°C to 52°C for 19 h. This soaking/drying cycle was repeated three times. All specimens were controlled for delamination after the first cycle and the third cycle if applicable. According to the standard, a PlyW panel meets the water resistance requirements for interior applications if 95% of the specimens (i.e., 19 of the 20 specimens) do not delaminate after the first soaking/drying cycle and 85% of specimens (i.e., 17 of the 20 specimens) do not delaminate after the third soaking/drying cycle. The ANSI/HPVA HP-1-2004 specifically provides the following definition of delamination: any continuous opening between two layers has to be longer than 5 cm and deeper than 0.635 cm and wider than 0.007 cm.

Preparation of SF-coated wood particles

For coating surface wood particles, SF (203.7 g, dry weight) and water (800 g) were sequentially added into a Hobart A-200 blender (Hobart, Topeka, KS) and stirred for 10 min at room temperature to form 20% SF slurry. Surface wood particles (2172.5 g, dry weight) were then added into the SF slurry in the Hobart blender and the resulting mixture was stirred for 10 min. The resulting wet SF-coated wood particles were put in a cloth bag and dried in a rotary dryer (Speed Queen, Ripon, WI) for 1 h. After drying, the SF-coated surface wood particles had an MC of 2%. SF-coated core wood particles (2% MC) were prepared by following the same procedure for the preparation of the SF-coated surface wood particles with SF (232 g, dry weight), water (910.5 g), and core wood particles (2968 g, dry weight).

Preparation of three-layer PB

NaOH (7 g) and water (133 g) were added into a 400 ml beaker and stirred with a magnetic stirrer for 30 min. The **II** solution (107 g) was further added into the beaker and stirred for another 5 min. The resulting solution was then sprayed onto the SF-coated surface wood particles (2376 g, dry weight) in a rotary drum blender. The resulting adhesive-coated surface wood particles had the adhesive usage of 12% (this was defined as the dry weight of SF, **II**, NaCl, and NaOH divided by the dry weight of the wood particles) and had an MC of 9%. A mixture of the **II** solution (122 g) and NaOH solution (7.9 g solid+water 117 g) was sprayed onto the SF-coated core wood particles (3200 g, dry weight) in the rotary drum blender. The resulting adhesive-coated core wood particles had the adhesive usage of 10% and had the MC of 7%. The adhesive usages of core and face in this study were higher than those in the commercial production of PB with UF resins (4–8% for core and 8–10% for face).

The adhesive-coated surface wood particles (970 g, dry weight) were added onto a forming box (60.96×60.96 cm^2) by hand to form a uniform layer. The adhesive-coated core wood particles (3297 g, dry weight) were evenly distributed on top of the surface wood particle layer followed by a uniform layer of the adhesive-coated surface wood particles (970 g, dry weight). The resulting three-layered wood particle mat was hand pressed with a flat PlyW panel (60.96×60.96 cm^2) and then hot pressed at 180°C for 270 s. The target thickness was 17.5 mm. The target density was 0.80 g cm^{-3}. Two PB panels were prepared for each set of experimental variables.

Mechanical properties of PB

PB was cut into 7.62×46.99 cm^2 rectangular specimens for the measurement of modulus of rupture (MOR) and modulus of elasticity (MOE) and into 5.08×5.08 cm^2 specimens for the measurement of internal bond strength (IB) in accordance with the ASTM D1037-99 (American Society for Testing and Materials 1999) using an MTS Sintech 1/G testing machine (**MTS** Systems Corp., Eden Prairie, MN). The crosshead speeds were 9 mm min^{-1} for the measurement of MOR and MOE and 1.5 mm min^{-1} for the IB measurement. For each PB panel, four specimens were cut for MOR and MOE and eight specimens for the IB determination.

Carbon, nitrogen, and chlorine contents

C and N content was simultaneously determined in a C&N analyzer (Leco CNS-2000 Macro Analyzer). The total chlorine content was determined in accordance with ASTM E442-91 (Standard Test Method for Chlorine, Bromine, or Iodine in Organic Compounds by Oxygen Flask Combustion). The inorganic chlorine content was determined by silver nitrate titration (Hu et al. 2003).

