

A new soy flour-polyepoxide adhesive system for making interior plywood

Jian Huang, Chunhong Li and Kaichang Li*

Department of Wood Science and Engineering, Oregon State University, Corvallis, OR, USA

*Corresponding author.

Department of Wood Science and Engineering, Oregon State University, Corvallis, OR 97331, USA
Phone: +1-541-737-8421
Fax: +1-541-737-3385
E-mail: Kaichang.Li@oregonstate.edu

Abstract

In this study, triglycidylamine (TGA) was synthesized and evaluated as a crosslinking agent for soy flour (SF) for making five-ply plywood from yellow poplar. Glycerol polyglycidyl ether (GPE) and trimethylolpropane triglycidyl ether (TTE) were also investigated as crosslinking agents for SF as adhesive for plywood. The plywood panels bonded with SF-TGA and SF-GPE adhesives did meet and those with SF-TTE adhesive did not meet the water-resistance requirement for interior application. The former two adhesives are formaldehyde-free, environmentally friendly, easy to use and readily available. They can be derived completely from renewable materials. The adhesion mechanisms are discussed in detail.

Keywords: adhesive; crosslinking; interior plywood; polyepoxides; soy flour; water resistance.

Introduction

Wood composite panels – such as plywood, particleboard, and medium density fiberboard – need an effective adhesive component. An estimated 1.8 million tonnes (t) of wood adhesives were consumed for this purpose in 2006 in North America (Orr 2007). Urea-formaldehyde (UF) resin – produced from petrochemicals – is the most common wood adhesive, accounting for approximately 60% of the wood adhesive market (Sellers 2001). However, a serious concern is that carcinogenic formaldehyde (FA) is emitted during production and use of panels (Myers 1983; Wiglus et al. 2002; Nakos and Athanassiadou 2006; Roffael 2006; Salthammer et al. 2010; Migneault et al. 2011; Ruffing et al. 2011). The California Air Resource Board (CARB) passed a strict regulation in April 2007, setting a very low emission limit of FA from wood composite panels. A national regulation of “formaldehyde standards for composite wood products act” was signed into law in 2010 in the USA (EPA 2011).

New adhesive systems derived from inexpensive renewable resources are very much expected to replace UF. Soybean is a renewable, abundant, readily available and inexpensive raw material. Soybean flour (SF) is mainly a mixture of soy protein and carbohydrates that contain a high amount of polar functional groups, such as hydroxyl, amino and carboxylic acid groups (Wool and Sun 2005). These characteristics are a good basis for the production of wood adhesives. It was demonstrated that soy-based adhesives suppress native FA emission and provide low FA emission levels (Birkeland et al. 2010). FA-free soy-based adhesives have recently been developed and one of them has proved the value for commercial production of interior plywood since 2004 (Li et al. 2004; Liu and Li 2004; Li 2007; Huang and Li 2008; Khosravi et al. 2010; Thames et al. 2010; Zhang and Sun 2010; Khabbaz and Fare 2011; Qi and Sun 2011). However, this commercial FA-free soy-based adhesive still contains polyamidoamine-epichlorohydrin (PAE, a petrochemical) as a curing agent (Li 2007).

The present study aims at the development of polyepoxides derived from renewable materials as curing agents to replace the petrochemical based PAE resin in soy-based adhesives. When successful, all components of the soy-based adhesive for interior plywood would be renewable materials.

Materials and methods

Sources of materials

Soy flour (SF) – 100 mesh; protein dispersibility index (PDI): 90; 93% solids content – was from Cargill Incorporated (Minneapolis, MN, USA). Epichlorohydrin (ECH) (99%) and ammonium hydroxide solution (NH_3 aq., 28–30% by wt.) were from Acros Organics (Morris Plains, NJ, USA). Ammonium trifluoromethanesulfonate and trimethylolpropane triglycidyl ether (TTE) were from Sigma-Aldrich (Milwaukee, WI, USA). NaOH was from BDH (West Chester, PA, USA). Yellow poplar veneer (*Liriodendron tulipifera* L) was from Columbia Forest Products (Greensboro, NC, USA). DENACOL EX-313 [glycerol polyglycidyl ether (GPE), weight per epoxide (WPE): 141] was from Nagase America Corp. (New York, NY, USA).

