Fundamental Bonding Properties of Douglas-Fir and Southern Yellow Pine Wood

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Abstract

Bonding properties of southern yellow pine (*Pinus* spp.) and Douglas-fir (*Pseudotsuga menziesii*) were compared in terms of density, chemical composition, surface energy, shear stress, percent wood failure, and delamination. Specimens were taken from two trees of loblolly pine (*Pinus taeda*) and one tree of Douglas-fir. Density measurements showed that for mature wood, southern pine exhibited a higher average density than Douglas-fir, but for juvenile wood, southern pine showed a lower average density than Douglas-fir. Chemical analysis determined that southern yellow pine contained higher percent hemicellulose, lignin, and extractives, whereas Douglas-fir had higher percent cellulose. Static sessile drop contact angle measurements revealed that southern yellow pine specimens exhibited a lower average contact angle than Douglas-fir and, accordingly, higher average surface energy. Shear strength, percent wood failure, and delamination due to accelerated weathering were measured for bonded specimens constructed with either a one-part moisture-cure polyurethane (PUR) or a two-part ambient-curing phenol-resorcinol-formaldehyde (PRF) and three different assembly time combinations. Shear strength for southern yellow pine was affected the most by assembly time, whereas Douglas-fir shear strength was affected by the type of adhesive and interaction with the growth region at the bond. Delamination results showed that southern yellow pine exhibited less delamination than Douglas-fir when using PRF. Delamination measurements from the PUR bonds were similar and extremely high for both wood types. Although statistically significant differences were found in a few wood factors, limited differences were found in shear strengths, percent wood failure, and delamination due to accelerated testing for the two wood types.

Douglas-fir (*Pseudotsuga menzesii*) and southern yellow pine (*Pinus* spp.) are the two main softwoods used for manufacture of engineered wood composites and structural lumber in the United States (Howard 2007). Wood from these trees is used to fabricate structural composites such as glued-laminated beams (glulam), plywood, laminated veneer lumber, and veneer strand products. These woods are also used for secondary assemblies such as I-beams and furniture. Both Douglas-fir and the various southern yellow pines are grown in plantations that undergo extensive forest management to increase growth rates and stem biomass. Intensive management practiced in the last 20 to 30 years has resulted in softwood trees with increasingly variable properties and greater proportions of juvenile wood (Gartner et al. 2002).

Although the two wood types seem similar in macroscopic features, there are noticeable differences in anatomical and chemical structure that may result in divergent bonding properties for a given adhesive. In fact, it has been noted in industry that southern yellow pine was harder to bond and provided qualification testing results below specifications as compared with Douglas-fir when testing for accelerated weather durability using the same adhesive. Increased knowledge about the bonding properties of these two wood types could lead to optimization of adhesive use and fewer bonding problems. The research objectives for this study were to characterize and compare bonding properties for both wood types and determine how the anatomical and chemical properties influenced bond durability and strength. Wood density, chemical composition, and surface energy were the material properties studied and shear stress, percent wood failure, and delamination were examined in terms of bonding strength and bond durability during accelerated weathering.

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Background

Variability in wood composites performance arises from many factors such as substrate properties, surface preparation, adhesive chemistry, adhesive application, composite fabrication, evaluation methods, and in-service parameters. A concise but comprehensive review showing the many variables that influence wood bonding has been provided by Frihart (2013). According to this review, variables associated with the wood component of a bonded composite are vast and include wood type, density, moisture content, plane of cut, heartwood versus sapwood, juvenile versus mature wood, earlywood versus latewood, reaction wood, grain angle, porosity, surface roughness, drying damage, machining damage, dirt and contaminants, extractives, pH, buffering capacity, and chemical surface. Many of the aspects of the review (Frihart 2013) have been thoroughly investigated but some have yet to be fully explored. Pizzi and Mittal (2003) stated that the chemistry of wood adhesives has been studied extensively and is now known well enough to allow for prediction of the results of altering the adhesive chemistry. This conclusion does not appear to be a universally held opinion within adhesives manufacturers, however. Complicated relationships between material characteristics and adhesive bonding illustrate that characterization of bonding performance cannot be determined by any one individual characteristic, but rather a combination of blended attributes is required.

Several theories are used to characterize adhesive bonding of wood. The most common are mechanical interlocking, electrostatic theory, adsorption or wetting theory, diffusion theory, chemical bonding, and the theory of weak boundary layers and interphases (Schultz and Nardin 1994, Pocius 2002). Each of these theories incorporates a chemical and an anatomical aspect of the wood and adhesive type at different scales. More than one mechanism may be in effect in a given adhesive bond at a given time depending on the adhesive and wood types. A state-of-the-art report (Dunky et al. 2002) indicated that because of wood's porous nature and its pronounced surface roughness, mechanical interlocking and valence forces (van der Waals forces, London forces, and hydrogen bonding) are now generally accepted as the main mechanisms through which bonds between adhesive polymers and the molecular structures of wood are formed. Wood anatomy, surface energies, adhesive viscosity, and wood moisture content were said to be the primary variables involved in the wetting and penetration of wood surfaces. Also, an optimum adhesive penetration is required to repair processing damage done to the wood surface and to allow better stress transfer between laminates (Scheikl et al. 2002).