Results and discussion

Preparations of I, II, and III

The preparation of curing agents **I**, **II**, and **III** from ECH and NH_4OH is shown in Figure 1. Compound **I** was readily prepared through the reaction of ECH and NH_4OH in isopropanol by following an established procedure (Connolly et al. 2005). Compound **I** contains approximately

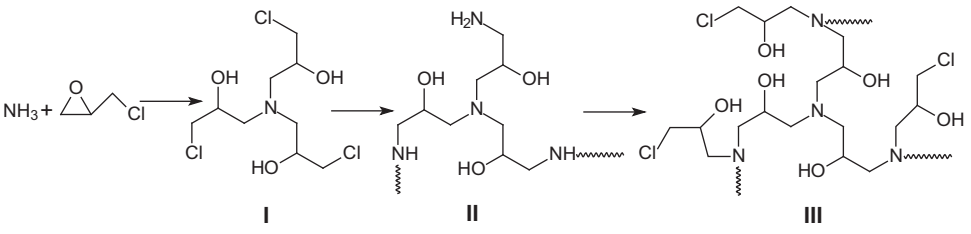

Figure 1 Preparation of compound **I**, **II**, and **III**.

4.8% inorganic Cl, implying that some organic chlorine was hydrolyzed during the reaction. The C, N, and organic Cl contents of **I** are close to those of the theory; thus, the major component in **I** is very close to that of the formula presented in Figure 1.

The compound **I** was directly reacted with NH_4OH without further purification to form **II**. NaOH was added to the crude **II-a** before the second vacuum drying for the removal of residual ammonium existed as NH_4Cl that is a byproduct in the reaction of **I** and NH_4OH. After this NaOH treatment, the N content measured from **II** should be all from amino groups (i.e., organic N). The N content (17.3%) of **II** indicates that **II** is truly a polyamine. The chemical structure of **II** (Figure 1) illustrates its multiple amino groups.

Treatment of **II** with ECH in water resulted in **III**. **III** was found to be a mixture of compounds containing various amounts of chlorohydrin ($CHOHCH_2Cl$) functional groups. The detailed structure of compounds in **III** was not characterized. Figure 1 illustrates the multiple chlorohydrin groups in **III**.

Water resistance of PlyW panels (SF-I adhesives)

Water resistances are presented in Table 1. Both $PlyW_7$ panels passed the three-cycle soak test (one panel had one specimen failed after the first cycle and the third cycle, and another panel had no specimen failed). Both $PlyW_5$ panels passed the three-cycle soak test (each panel had one specimen failed after the first cycle and three specimens failed after the third cycle). Both $PlyW_7$ and $PlyW_5$ panels meet the water resistance requirement for interior application.

		Number of fails from 20	
Type of plywood	**#**	**First cycle**	**Third cycle**
$PlyW_7$-SF-**I**			
M/F/P/F/P/F/M[a]	1	1/20	1/20
	2	0/20	0/20
$PlyW_5$-SF-**I**			
Y/Y/Y/Y/Y[b]	1	1/20	3/20
	2	1/20	3/20
$PlyW_3$-SF-**II**			
Y/Y/Y[b]	1	20/20	N.D.
	2	20/20	N.D.
$PlyW_3$-SF-**III**			
Y/Y/Y[b]	1	0/20	0/20
	2	0/20	0/20

Table 1 Water resistances of various PlyW panels ($PlyW_n$) bonded with SF-**I**, SF-**II**, and SF-**III** adhesives.
The index n indicates the number veneer layers. Data are for the number of failed samples from 20 in a three-cycle soak test. [a]Maple/fir/pine/fir/pine/fir/maple. [b]Yellow poplar. N.D., not determined.

Curing mechanisms of the SF-I adhesive

The intermediates of the curing are proposed in Figure 2. Kim et al. (1996) demonstrated that the OH group in the chlorohydrins (i.e., the 3-chloro-2-hydroxypropyl group) has a neighboring-group participation effect on facilitating the replacement of the chloride group in the chlorohydrin group by a nucleophilic group. This neighboring-group participation effect might facilitate the formation of an azetidinium ring, an epoxy ring, or direct replacement of the chloride group with a nucleophilic group in SF. The four-member-ringed azetidinium group and chlorohydrins have been proposed to be essential for reaction with carboxylic acid and amino groups in soy protein; they facilitate the cross-linking of SF into a water-insoluble network during the hot pressing (Li et al. 2004; Rogers et al. 2004). The curing agent **I** has three chlorohydrin groups and each of them might be converted to a hydroxyl-azetidinium group on heating under basic conditions. After reaction, the remaining chlorohydrins groups could be converted into a new azetidinium group again that might further react with nucleophilic functional groups in soy protein. These lead again to a water-insoluble cross-linked network. It is well known that the chlorohydrin group converts to an epoxy ring in alkaline solution (Alferiev and Levy 2005; Connolly et al. 2005). The newly generated epoxy ring could react with carboxylic acid or amino groups in SF, thus resulting in a cross-linked water-insoluble network. The direct replacement of the chloride group on the chlorohydrin groups with nucleophilic groups in SF could also lead to a cross-linking. At present, the relative contributions of the azetidinium, epoxy, and direct replacement of the chloride group in the cross-linking of SF are not well understood.