The route of the experimental design is presented in Figure 1. Triglycidylamine (TGA) was prepared according to Alferiev and Levy (2005). ECH (99%, 4.04 mol, 316 ml), isopropanol (300 ml), and ammonium trifluoromethanesulfonate (1.68 g, 10 mmol) were added to a three-neck 1 l flask in a water bath. NH_3 aq. (28–30%, 0.84 mol, 55 ml) was then added to the flask. The mixture was stirred at 20–24°C for 48 h. The reaction solution was then stirred at 30–35°C for 3 h. The isopropanol was removed with a rotary evaporator at 40°C and 15–25 mm Hg. The resulting solution was dissolved in toluene (250 ml) and *tert*-butanol (70 ml) and then concentrated in a rotary evaporator at 40–45°C and 15–25 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 in a rotary

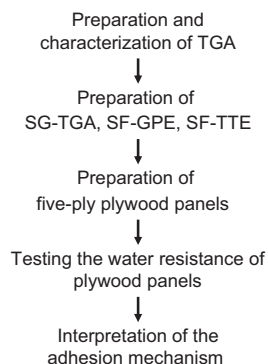


Figure 1 The route of experimental design.

evaporator under the same conditions to further remove residual ECH. Crude *tris*(3-chloro-2-hydroxypropyl)amine (**I**) (254 g) was obtained. Crude **I** (160 g) was dissolved in THF (44 ml), *tert*-butanol (8 ml), and toluene (244 ml) in a 1 l three-neck flask that was equipped with a mechanical stirrer, a thermometer, and an addition funnel. A solution of NaOH (50%, 320 g) in water was added dropwise over 50 min at 18–22°C under vigorous stirring. An ice-water bath was used for controlling the reaction temperature. After the addition of NaOH, the mixture was further stirred at the same temperature for 2 h. Ice water (250 g) and toluene (54 ml) were sequentially added to the reaction mixture while maintaining the temperature below 25°C. After stirring for an additional 5 min, the mixture was transferred into a 1 l separation funnel. The top organic layer was separated from the aqueous layer. The latter was extracted with toluene (82 ml) and the resulting organic phase was separated. All organic phases were combined and dried overnight with anhydrous K_2CO_3 at 5°C. The K_2CO_3 was filtrated off and washed with toluene (44 ml). The filtrate was concentrated in a rotary evaporator at 50°C and 15–25 mm Hg to yield viscous clear liquid TGA (60 g). The yield was approximately 62%.

Three polyepoxide products were prepared by following the procedures in the preceding paragraph, but two different ECH/ NH_3 molar ratios were applied and recycled isopropanol was used in the mixture with 3:1 ECH/ NH_3 ; more specifically, the input was: ECH (99%, 2.52 mol, 197 ml), NH_3 aq. (28–30%, 0.84 mol, 55 ml), and a solution of NaOH (50%, 320 g). The yield of TGA product from the 3:1 ECH/ NH_3 was 55%. For the preparation of 2:1 ECH/ NH_3 , ECH (99%, 1.68 mol, 131 ml), aq. NH_3 (28–30%, 0.84 mol, 55 ml), and a solution of NaOH (50%, 214 g) were used.

For making SF-TGA adhesive, TGA (80 g, 1.3 mol of epoxy group, calculated) and water (1096 ml) were sequentially added to a KitchenAid mixer and mixed for 1 min at room temperature (r.t.). SF (560 g dry weight) was added and further mixed for 5 min. The total solids content of the resulting adhesive was 36%. SF-TTE and SF-GPE adhesives were prepared in the same way, except that TGA was replaced by either TTE or GPE based on the same molar ratio of the epoxy group.