Wood density is one expression of a tree's response to its growing environment and, in general, is a good estimator of other physical properties of wood such as stiffness and strength. Variation in wood density in the softwoods is related to the relative proportion of earlywood to latewood within growth rings and the portion of juvenile wood. The impact of density on bonding wood materials relates to ease of flow and penetration of an adhesive into the cellular structure, compaction factors that affect the consolidation processes, dissimilarity in adhesion between earlywood and latewood and mature wood versus juvenile wood, and the extent of damage on the bonding surfaces created by pressure and surfacing (Frihart 2013). Douglas-fir and the southern yellow pines are resinous softwoods that exhibit abrupt transition from earlywood growth to latewood growth within a given growth ring and large density differences between earlywood to latewood regions. Density often varies within different growth regions in trees, e.g., juvenile and mature wood zones, and also varies with axial and radial location along the tree stem (Gartner et al. 2002).

Woody material consists of three major chemical components—cellulose, hemicellulose, and lignin—that combine in different proportions to make up the cell wall structure. The chemical units of these components provide a surface upon which an adhesive can form chemical bonds and diffuse into the cell wall structure if the molecular weight and chemical nature of the adhesive are suitable. When considering adhesion, the chemical components of wood could affect adhesive flow and diffusion, chemical bonding, acid–base interactions, surface energy, and wettability (Frihart 2013).

Extractives, which fall into a broad category of chemical compounds that occur in trees during the sapwood-to-heartwood transition, play a large role in the bonding of woody materials where content and quantity vary between different wood types and within different regions of tree growth in individual trees. Extractives can negatively affect wettability of the wood because of chemical interference that hinders favorable bonding sites (Frihart 2013). In addition, migration of extractives to the surface can prevent or obstruct adhesive penetration into the cell structure. Consequently, woods with a higher percentage of extractives are often said to be more difficult to bond. Extractives migrate to the wood surface (either naturally or during wood-drying processes) and thus influence surface measurements (Hse and Kuo 1988). Wood extractives can be both polar (e.g., tannins, phenolic compounds, and water-soluble oligomeric carbohydrates) and nonpolar (e.g., free and esterified fatty acids and sterols; Widsten et al. 2006). Nonpolar extractives lower wood surface polarity, consequently reducing polar liquid wetting (Chen 1970, Widsten et al. 2006). The presence of surface extractives poses a problem for surface measurements because they can contaminate the liquid and lower liquid surface tension, which consequently decreases the contact angle. Walinder and Johansson (2001) determined the impact of liquid extractive contamination with nonextracted and extracted wood specimens by measuring the decrease in liquid surface tension after an immersion measurement.

Wetting of a solid surface is said to occur when there is contact between liquids such as an adhesive and the solid. Quality and nature of wetting by an adhesive has been characterized by the contact angle method in which the angle of contact between a liquid droplet and the solid surface is determined (Good 1992, Johnson and Dettre 1993). Contact angles less than 90° are considered favorable wetting, but angles greater than 90° are considered unfavorable (Burch 2015). Measurement of contact angles is also used as a method to estimate surface energy of a solid, which can be useful information about wettability of the surfaces but also useful in formulating adhesives that favorably wet a surface (Scheikl and Dunky 1998, de Meijer et al. 2000, Gindl et al. 2001). Because surface energy is the sum total of all intermolecular forces on the surface of a material, it represents the degree of attraction or repulsion force the material exerts on other materials such as liquids and adhesives. Water, for example, penetrates more rapidly

into high surface-energy wood, and likewise, wetting and penetration is slower or prevented on low surface-energy woods.

Bond durability against delamination due to weathering has been examined for many adhesive and wood systems (Custodio et al. 2009, Frihart 2009). Among the numerous factors that have been found to affect bond durability, the ability to distribute the stress that occurs due to moisture changes and how the adhesive properties contribute to those changes at the bond line are frequently reported to be the most influential (Frihart 2009). Dimensional change and stress created by shrinkage and swelling in the wood component can overpower bond integrity if the forces exceed the matrix strength. Research studies have found that adhesives that polymerized in situ facilitated stress distribution away from the adhesive bond line, whereas prepolymerized adhesives with longer polymer chains allowed for more flexibility at the bond line (Frihart 2009). Surface preparation has been reported by many to be critical in creation of suitable wood bonding (River et al. 1991, Liptakova et al. 1995, Frihart 2013, Hass et al. 2014, Jiang et al. 2014). A study of the impact of surface preparation using several softwood-bonded assemblies found that the largest factors influencing delamination and shear strength were the time elapsed between surfacing and bonding and the level of damage created by surfacing (Jiang et al. 2014). However, other studies have shown that different surfacing effects on several softwoods provided no definite impact on shear strength and percent wood failure using polyurethane (PUR) and phenol-resorcinol-formaldehyde (PRF) adhesives (Hass 2014).

PRF adhesives were introduced to help lower the high cost of ambient-curing resorcinol adhesives (Frihart 2009). PRF adhesives are frequently used in glued-laminated timbers (glulam) and other engineered wood-based composites such as plywood, oriented strand board, and others. PRF adhesives are reported to produce bonds that are favorable for weathering durability, high percent wood failure, and high bond strengths in wood composites (Okkonen and Vick 1998, Lopez-Anido et al. 2000, Zhang et al. 2011). Possible reasons for the favorable properties created with PRF adhesives and wood materials are that PRF infiltrates the wood cell walls through diffusion and a high degree of irreversible cross-linking can occur (Frihart 2009). Infiltration and cross-linking within cell walls could lead to reduced shrinking and swelling of the bond-line region when in contact with water and subsequent moisture content changes. In addition, PRF exhibits water sorption properties similar to wood materials, which could also lead to reduced stresses created by differential shrinkage and swelling properties (Wimmer et al. 2013).