Water resistance of PlyW panels with SF-II

As shown in Table 1, all specimens of both panels delaminated after only one cycle of the soak test. Amino groups can form salts with carboxylic acid in soy protein and the dehydration of the salts can lead to formation of amides. However, the effective formation of amides requires a

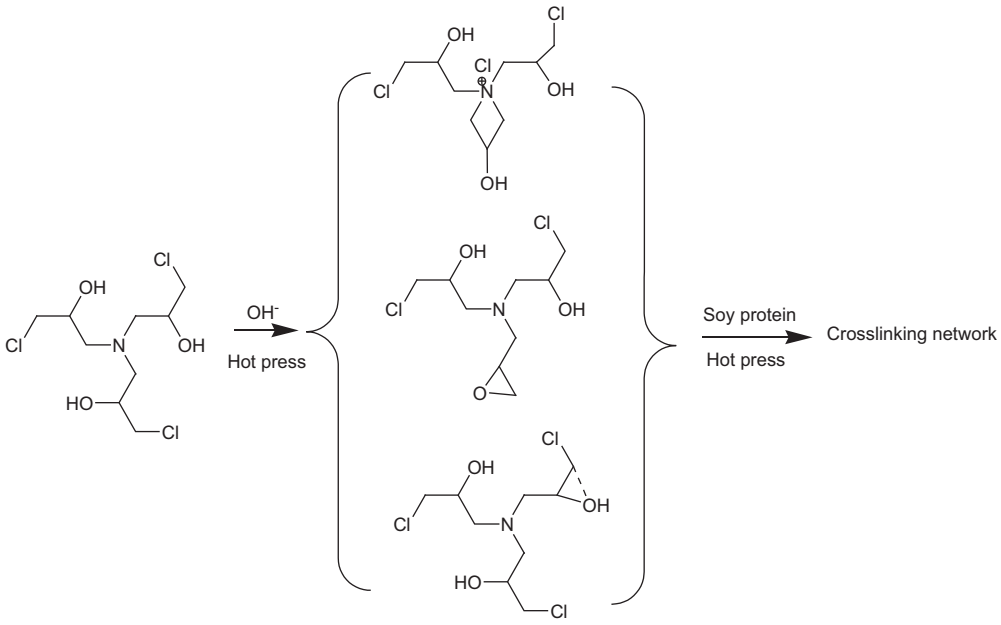

Figure 2 Proposed reactions between soy protein and **I** in hot pressing.

relatively high temperature and long reaction time (Jursic and Zdravkovski 1993; Arnold et al. 2006). $PlyW_3$ panels were made at 120°C for 5 min. Sufficient amounts of amides were unlikely formed from the salts under such conditions. Therefore, cross-linking in the SF-**II** adhesive mainly relied on the salt bridges between amino groups in **II** and carboxylic acid groups in SF. The salt bridges could be disrupted during the water soak test, which explains the failure of these specimens.

Mechanical performance of PBs with SF-II

PB panels bonded with the SF-**II** adhesive had the average IB of 0.76 MPa, which is higher than the industrial requirement of 0.45 MPa for M-2 grade PB (one of the most common PB panels). The average MOE (4.0 GPa) and the average MOR (23.2 MPa) for the PB panels bonded with SF-**II** adhesive also fulfilled the industrial requirements of MOE (2.25 GPa; horizontal dashed line) and MOR (14.5 MPa; horizontal solid line; Figure 3). The PB was prepared at 180°C that is higher than 120°C applied for PlyW. The higher temperature may facilitate the dehydration of the salts to form amide linkages, thus affording good mechanical properties of the PB. More importantly, the IB, MOR, and MOE are dry strengths of the PB panels. M-2 grade PB panels are produced for interior applications and there is no need for water resistance tests.