Preparation of five-ply yellow poplar plywood panels

A SF-polyepoxide adhesive was applied to both sides of a veneer (61 cm×61 cm; moisture content, 12%; thickness, 3.7–3.9 mm) by an adhesive roller-coater (80 g m⁻² adhesive on a dry weight basis). The adhesive-coated veneer was stacked between two uncoated veneers with the grain directions perpendicular to each other. Another adhesive-coated veneer was put on the stacked panel and covered with

an uncoated veneer. The structure of the panel was uncoated/coated/uncoated/coated/uncoated. The stacked veneers were kept at ambient environment for 5 min, cold-pressed at 0.69 MPa (r.t.) for 5 min, and kept again at ambient environment for 5 min and hot-pressed at 1.03 MPa at 120°C for 5.5 min. Then, the panel was stored at ambient environment for at least 24 h before being evaluated for its water resistance. Two plywood panels were prepared for each adhesive.

The water resistance of plywood panels for interior application was determined with 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). Twenty plywood specimens (5 cm×12.7 cm) cut from each plywood panel were soaked in water at 24±3°C for 4 h, and then dried at 49–52°C for 19 h. This soaking/drying cycle was repeated three times. The delamination was checked after the first and the third cycle, if applicable. According to the standard, 95% of the specimens (19 out of the 20) should not delaminate after the first cycle and 85% (17 out of 20) after the third cycle. ANSI/HPVA HP-1-2000 specifies the 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.

Results and discussion

Characterization of TGA

Preparation of TGA from ECH and aq. NH_3 is shown in Figure 2a. The reaction of the components readily generated compound **I**. Excessive ECH was removed through evaporation of toluene and *tert*-butanol. The crude **I** without further purification was directly treated with NaOH to generate TGA. The resulting TGA was directly reacted with SF for preparation of the adhesive. The proton NMR spectrum of TGA (identical with that of Connolly et al. 2005) was very clean indicating high purity of the crude TGA.

Water resistances of plywoods

Water resistance of plywood panels bonded with SF-TGA, SF-GPE, and SF-TTE adhesives, respectively, is listed in Table 1. The swelling and shrinkage creates high stress on the adhesive line. Therefore, in addition to dry strength of the panel, the adhesive line itself has to be water resistant, strong, and tough, so that the resulting plywood survives the three-cycle soak test. Both panels bonded with the SF-TGA adhesive fulfilled this requirement. Also, the two panels bonded with the SF-GPE adhesive passed the three-cycle soak test. However, one panel had one failed specimen after the third cycle, and another panel had one failed specimen after the first cycle and two failed specimens after the third cycle. Accordingly, the SF-TGA adhesive was superior to the SF-GPE adhesive in terms of the water resistance of the plywood panels. Both panels bonded with SF-TTE failed to pass the three-cycle soak test. One panel had eight out of 20 failed specimens after the first cycle and 17 out of 20 specimens failed after the third cycle; and another panel had five out of 20 failed specimens after the first cycle and 13 out of 20 failed specimens after the third cycle, which indicates that the SF-TTE is a very poor adhesive for bonding wood.