PUR adhesives are usually a one- or two-part system depending on the application. The one-part PUR moisture cure adhesives are used for normal room-temperature and humidity conditions. One-part PUR reacts with moisture in the surrounding air to create cross-linking. Two-part PUR adhesives have an isocyanate portion and an isocyanate-reactive portion that are mixed before bonding. Two-part PUR adhesives are more commonly used for preassembly in manufactured housing and other house construction applications (Frihart 2005). Portions of the PUR adhesive exposed to air form a thick layer that assists moisture diffusion as the primary mechanism for curing. One-part PUR adhesives are reported to provide favorable shear strength and percent wood failure under dry conditions but not in wet conditions (Klausler et al. 2013). PUR has a long polymer chain that is flexible and allows stress from wood shrinkage and swelling at the bond line to be distributed rather than concentrated in the bond line (Frihart 2009). Testing two one-part PUR adhesives and a PRF-cured resin in tensile strength after soaking in water showed that PUR was a flexible material, with the strain at failure reported as being approximately 25 percent for the PURs but 2.5 percent for the PRF (Frihart 2005).

Methods and Materials

Sample preparation and testing of wood property variables

Test specimens were prepared from loblolly pine (*Pinus taeda*) and Douglas-fir trees freshly harvested for this research. Two loblolly pine trees, each about 40 years old, were removed from the Reynolds Homestead Forest Resources Research Center in Critz, Virginia, and a single Douglas-fir tree about 47 years old was harvested from the McDonald–Dunn research forest in Benton County, Oregon. No silvicultural treatments had been applied to these trees and all were growing in natural settings. Trees were felled, delimbed, and cut into bolts for transport to the Brooks Forest Products Center in Blacksburg, Virginia, for further processing. Boards were sawn from the bolts using a Timber King portable sawmill and subsequently dried to final a moisture content of 12 percent in the SII dry kiln at the Brooks Forest Products Center. Boards were further processed into specimens for the various analyses as described below. Test specimens were prepared from juvenile and mature wood growth regions taken from several heights within the trees. Distinguishing between juvenile and mature wood was based on visual analysis of the growth ring width patterns before processing the logs into boards (Douglas-fir [Abel-Gadir and Krahmer 1993] and southern yellow pines [Clark and Saucier 1989]) and density trends as measured with the densitometer scans described below. The adhesives used in this study were chosen by industrial colleagues because of their particular interest in our findings for PRF and PUR adhesives for bonding the two wood types studied. A two-part PRF adhesive was provided by Hexion Inc. This adhesive is one part phenol-resorcinol, known as Cascophen LT-5210, which has a 55 percent solids content, and one part paraformaldehyde, marketed as Cascoset FM-7400. The PUR adhesive was a one-part moisture-reactive Purbond HB E202 provided by the Henkel Corporation. Viscosity of the two adhesives was tested after mixing according to the manufacturer's specifications and settling for 5 minutes at room temperature. The shear rate was from 0.1 to 500 (PRF) or 1,000 (PUR) (1/s) over a time period of 1,400 seconds. Viscosity was not modified with any additional factors so that the mixtures could be considered typical industrial usage. Viscosity of both of the adhesives across the shear rates studied were below maximum values considered to provide good spreadability. Details of specimen preparation can be found in Mirabile (2015).

Density was measured with a QMS model QTRS-01X tree ring scanner (Quintek Measurement Systems, Inc., Knoxville, Tennessee), which uses the attenuation of a collimated X-ray beam passed through a thin strip of material to measure density. Density at each measurement

point is based on the relationship between X-ray beam attenuation and density as expressed in Equation 1 (QMS 1999):

$$\frac{I}{I_o} = e^{-\mu\lambda t} \qquad (1)$$

where I is the intensity of the radiation beam after passing through the sample, I_o is the intensity of the radiation beam without passing through the sample, $\mu\lambda$ is the sample linear attenuation coefficient (cm^{-1}), t is the sample thickness (cm), and e is the natural logarithm base. Once I and I_o are measured for each point, $\mu\lambda$ is calculated for each point. The linear attenuation coefficient, $\mu\lambda$, is then related to density by Equation 2 (QMS 1999):

$$\mu\lambda = \mu_m \times \rho \qquad (2)$$

where μ_m is the sample mass attenuation coefficient (cm^2/g) and ρ is the sample density (g/cm^3).

Measurements were taken every 0.02 mm from strips of wood cut to target measurements of 1.59 by 152 by 25.4 mm, longitudinal by radial by tangential dimension and conditioned to 12 percent moisture content. Strips taken from several heights and growth regions within the trees were scanned along the radial direction to determine density characteristics at several locations within the trees.

Extractives content and compositional analyses were performed to determine the chemical characteristics at numerous locations within the trees. Determination of the extractives percentage involved removal of the extractives from the wood particles using acetone extraction at room temperature. Twenty milliliters of acetone was added to 20 mL of the dry milled material and shaken for 10 minutes on a high setting of a vortex shaker. The specimen was held stationary for 5 minutes and then shaken for an additional 10 minutes. Specimens were kept stationary for the next 24 hours and then centrifuged at 5,000 rpm for 30 minutes. Specimens were decanted and washed with water and agitated twice to remove any acetone residue. Specimens were dried in a 100°C oven until weight change was less than 2 percent. Initial specimen weight was subtracted from the final weight to report extractives on a percent dry weight basis.

