

Interfacial Properties of Loblolly Pine Bonded with Epoxy/Wood Pyrolysis Bio-oil Blended System

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The bonding interface of loblolly pine veneers cured with epoxy/wood pyrolysis bio-oil resins was studied. The shear strength of the adhered strands was calculated to examine the effect of bio-oil addition on epoxy resin performance. The chemical structure, curing behavior, and microstructure were investigated to analyze the interaction between wood substrate and resins. Results showed that the strength of pine wood-resin joints gradually decreased as more bio-oil was added. However, this effect was not apparent when the substitution rate was lower than 30%. ATR-FTIR analysis confirmed that complex chemical reactions take place between wood constituents and epoxy/bio-oil resins involved in the cross-linking at the interface. The reaction degree of -OH and C-O-C functional groups plays a key role in regulating the bonding stress of the wood bond line. The addition of bio-oil accelerated the polycondensation cross-linking process, resulting in a decreased cure temperature. SEM and optical microscopy showed that the epoxy/bio-oil resin formed gel nails in the pit and tracheid gaps, leading to the closing of the capillaries of the wood's cell walls and the colloidal interface extending into the timber micro-capillary system.

Keywords: Interface; Cross-linking; Bio-oil; Epoxy; Loblolly pine; Bond

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INTRODUCTION

Resins such as urea-formaldehyde (UF) and phenol-formaldehyde (PF) have been widely used in the wood industry during the manufacture of plywood, fiberboard, particleboard, and other non-structural products. These resins have the advantages of high reactivity, fast curing, easy operation, and cost efficiency (Pizzi 1994; Gao *et al.* 2013; Zhang *et al.* 2013). However, poor water resistance, formaldehyde emissions, and lower bond strength have limited the application of UF in outdoor structural composites, while volatile organic compound (VOC) emissions are becoming more of a concern for PF.

Epoxy resin has the potential to be used for wood structural bonding because of its strong wood-to-epoxy bond strength under dry conditions, low consumption ratio, and low environmental impact, but its high cost and brittleness needs to be improved to be competitive on a commercial scale (Pizzi 1994; Vick *et al.* 1995). Using wood-derived bio-oil to modify epoxy resin is a promising method to lower costs (Mohan *et al.* 2006; Wei *et al.* 2014). These bio-oils are derived from renewable resources, rather than from

oil derivatives. They are low-cost, environmentally friendly, and contain a large quantity of -OH active groups, and these can positively react with the resin mixture (Xie and Chen 2005; Effendi *et al.* 2008; Cheng *et al.* 2012; Li *et al.* 2014).

Efforts have been made to develop new bio-oil-based wood resins that have no/low formaldehyde emission and good bonding performance (Kobayashi *et al.* 2000; Kishi *et al.* 2006, 2011; Sasaki *et al.* 2013). Some researchers have successfully introduced wood bio-oil into the epoxy resin system. They found that the -OH groups of the liquefied wood react with epichlorohydrin under alkaline conditions. Their results suggested that wood-derived molecules were chemically incorporated into the resin to form a densely cross-linked copolymer network structure. The liquefied wood bio-oil/epoxy resin presented a shear bonding strength similar to the commercial epoxy resins.

In addition to the cross-linking of the epoxy polymer, the interaction with the resin to substrate interface is also critical. However, the bonding of wood with epoxy is quite different from traditional adhesion because the wood's dimensional stability causes forces that exceed the adhesive bond line strength, resulting in delamination. What is less understood is the chemical characteristic and polymer network of the wood-resin bonding interface, and more detailed research on the micromorphology of the bond line is worth further exploration (Frihart 2006).

The aim of this study was to investigate the interfacial properties of loblolly pine bonded with an epoxy/wood pyrolysis bio-oil blended system. The bond strength of pine joint veneers was calculated to examine the effect of bio-oil addition on epoxy resin performance. The chemical structure, curing behavior, and microstructure properties were determined to characterize the interactions between pine wood and epoxy/bio-oil-based resins. These findings aid in understanding the mechanisms of the bio-resin's penetration and cross-linking with the wood substrate and could improve the ability to use these systems for wood structural applications.