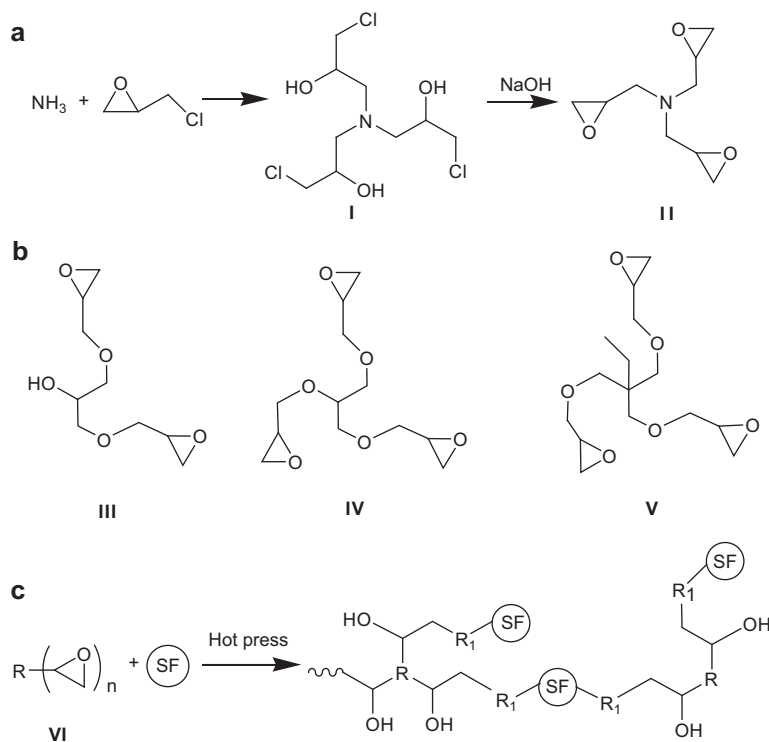


Figure 2 (a) Preparation of TGA from epichlorohydrin and ammonium hydroxide; (b) structures of glycerol diglycidyl ether (III), glycerol triglycidyl ether (IV), and trimethylolpropane triglycidyl ether (V); (c) the curing process of soy flour and polyepoxide (R_1 , -COO-, -NH-, -O- or -S-; R, backbone moiety of polyepoxide, $n=2$ or 3).

Adhesion mechanism

TGA (II in Figure 2a) and TTE (V in Figure 2b) have very similar chemical structures, each containing three epoxy rings. GPE is a mixture that mainly consists of glycerol diglycidyl ether containing two epoxy rings (III in Figure 2b) and glycerol triglycidyl ether containing three epoxy rings (IV in Figure 2b) (Imamura et al. 1992). Epoxy groups can react with a wide variety of functional groups, such as hydroxyl, amino, mercapto, and carboxylic acid groups in SF (May 1988). Therefore, the polyepoxides are proposed to serve as crosslinking agents that convert flowable SF into water-insoluble crosslinked networks during the hot-pressing step of plywood production. The curing mechanisms of the SF-polyepoxide

adhesives (VI) are proposed in Figure 2c. In the commercial production of plywood, the hot-press time is typically around 5–6 min at 120°C for making five-ply plywood panels (personal communications with plywood manufacturers). Under competitive industrial conditions, the hot-press time should not be significantly longer than 6 min, whereas the curing of a typical epoxy resin with an amine or a carboxylic acid is typically carried out at 80–200°C for 0.5–6 h (Tomotaki et al. 2000). Thus, the 5–6 min pressing at 120°C is too short to fully cure a SF-polyepoxide adhesive. This is the reason why polyepoxide has not yet been used as a crosslinking agent for natural materials, such as SF for commercial production of plywood panels.

TTE has been tested as a crosslinking agent for SF in the presence of various catalysts to enhance its reactivity without success in terms of satisfactory water resistance (Huang 2007). TGA contains a tertiary amino group (a known catalyst for epoxy resins) that can potentially activate its epoxy rings (Dolbey 1996), thus making TGA a good crosslinking agent for SF. This may explain why SF-TGA was a much better adhesive than SF-GPE or SF-TTE for making water resistant plywood panels. To be an effective crosslinking agent, a polyepoxide must have sufficiently high water solubility for mixing with SF in aqueous solution. In the case of low water solubility, a polyepoxide tends to aggregate in the presence of SF and thus the crosslinking during hot-pressing will be poor. GPE is fairly water soluble, i.e., in a GPE/water ratio of 1/9 at room temperature (Material safety data sheet for DENACOL

Table 1 Comparison of water resistances of plywood bonded with SF-polyepoxide adhesives, i.e., number of 20 specimens failed in a three-cycle soak test.

Polyepoxide	Panel #	Number of fails from 20	
		First cycle	Third cycle
TGA	1	0/20	0/20
	2	0/20	0/20
GPE	1	0/20	1/20
	2	1/20	2/20
TTE	1	8/20	17/20
	2	5/20	13/20

EX-313; Nagase ChemteX Corporation). No data on the water solubility of TGA are available. In our experiments, TGA was at least as water soluble as GPE. However, the water solubility of TTE is poor. The high water solubility and the presence of an internal tertiary amino group of TGA might account for the superior properties of the SF-TGA adhesive. The low water solubility and low reactivity of TTE might explain why it failed as a crosslinking agent for SF-TTE adhesive. GPE might not have high reactivity, but it has good water solubility, which explains why GPE was worse than TGA, but better than TTE.