Compositional analysis of the structural carbohydrates and lignin in the extracted test specimens was completed according to procedures outlined in a National Renewable Energy Laboratory (NREL) standard (NREL 2011). A Metrohm ion chromatograph equipped with a pulsed amperometric detector was used to analyze chemical composition of mature and juvenile wood specimens. Deionized water was the eluent and 350 mmol/liter sodium hydroxide was used for the postreaction. The eluent was run with a flow rate of 1 mL/min and the Hamilton RCS-30 column at a temperature of 32°C. Postreaction sodium hydroxide was run at a flow rate of 0.43 mL/min after column separation to help identify the carbohydrates in the pulsed detector at a temperature of 35°C.

Contact angle measurements were completed to determine surface energy using a static sessile drop method and three liquids. Test specimens were taken from the juvenile and mature growth regions but at one stem height only (4.88 m up from tree base). Our experiments showed that density and chemical composition did not vary appreciably along the stem axes; therefore, one stem height was used for

characterization of contact angles. Microtomed specimens have been reported to show the least amount of surface roughness and are often considered the most ideal for wetting measurements; sanded surfaces exhibit torn and damaged wood elements, which complicate wetting measurements (Liptakova et al. 1995). Blocks were softened before microtoming by placing them in a beaker containing water and a vacuum pulled until the blocks were saturated and they sank in the water. A Leica SM2500 microtome was used for surfacing the tangential–longitudinal plane of saturated blocks. Earlywood surfaces were prepared for analysis because of the degree of difficulty and likely creation of artifact when surfacing latewood of these two wood types. A First Ten Angstroms (FTA) 200 dynamic contact angle analyzer was used to place droplets of water, methylene iodide, and formamide on the tangential surface of the blocks. Initial images were recorded at 0.3 second for uniformity across all specimens and to minimize vibration upon initial contact and every 0.1 second thereafter over a 10-second period for a total of 100 images per block. Surface energy calculations using the initial contact angle were performed using the FTA 32 version 2.1 software and the acid–base theory (Gindl et al. 2001, Burch 2015) to gather as much information about surface energy through contact angle analysis as possible.

Time dependency of droplets of liquids as they transition from an initial contact angle to an equilibrium contact angle can be represented as a K value (Shi and Gardner 2001). K values reflect modification of the contact angle over time until an equilibrium is reached (Shi and Gardner 2001). Time-dependent properties provide information not just on liquid spreading but also on penetration of the liquid as time passes, which can then be used to interpret favorable or unfavorable wetting by determining how fast a liquid decreases or spreads on a surface. A larger K value indicates a higher amount and rate of spreading and penetration to reach an equilibrium state in which no additional changes take place. The wetting model to quantify the amount of change in contact angle over time is shown below in Equation 3 (Shi and Gardner 2001).

$$\theta = \frac{\theta_i \theta_e}{\theta_i + (\theta_e - \theta_i)\exp\left[K\left(\frac{\theta_e}{\theta_e - \theta_i}\right)t\right]} \qquad (3)$$

where θ_i is the initial contact angle at time 0 seconds, θ_e is the equilibrium contact angle, t is time, and K is the constant intrinsic relative contact angle decrease rate (1/s). A high K value represents a liquid that spreads and penetrates quickly and a low K value one that spreads and penetrates slowly. A K value of zero would mean no change between initial and equilibrium contact angles.

Sample preparation and testing of bond strength and durability

Specimens for shear strength, percent wood failure, and delamination testing were prepared in accordance with ASTM D2559 (ASTM International 2014) and D905 (ASTM International 2013a). ASTM D2559 is a severe test of resistance to delamination and is the specification used by industry to qualify adhesives for use in structural laminated wood products destined for exterior exposure. Preparation of the bonded assemblies followed guidance from the adhesives' manufacturers for adhesives application, assem-

bly times, pressing time, and pressure levels. Assembly times were varied according to specifications found in ASTM D2559 to provide information about the impact on bond strength and durability of the two adhesives being studied. For the PRF adhesive, minimum open time was essentially immediately after application of the adhesive and minimum closed time was 5 minutes; maximum open time was 1 minute and maximum closed time was 20 minutes. Assembly times for the PUR laminates were minimum open time immediately after adhesive application, minimum closed time 10 minutes, maximum open time 1 minute, and maximum closed time 15 minutes. Laminates were constructed of one wood type and either mature wood bonded to mature wood or juvenile wood bonded to mature wood. After construction, the assemblies were further subdivided into shapes and sizes specified in the ASTM testing standards.

Shear block specimens were prepared using a two-ply, stair-step assembly configuration. An average of 20 shear stress tests was conducted for each wood type, assembly time, growth region, and adhesive combination. Shear blocks were conditioned to 12 percent moisture content and tested more than 2 weeks after conditioning. Shear strength tests followed ASTM D2559 (ASTM International 2014) and D905 (ASTM International 2013a) procedures. Blocks were tested to failure and percent wood failure visually estimated by applying a grid to the specimen surface after testing. Percent wood failure was approximated in accordance with ASTM D5226 (ASTM International 2013b).