EXPERIMENTAL

Materials

The wood pyrolysis bio-oil was produced at Red Arrow International (Manitowoc, WI, USA) by a circulating fluidized bed at 1500 to 1700 kg/h. The feedstock was the common American hardwoods used for the manufacture of liquid smoke (Steele *et al.* 2012). Most of the water was removed prior to shipping from the manufacturer. Upon acquisition, the crude bio-oil was stabilized and homogenized with the addition of 80% to 100% V/V reagent-grade methanol. Methanol is a common solvent for phenolic compounds. It provides a means to reduce polymerization and the accompanying rise in the viscosity of the bio-oil feedstock (Mohan *et al.* 2006; Robinson *et al.* 2011). The diluted bio-oil was vacuum-filtered through #1 Whatman paper to separate the solid particulates and then vacuum rotary distilled at 70 °C to remove the methanol and some water fractions. The water content of the pretreated bio-oil was below 15%. After that, the bio-oil was stored in a refrigerator at 4 °C until use.

Epon 828 (EV Roberts and Associates INC, USA) is a commercial type of low molecular weight bisphenol A/epichlorohydrin-derived liquid epoxy resin. Loblolly pine wood (*Pinus taeda* L.) was cut in Florida, which is located in the southeast region of the United States. The sapwood of loblolly pine was saw cut and prepared into 80 mm × 20

mm × 5 mm veneers. The moisture content of the wood veneers was air dried to less than 10%, and the specific gravity was 0.45.

Preparation of Epoxy/Bio-oil Blended System

Bio-oil was added into the epoxy resin at 10%, 30%, and 50% by weight. The viscosity of the blended resins was 485, 754, and 1150 mPa•s at 25 °C, respectively. The mixtures were stirred uniformly to form a homogeneous system before use.

Preparation of Bonding Samples

Two layers of solid loblolly pine veneers were bonded according to the standard EN 205:2003 (Atta-Obeng *et al.* 2013). Resin curing was catalyzed using 10% ethylene diamine tetraacetic acid (EDTA) by weight. The pure epoxy resin was used as a control. The resins were applied at a consumption rate of 140 g/m². The bonded samples were completely wrapped in aluminum foil and hot-pressed at 150 °C for 15 min with a pressure of 0.9 MPa. After that, the samples were stored at 105 °C for 4 h and then cooled to 23 °C. All the samples were shear stretched using a mechanical testing machine (Zwick Roell testxpert II) with a loading speed of 1 mm/min. Six replicates per condition were tested. Additional replicates were added if the failure rate was lower than 75% in the epoxy/bio-oil composite interface.

ATR-FTIR Characterization

Attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR) analysis of the interface chemical structure of bonded samples was performed using a FT-IR spectrometer (PerkinElmer Spectrum 400). The bonding interface of veneer samples after shear failure was selected and applied directly on the diamond crystal. The spectrum was recorded by 32 scans over the range of 4000 to 650 cm⁻¹ with a 4-cm⁻¹ resolution.

DSC Measurement

The curing behavior of the epoxy/bio-oil resins bonded with loblolly pine powder (40 to 60 mesh, the average particle size was 0.42 to 0.25 mm) was evaluated using a TA Q2000 calorimeter. The pure epoxy resin, and resins with three bio-oil substitution rates (10%, 30%, and 50%) and pine powder were mixed at a weight ratio of 1:2, respectively. For each scan, 5 ± 0.5 mg of the mixture (10% EDTA added) was used. The curing reaction was conducted by increasing the temperature from 20 to 200 °C with a heating rate of 10 °C/min in a 50-mL/min nitrogen flow.

SEM and Optical Microscope Analysis

To analyze the microstructure properties of the bond line that formed during the bonding of the wood with the epoxy resin and epoxy/bio-oil resins, the samples were cut into slices and observed using an SEM (EVO 50VP; Zeiss, Germany) and an optical microscope (BX 53 system; Olympus, Japan) (Pan *et al.* 2014).

RESULTS AND DISCUSSION

Bond Strength

The effect of bio-oil addition on the shear strength of loblolly pine veneer bonded by the epoxy resin and epoxy/bio-oil resins is presented in Fig. 1. The epoxy/bio-oil

resins yielded wood joints with lower bond strength than the epoxy resin control. The strength gradually decreased as more epoxy was substituted with bio-oil. However, this effect was not apparent when the substitution rate was lower than 30%. Amen-Chen *et al.* (2002) reported a similar result in which the mechanical properties of three-layer panels made with bio-oil/PF resins (50% bio-oil substitution at the surface and 25% bio-oil substitution in the core) were higher than the Canadian standard (CSA O437.0-93) requirements. Li *et al.* (2014) used an urea-formaldehyde resin with 15% by weight of wood-derived bio-oil, and its mechanical performance still reached the Chinese standard (GB/T 9846.3-2004). These findings are important, as producers prefer to operate at a level that allows for a considerable bio-oil substitution rate while maintaining a cost advantage at acceptable bond strength.