The effect of ECH/NH₃ molar ratio

Excess ECH (5:1 ECH/NH₃ by mole) was applied for the preparation of pure TGA (Alferiev and Levy 2005). However, the extra ECH was wasted in the process. The superior results of TGA prompted us to further investigate a more economical way of making TGA based on a mixture of 3:1 ECH/NH₃. The proton NMR spectrum of this compound displayed many extra signals in comparison to pure TGA; thus, it was not as pure as the compound made of a mixture with 5:1 ECH/NH₃. A gel instead of a water-soluble product was obtained when an intermediate product from the reaction of ECH and aq. NH₃ at 2:1 ECH/NH₃ was subjected to the second step ring-closure reaction. In other words, a useful crosslinking agent could not be prepared from ECH under these conditions.

Isopropanol recovered from concentration of the ECH/NH₃ reaction mixture in making compound **I** was directly re-used without further purification. In doing so, the yield of final TGA product was only 30%, which is significantly lower than that in the case of fresh isopropanol. It can be assumed that water contained in recycled isopropanol led to hydrolysis of ECH.

TGA products from 3:1 ECH/NH₃ and with fresh or recycled isopropanol were found to be effective crosslinking agents for SF (Table 2). All plywood panels passed the three-cycle soak test. Results from Tables 1 and 2 demonstrate that TGA(ECH/NH₃=3/1) product is equally effective as that (ECH/NH₃=5/1) as a crosslinking agent with SF. The 3:1 ECH/NH₃ ratio is preferable for large-scale production of the TGA product.

ECH is industrially manufactured from propylene in the following processes: reaction of propylene with chlorine gas to form allyl chloride that is further converted to dichloropropanol with peroxide, and treatment of dichloropropanol with NaOH to form ECH. ECH can also be produced from glycerol, a byproduct from biodiesel production (Pagliaro et al. 2007). Glycerol is first treated with HCl in the presence of an acid catalyst to form 1,2-dichloropropanol and 1,3-dichloropropanol that are treated with NaOH to provide ECH. Several patents exist for different acid catalysts and improvements of the yields of the dichloropropanol compounds and overall production efficiency (Schreck et al. 2006; Siano et al. 2006). Solvay started a plant in April 2007 to produce 10,000 t/year of ECH from glycerol supplied from the biodiesel producer Diester Industrie based on their patented Epicerol process (Pagliaro

Table 2 Water resistances of plywood panels bonded with SF-TGA product (prepared with fresh or recycled isopropanol) adhesives, i.e., number of 20 specimens failed in a three-cycle soak test.

Molar ratio ECH/NH ₃	Isopropanol	Panel #	Number of fails from 20	
			First cycle	Third cycle
3/1	Fresh	1	0/20	0/20
		2	1/20	1/20
3/1	Recycled	1	0/20	0/20
		2	0/20	0/20

et al. 2007). More plants for production of ECH from glycerol are expected to be built in next few years. Therefore, ECH can be considered as an available chemical based on a renewable material. GPE is derived from glycerol and ECH (Condo and Schroeder 1956). SF is abundant, renewable, inexpensive, and readily available. Hence, SF-TGA and SF-GPE adhesives can be regarded as 100% renewable materials.

Conclusions

SF-TGA and SF-GPE adhesives are effective for bonding five-ply panels made of yellow poplar. The plywoods passed the three-cycle soak test that is required for interior plywood. TGA could be readily prepared from ECH and ammonium hydroxide. Plywood bonded with SF-TGA adhesive is less expensive and easier to produce with a 3:1 ECH/NH₃ than that with 5:1 ECH/NH₃ (in the case of fresh isopropanol). Recovered isopropanol from the ECH/NH₃ reaction leads to a lower yield of TGA. The tertiary amino group in TGA probably enhances the reactivity of TGA towards nucleophilic groups in SF. The superiority of TGA and GPE to TTE can be explained by the good water-solubility of TGA and GPE.

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