Resistance to accelerated weathering and delamination characteristics were determined with ASTM D2559. This test requires a series of treatment conditions that are considered a maximum severity level for testing moisture effects and exposure to weathering (ASTM International 2014). Specimens are subjected to several testing cycles inside a pressure vessel that include application of a vacuum and pressure, steaming, and alternating oven-drying. Delamination along the bond lines was measured with a caliper on both end-grain surfaces of the assemblies. Total delamination length for a particular specimen was the sum of all measurements from both end-grain surfaces. Three specimens were tested for each wood type, assembly time, growth region, and adhesive combination. Averages for all shear strength, wood failure, and delamination test results were used to represent each different testing combination. Specimens were tested in random order.

Statistical analyses

Various statistical analyses were conducted for each experiment. Data from ASTM D2559 and D905 testing required a nested factorial model because the assembly time was varied (nested) within each adhesive type. Factors were wood type, growth region at the bond line, adhesive type, and assembly time. The nested factor was assembly time because it was varied within each adhesive type. A two-sample t test was used for statistical comparisons of results from the density and chemical composition tests. Additional tests included Tukey's honestly significant difference (HSD) test for pairwise comparison of treatment groups. Specific details and extensive tables of all statistical analyses may be found in Mirabile (2015). Tukey's HSD is considered a rather conservative test if the sample sizes differ, as was the case in this study. If an effects P value was less than 0.05, it

was thought that the treatment group likely had an effect on the test results. Considerations in the statistical analyses were number of parameters, degrees of freedom, sum of squares, and F ratio. The F ratio in effects testing is used to determine if the effect (testing variable) on the response variable is statistically significant. If the effect being studied was found to be significant, then Tukey's HSD testing was completed. Objectives for this study were to identify differences between two wood types bonded with the same adhesive and not to compare juvenile wood with mature wood; therefore comparisons and analyses were confined to comparisons of mature wood bonded to mature wood and comparisons of juvenile wood bonded to mature wood. The two growth regions were considered separate specimen types because of the vast differences in anatomical and chemical properties and were analyzed separately.

Results

Wood properties

Density characteristics as shown in Figure 1 were recorded at several heights and growth regions within the tree stems. Variation was found to be minor from base to top of the trees as illustrated by standard deviation bars in Figure 1. Consequently, specimen location along the stem height likely had little or no impact on data variability. Overall average density values shown in Table 1 indicate that mature wood from the southern yellow pine specimens exhibited a higher overall average density than mature Douglas-fir wood; however, juvenile wood of the Douglas-fir had a higher average value than juvenile wood of southern yellow pine. Comparisons with a two-sample t test of average wood density across the two wood types indicated that the values for the two wood and growth types were statistically different. Because mature wood of the pine specimens had a higher average density, the pine specimens might be expected to exhibit higher mechanical strength in general. However, higher densities might also hinder thorough and widespread adhesive penetration within the southern yellow pine specimens.

Chemical composition is reported along the tree stems and within growth regions in Table 2. Similar percentages of extractives and structural components were found at all specimen heights within the trees and, as with density, it is supposed that chemical composition along the tree heights did not significantly affect later property measurements. It was determined that most of the components were statistically significantly different from each other with the exception of the mannose pine comparison of mature with juvenile wood, the lignin of juvenile pine compared with juvenile Douglas-fir, and the galactose of the juvenile pine compared with the juvenile Douglas-fir. Chemical composition affects bonding of wood with adhesives because some

Table 1.—Overall average density values for the southern yellow pine and Douglas-fir specimens.

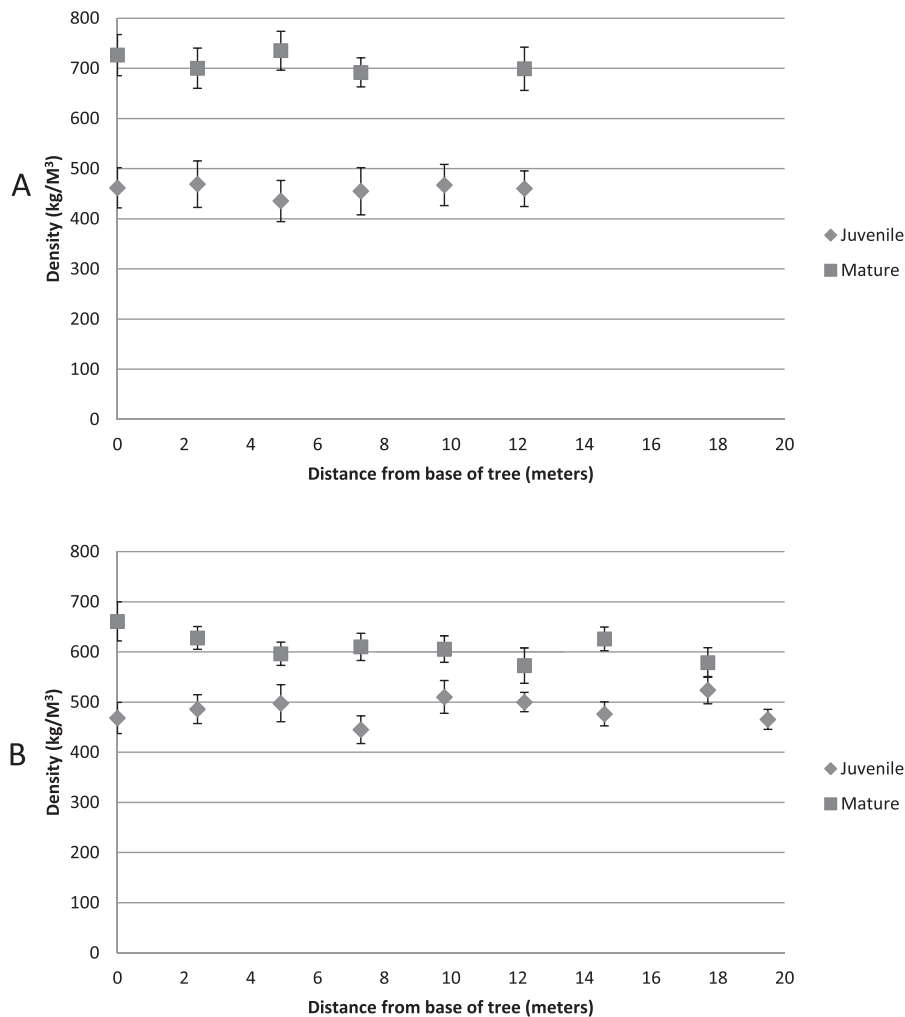|	Juvenile wood		Mature wood	
	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir
Average (kg/m³)	458.10	485.84	710.51	609.82
SD (kg/m³)	83.75	54.95	76.92	56.67
No. of specimens	12	10	14	10