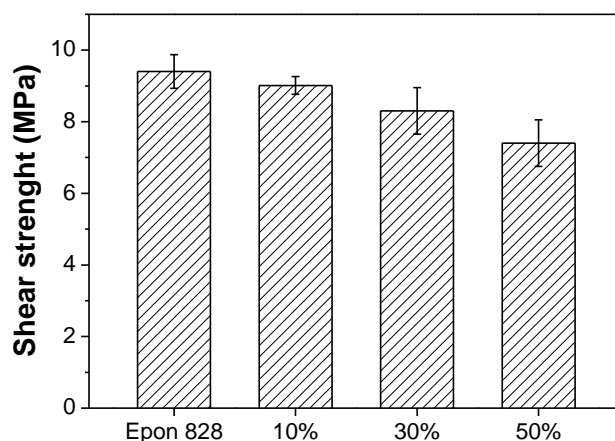


Fig. 1. Shear strength of loblolly pine veneer bonded by the pure epoxy resin and epoxy resins with bio-oil substitutions of 10%, 30%, and 50%

Although there was a small decrease in strength (Fig. 1), most of the strength was still maintained even at a 50% substitution rate. This suggests that the precise tuning of bio-oil concentrations is an optimization method for regulating the interaction between pine wood and resins while assuring acceptable bond strength.

Chemical Structure at the Interface

ATR-FTIR spectroscopy was used to characterize the interfacial chemical structure of loblolly pine veneer bonded with the epoxy resin and epoxy/bio-oil resins (Fig. 2). Compared with the spectrum of Figs. 2A and 2B, the interfacial bonding with epoxy/bio-oil resin showed a sharper characteristic C=C peak of benzene rings at 1606 cm^{-1} (Li *et al.* 2014), as well as a functional C-O-C peak of epoxide rings at 828 cm^{-1} (Khalil *et al.* 2011). These results confirm that the phenolic compounds of bio-oil and epoxide groups of the epoxy resin were both successfully interacted in the wood-resin bond line. Noticeable changes were observed for different bio-oil substitution rates (Fig. 2C and 2D). The C-O-C group of epoxy resins and the absorbance at 3280 cm^{-1} , which was attributed to -OH stretching (Wei *et al.* 2014) of wood components and/or bio-oil were the two main functional groups in the interaction. However, further work needs to be carried out for better understanding of the complex mechanism of the curing reaction between epoxy resin, bio-oil, and wood components.

In the Fig. 2B, the interface cured with the epoxy resin showed a reduction of absorbance at 3280 cm^{-1} . However, this absorbance presented a strong increase when bonded with epoxy/bio-oil resin with a 50% bio-oil substitution (Fig. 2D). The sharpness of this band, combined with the mechanical performance (Fig. 1) analysis of the veneer glued joint, indicated that part of the epoxy/bio-oil resin was not fully engaged in the cross-linking action.

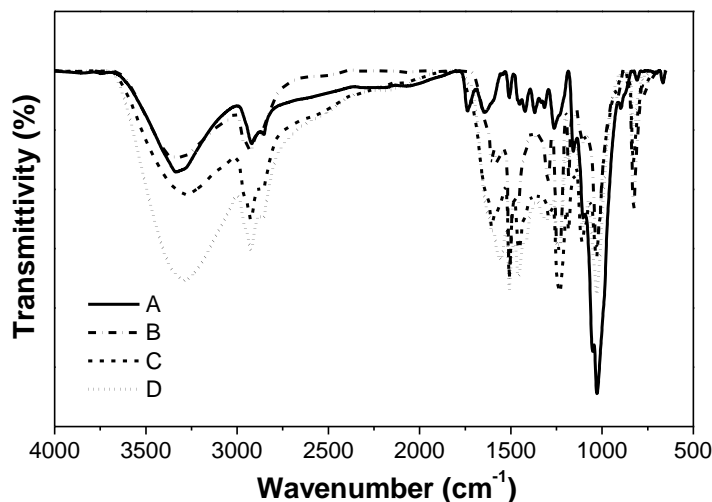


Fig. 2. ATR-FTIR curves of (A) loblolly pine solid wood and the interface of (B) solid wood bonded with the epoxy resin, (C) solid wood bonded with the epoxy resin at 10% bio-oil substitution, and (D) solid wood bonded with the epoxy resin at 50% substitution

It was concluded that complex chemical reactions between the wood and epoxy/bio-oil resins were present and contributed to the overall cross-linking of the system. The reaction degree of -OH and C-O-C played a key role in controlling the bonding stress of the loblolly pine joint.