Water resistance of PlyW panels with SF-III

Water resistances of $PlyW_3$-SF-III yellow poplar panels are listed in Table 1. Both panels passed the three-cycle soak test without any delamination. **III** was a better curing agent than **II** but was comparable with **I** in terms of the water resistance of the PlyW panels. The major functional groups in **III** are the same as those in **I** (chlorohydrins); thus, the curing mechanisms are supposed to be very similar. **III** has probably a higher molecular weight and

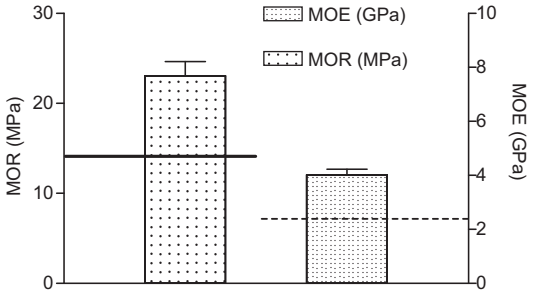

Figure 3 MOE and MOR of particleboard bonded with the SF-**II** adhesive.
Explanation of some details: surface adhesive usage (dry basis on wood particle), 12 wt%; core adhesive usage (dry basis on wood particles), 10 wt%; SF/**II**/NaOH, 7/1.0/0.24; hot pressing time, 270 s; hot pressing temperature, 180°C; the targeted particleboard density, 0.80 g/cm³. Data are the means of four replications, and the error bar represents one standard error of the mean.

more branches than **I**, which appeared to be not the critical factors for effective cross-linking of SF.

The water resistance performance of SF-based PlyW with **I** and **III** are comparable with that made with PAE. **I** was prepared in a simple one-step reaction, whereas three steps were required for the preparation of **III**. **I** is a preferred curing agent over **III** in terms of the cost-performance ratio. However, a large amount of isopropanol is required for the preparation of **I**, which is not desirable. The manufacturing of **I** in water and its performance in PlyW and PB are topics of ongoing research in our laboratory (Jang et al. 2011; Gu et al. 2012).

SF-I, SF-II, and SF-III from the environmental point of view

The curing agents should not contain residues of the dangerous ECH and other hazardous volatile organic compounds (VOCs). The crude **I** was diluted with toluene and tert-butanol and then evaporated under diminished pressure for the removal of these undesired compounds. In the presence of NaOH, the chlorohydrin in the curing agent **I** reacts with OH and amino groups and other nucleophiles in SF to form stable cross-linked adhesive networks with NaCl as a byproduct. The curing reactions of the SF-**I** adhesive are thus unlikely to generate hazardous VOCs.

The curing agent **II** was treated with NaOH solution and dried under high vacuum for the removal of residual ammonia. Expectedly, reactions between the polyamine **II** and SF will not generate hazardous VOCs during the hot pressing of PlyW and PB manufacturing; thus, the SF-**II** adhesive can be considered as environmentally nonhazardous.

The curing agent **III** is even less volatile than **II** because of its higher molecular weight. However, it is possible that **III** contains trace amounts of ECH and its hydrolysis products such as 1,3-dichloropropan-2-ol (DCP) because SF-**III** was formed by the crude **III**. Also in this case, the residual ECH will be consumed by SF in the presence of NaOH based on the high reactivity of ECH toward NaOH, OH and amino groups, and other nucleophiles in SF. Accordingly, the trace amounts of ECH or DCP, if any, will become an integral part of the adhesive network. NaCl as a byproduct is not toxic. Therefore, the PlyW panels bonded with the SF-**III** are expected to be unproblematic regardless of the presence of trace amounts of ECH and DCP. Of course, curing agent **III** has to be analyzed for ECH and DCP before industrial application.

Conclusions

Curing agents **I**, **II**, and **III** were successfully prepared and evaluated as curing agents of SF for making PlyW and PB. PlyW panels bonded with SF-**I** and SF-**III** adhesives met the requirements for interior application. PlyW panels bonded with the SF-**II** adhesive had poor water resistance, whereas PB panels bonded with the SF-**II** adhesive had superior IB, MOE, and MOR, which all exceeded the industrial requirements for M-2 grade PB.

Acknowledgements: This project was financially supported by a grant from a USDA National Research Initiative Competitive Grants Program (award no. 2008-35504-19204). We thank Columbia Forest Products for providing us with veneers, Cargill, Inc., for SF, and Flakeboard for wood particles.

Received June 15, 2012; accepted November 1, 2012; previously published online xx

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