Figure 1.—Average density determined at several distances from the base of the tree along the tree stem axis. (A) Data from the southern yellow pine specimens; (B) data from the Douglas-fir specimens.

components are more favorable than others (Frihart 2013). Hemicellulose has been linked to having the most hydroxyl bonding sites when compared with the other structural polymers in wood and this feature is one of the main secondary bonding mechanisms with wood substrates (Walinder and Johansson 2001). By summing the components of hemicellulose listed in Table 2 and comparing all values with statistical tests, it was determined that southern yellow pine had more hemicellulose, lignin, and extractives than Douglas-fir, whereas Douglas-fir had more cellulose than the pine specimens. The higher hemicellulose content of southern yellow pine could lead to higher bond strengths and resistance to delamination. However, confounding this supposition, southern yellow pine specimens also showed higher extractives content, which has been shown to be a negative factor in wood bonding by possible contamination of liquids applied to the surfaces and chemical alteration of surface properties (Walinder and Johansson 2001).

Wettability of the two wood types and growth regions was characterized using contact angle analysis as a measure of surface energy. When liquid adhesives are applied to surfaces or ''wet'' the surface, an angle is formed between the liquid droplets and the surface, i.e., the contact angle. Wetting of a surface is considered favorable if the contact

angle is less than 90° and unfavorable if the angle is greater than 90° (Burch 2015). Averaged contact angle results are shown in Table 3. It is noted from Table 3 that contact angles were lower for all three liquids and both growth regions on the southern yellow pine specimens. Because lower contact angles indicate more favorable spreading of liquids, southern yellow pine specimens might be expected to exhibit more favorable bonding surfaces than the Douglas-fir specimens on the basis of contact angle data alone. Statistical t tests of data in Table 3 indicate that when comparing the same growth region across the two wood types (i.e., juvenile southern yellow pine compared with juvenile Douglas-fir) for each liquid, all the paired contact angles were significantly different from each other. Surface energy values calculated using the acid–base approach (Burch 2015) for all three liquids are provided in Table 4. Lower surface energies were found for the Douglas-fir specimens across all components of dispersive, polar, acid, and base measurements and both growth regions, and together with higher contact angles, less favorable bonding might have been expected with the Douglas-fir specimens. In contrast, southern yellow pine, with lower contact angles and higher surface energies, might exhibit more liquid

Table 2.—*Results of compositional analysis completed on the basis of the National Renewable Energy Laboratory (NREL) standard for determination of chemical composition of biomass.*[a]