Curing Behavior at the Interface

Typical DSC curves of pure epoxy resin, and loblolly pine wood powder cured with the pure epoxy resin and epoxy resins with various bio-oil replacement rates are shown in Fig. 3.

Because it is a thermosetting polymer composite, the pine wood-resin mixture exhibited an exothermal reaction range from 45 to $145\text{ }^{\circ}\text{C}$. The composition and chemical structure of the resin system effects the curing reaction (Pizzi 1994); thus, the curing exothermic peaks of different resins occur at different temperatures (Fig. 3). The exothermic reaction of pure epoxy reacted with wood powder ranged from 70 to $145\text{ }^{\circ}\text{C}$ (Fig. 3A), which is great different form the pure epoxy resin cured without wood powder (Fig. 3E); this is due to the condensation reactions between epoxy groups of the epoxy resin, EDTA and reactive groups of wood, such as hydroxyls and/or hydroxymethyls.

After introducing bio-oil, the exothermic peak was reduced (Fig. 3B, 3C, and 3D). This is due to the polyphenolic compounds in the bio-oil (rich in phenolic hydroxyl groups) (Ren *et al.* 2013), which become cross-linked with the epoxy and wood by ternary copolycondensation reactions (Fig. 2). As the bio-oil replacement was increased from 0 to 50%, the exothermic peak gradually migrated to a lower temperature. This happened because the reaction activation energy decreased as the active phenolic content

in the cured system increased through nucleophilic interactions. This aggravated the polycondensation crosslinking process and reduced the cure temperature.

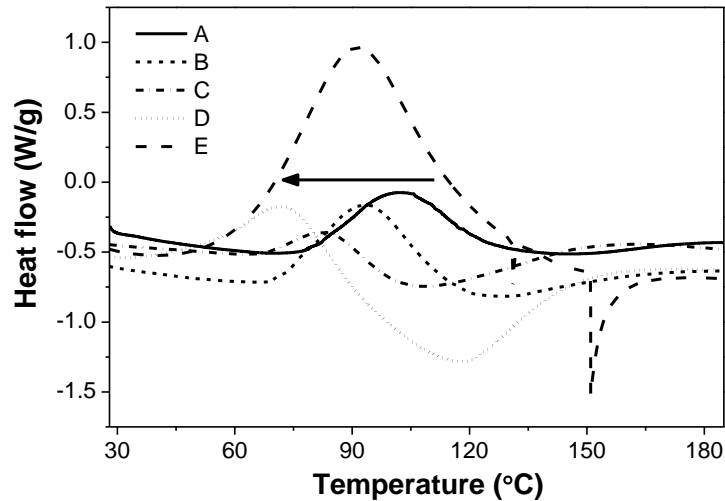


Fig. 3. DSC curves of loblolly pine wood powder cured with (A) the epoxy resin and (B) epoxy/bio-oil resins at 10%, (C) 30%, and (D) 50% substitution, and (E) pure epoxy resin

Microstructure Properties of Interface

The interfacial morphologies of loblolly pine bonded by the pure epoxy resin and epoxy/bio-oil blended resins are shown in Fig. 4.