Height (m)	Extractives	Lignin	Arabinose	Galactose	Glucose	Xylose	Mannose	Total
				%				
Mature southern yellow pine								
0–2.4	3.52	28.68 (0.38)	1.21 (0.02)	1.53 (0.02)	43.37 (0.37)	6.42 (0.02)	11.26 (0.03)	95.99
2.4–4.9	2.91	32.39 (0.16)	1.23 (0.03)	3.64 (0.04)	38.19 (0.69)	7.45 (0.03)	9.60 (0.08)	95.42
4.9–7.3	3.29	28.81 (0.61)	1.17 (0.02)	1.85 (0.69)	43.40 (0.99)	6.27 (0.12)	10.72 (0.39)	95.50
7.3–9.8	3.26	30.12 (0.65)	0.94 (0.16)	2.34 (0.39)	37.51 (0.62)	6.08 (0.01)	9.48 (1.60)	89.72
9.8–12.2	3.88	32.33 (0.15)	1.02 (0.05)	3.62 (0.21)	40.48 (1.88)	6.41 (0.24)	9.40 (0.36)	97.13
12.1–14.6	3.87	30.62 (0.07)	1.17 (0.04)	2.78 (0.09)	42.70 (1.23)	7.20 (0.27)	10.06 (0.32)	98.41
0 –2.4	3.89	27.78 (0.78)	1.01 (0.11)	2.01 (0.25)	40.98 (0.48)	5.97 (0.68)	11.35 (1.28)	92.99
2.4–4.9	3.71	27.50 (0.14)	1.31 (0.02)	1.56 (0.04)	46.01 (0.60)	6.53 (0.11)	11.09 (0.17)	97.72
Average	3.54	29.8	1.13	2.42	41.58	6.54	10.37	95.36
Juvenile southern yellow pine								
0–2.4	5.89	32.27 (0.84)	1.20 (0.02)	3.57 (0.01)	38.64 (0.56)	7.86 (0.16)	9.21 (0.16)	98.64
2.4–4.9	5.75	31.57 (0.02)	1.33 (0.01)	2.57 (0.18)	38.56 (0.08)	7.77 (0.09)	9.47 (0.07)	97.01
4.9–7.3	6.02	31.80 (0.82)	1.32 (0.02)	3.37 (0.04)	39.37 (0.61)	7.51 (0.14)	10.17 (0.22)	99.57
7.3–9.8	6.17	31.07 (0.11)	2.10 (0.01)	3.61 (0.05)	40.06 (0.71)	7.15 (0.03)	9.02 (0.07)	99.18
9.8–12.2	5.78	30.42 (0.47)	1.32 (0.01)	2.01 (0.02)	41.16 (0.29)	8.23 (0.02)	10.74 (0.01)	99.66
12.1–14.6	4.05	30.41 (0.25)	1.11 (0.22)	2.09 (0.44)	36.12 (1.59)	6.92 (1.43)	9.02 (1.89)	89.70
0–2.4	4.27	29.54 (0.73)	1.41 (0.02)	3.51 (0.04)	40.44 (0.81)	7.28 (0.03)	11.11 (0.14)	97.56
2.4–4.9	4.18	30.62 (0.96)	1.39 (0.06)	4.05 (0.06)	39.33 (0.37)	7.25 (0.11)	9.68 (0.10)	96.51
Average	5.26	30.9	1.40	3.10	39.21	7.49	9.80	97.23
Mature Douglas-fir								
0–2.4	1.35	25.64 (0.94)	0.81 (0.02)	1.74 (0.05)	45.62 (1.35)	3.35 (0.07)	14.91 (0.50)	93.42
2.4–4.9	0.77	24.99 (0.60)	0.89 (0.03)	1.69 (0.03)	45.68 (0.80)	3.31 (0.02)	14.40 (0.28)	91.73
4.9–7.3	2.06	25.97 (0.29)	0.89 (0.02)	1.73 (0.01)	45.29 (0.83)	3.54 (0.10)	14.42 (0.12)	93.90
7.3–9.8	1.05	26.02 (0.45)	0.91 (0.01)	1.75 (0.01)	46.30 (0.30)	3.63 (0.01)	13.96 (0.01)	93.62
9.8–12.2	1.09	27.32 (0.48)	0.98 (0.02)	1.81 (0.03)	45.58 (0.34)	3.83 (0.01)	13.81 (0.08)	94.41
12.1–14.6	1.64	27.24 (0.24)	1.00 (0.02)	1.91 (0.02)	45.38 (1.07)	3.91 (0.07)	13.78 (0.33)	94.86
14.6–17.1	1.22	26.54 (0.19)	0.91 (0.01)	1.68 (0.06)	45.70 (1.70)	3.17 (0.12)	13.42 (0.50)	92.63
17.1–19.5	1.32	29.36 (0.36)	0.80 (0.02)	2.61 (0.03)	43.76 (0.63)	3.43 (0.07)	12.35 (0.24)	93.62
Average	1.31	26.6	0.91	1.77	45.64	3.59	14.21	93.66
Juvenile Douglas-fir								
0–2.4	3.30	31.61 (0.26)	0.56 (0.02)	3.16(0.33)	41.92 (0.25)	4.76 (0.01)	13.28 (0.07)	98.59
2.4–4.9	3.44	31.43 (0.11)	0.50 (0.01)	2.84(0.01	42.88 (0.67)	4.52 (0.05)	13.18 (0.17)	98.79
4.9–7.3	3.00	30.95 (0.04)	0.54 (0.03)	2.78(0.05)	43.41 (0.06)	4.24 (0.01)	13.33 (0.01)	98.25
7.3–9.8	2.28	31.16 (0.43)	0.65 (0.05)	2.91(0.12)	42.23 (0.41)	4.72 (0.01)	13.34 (0.09)	97.30
9.8–12.2	3.21	30.76 (0.49)	0.62 (0.01)	2.72(0.09)	43.26 (0.09)	4.42 (0.03)	13.45 (0.09)	98.44
12.1–14.6	2.42	30.28 (0.09)	0.74 (0.02)	2.30(0.04)	43.00 (0.07)	4.33 (0.02)	13.31 (0.05)	96.38
14.6–17.1	3.00	30.34 (0.43)	0.86 (0.05)	2.99(0.12)	41.89 (0.80)	4.65 (0.01)	13.56 (0.03)	97.29
17.1–19.5	1.52	27.56 (0.67)	1.08 (0.01)	2.65(0.03)	40.61 (0.39)	4.56 (0.16)	12.98 (0.02)	90.96
19.5–21.9	3.32	28.54 (0.31)	1.00 (0.18)	2.91(0.05)	39.32 (0.02)	4.16 (0.02)	12.15 (0.01)	91.39
Average	2.83	30.2	0.60	2.79	42.78	4.50	13.32	97.96

[a] Percentages are on a dry basis. Standard deviations are in parentheses. It should be noted that the total does not sum to 100 percent because of slight loss of material during filtration and other material handling steps.

spreading (higher degree of wetting) and more favorable bonding surface qualities.