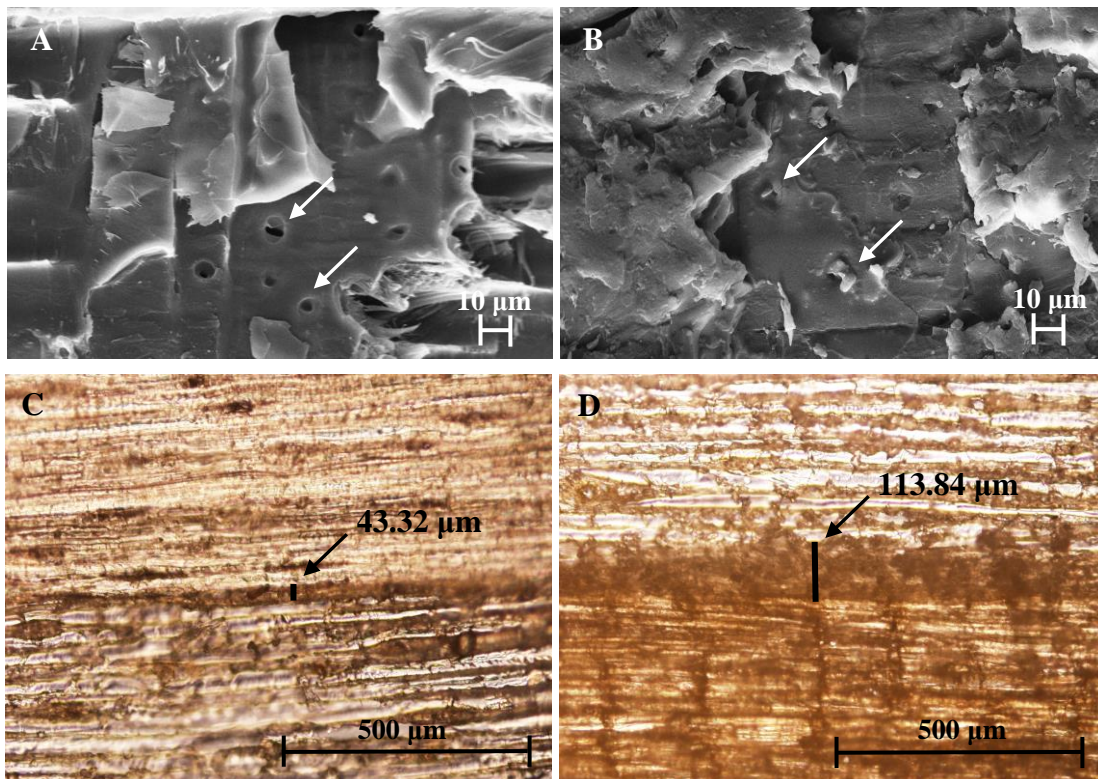


Fig. 4. SEM and optical microscope micrographs of the loblolly pine interface bonded by (A, C) pure epoxy resin and (B, D) epoxy/bio-oil resin

The epoxy resin diffused into the interface and then cured into a transparent, hard, and brittle material. However, its compatibility with the wood micro-capillary system (e.g., pits and tracheids) was insufficient (Fig. 4A, 4C). This linkage connects the pine wood substrate and epoxy resin but is possibly considerably weakened after circular hygroexpansion during outdoor exposure to moisture. This is because the stresses at the bond line increase during shrinking or swelling as the bound moisture content changes. The interface fails if the stresses exceed the interfacial strength (Vick *et al.* 1995; Brockmann *et al.* 2008).

The addition of bio-oil to wood helps resist moisture and consequent swelling (Robinson *et al.* 2011). Figure 4B and 4D illustrate that the addition of bio-oil endowed the epoxy resin became darkness but better permeability. The bond line in Fig. 4D is much wider (113.84 μm) than that in Fig. 4C (43.32 μm). When the bio-oil interacts with the wood substrate during hot pressing, there is synchronous crosslinking with the epoxy, resulting in better resin bonding distribution in the wood's microstructure. Additionally, the pit capillaries on the wood cell walls became congested with the epoxy/bio-oil crosslinked polymer. Interaction or polymerization with the wood cell wall components is an effective way to provide a stable interphase region at the pit structure. Because the bio-oil/epoxy resin better penetrates into the cell wall, the diffusion of low-molecular weight material, followed by polymerization, can generate nanoscale mechanical interlocking (Frihart 2006; Kasemsiri *et al.* 2011). These are beneficial in creating a better shrinking and swelling tolerance to moisture exposure at the bond line.

During the curing process, the resins formed a gel nail structure in the pit and tracheid gaps (Fig. 4B and 4D), extending the colloidal interface into the timber micro-capillary system. This limited cell wall expansion and improved the environmental tolerance of the resin interface.

CONCLUSIONS

1. The shear strength of loblolly pine wood bonded with epoxy/bio-oil resins gradually decreased as more bio-oil was added to the epoxy. However, there was not an apparent amount of strength lost, even when the substitution rate was as high as 50%. The precise tuning of bio-oil addition was an effective method for controlling cross-linking while ensuring acceptable bond strength.
2. ATR-FTIR analysis confirmed that complex chemical reactions were present between the pine wood constituent and epoxy/bio-oil resins. The reaction degree of -OH and C-O-C played a key role in regulating the bonding stress of the wood bond line.
3. The addition of bio-oil led to a decrease in the curing activation energy, which improved the polycondensation crosslinking process, resulting in a reduction in cure temperature.
4. SEM and optical microscopy showed that the epoxy/bio-oil resins formed gel nail structures in the pit and tracheid gaps, leading to the closing of capillaries in the wood cell walls. The colloidal interface extended into the timber micro-capillary system, leading to a better shrinking and swelling tolerance to moisture exposure at the bond line.

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