K values determined in this research for the three liquids are shown in Table 5. Water and methylene iodide exhibited higher initial contact angles and higher *K* values for Douglas-fir than for southern yellow pine, but in contrast, the formamide exhibited higher initial contact angles in Douglas-fir than in southern yellow pine but lower *K* values in Douglas-fir than in southern yellow pine. *K* values for formamide were highest of all three liquids on both wood types and growth regions, indicating that formamide spread or penetrated the wood substrates more readily than did the water and methylene iodide. Water and formamide are polar liquids, whereas methylene iodide is nonpolar. Formamide

wetting was more favorable than the water and methylene iodide, as reflected in the larger *K* values. All testing was conducted at room temperature.

Surface energy and contact angle results were confirmed in related research on sensitivity to thermal deactivation and time-dependent wetting of two woods from Australia compared with Douglas-fir and loblolly pine (Burch 2015). Burch (2015) used water and methylene iodide to obtain *K* values and equilibrium contact angles on specimens prepared from the same trees used in this study. As in the present study, this additional study found that time-dependent behavior was more favorable on Douglas-fir than on the pine specimens for the unheated specimens and with water as the liquid. Methylene iodide time-dependent

Table 3.—Average contact angle (degrees) for each liquid on each wood type and growth region.

Wood type	Water Juvenile	Water Mature	Methylene iodide Juvenile	Methylene iodide Mature	Formamide Juvenile	Formamide Mature
Southern yellow pine						
Average (°)	60.6	51.1	30.3	29.2	29.4	27.6
Std. (°)	5.38	3.73	5.06	2.67	2.72	3.41
COV[a]	0.09	0.07	0.17	0.09	0.09	0.12
Douglas-fir						
Average (°)	73.85	87.04	43.81	42.29	60.25	67.76
Std. (°)	9.68	10.56	6.38	5.54	11.15	9.22
COV	0.13	0.12	0.15	0.13	0.19	0.14

[a] COV = coefficient of variation.

wetting measured with K values on unheated specimens also showed higher K values for Douglas-fir. However, reduction in the K values was more rapid with the Douglas-fir and in general, Douglas-fir exhibited larger variability in time-dependent wetting than the southern yellow pine.

Bond strength, percent wood failure, and delamination due to accelerated weathering

Shear block testing to determine shear strength and percent wood failure followed ASTM D2559 (ASTM International 2014) using the alternative two-ply assembly for the test specimens. Results are shown in Tables 6 and 7. Using Tukey's HSD test to compare the average shear stress values of southern yellow pine and Douglas-fir specimens bonded with the same adhesive, it was determined that four combinations showed averages that were statistically different (these are bold in Table 6): the mature-to-mature wood bonds with an assembly time of minimum open and minimum closed for both the PUR and PRF adhesives, the mature-to-mature bonds for the maximum open and maximum closed bonds for the PUR adhesive, and the minimum open and minimum closed assembly times with the PRF adhesive. All other averages were found to be essentially the same. It is interesting to note that the overall largest and smallest average shear stress values (13,343 kPa for loblolly pine compared with 10,241 kPa for Douglas-fir) were found with the minimum open and closed assembly times and the PUR adhesive. Southern yellow pine average shear strengths were higher for all minimum–minimum assembly times. Other combinations of assembly times, wood types and growth regions, and adhesives did not exhibit statistically significant trends. Only the minimum open and closed assembly times had a significant impact on shear strength values when comparing the two wood types bonded with the same adhesive. Effects statistical testing determined that the average shear strength of the southern

Table 5.—K values for the two wood types and three test liquids used to conduct contact angle tests.

	Initial contact angle (°)	K value (1/s)	Model fit R^2 (%)
Southern yellow pine			
Water			
Juvenile	55.6	0.262	99
Mature	43.4	0.306	99
Methylene iodide			
Juvenile	28.4	0.129	95
Mature	28.2	0.073	98
Formamide			
Juvenile	23.8	1.82	98
Mature	22.5	1.52	99
Douglas-fir			
Water			
Juvenile	72.7	0.170	98
Mature	83.8	0.123	99
Methylene iodide			
Juvenile	42.5	0.0151	98
Mature	41.1	0.0216	98
Formamide			
Juvenile	49.3	0.569	82
Mature	61.6	0.538	98

yellow pine assemblies was affected the most by the assembly times and Douglas-fir by adhesive type.

Results from visual approximation of the percent wood failure (Table 7) after shear strength testing indicated that all average values were above the minimum ASTM requirements of 75 percent. Douglas-fir was found to be affected the most by the growth region at the bond in combination with the assembly time for each adhesive, and southern yellow pine was not statistically affected by any factor or interaction of factors.

Resistance to delamination during accelerated weathering experiments was determined according to ASTM D2559 (ASTM International 2014). Large delamination values occurred in the PUR assemblies for both wood types and growth regions compared with the PRF-bonded assemblies as seen in Table 8. Of particular note is that the group of southern yellow pine specimens bonded with juvenile wood to mature wood using the PRF adhesive and minimum open and closed assembly times had several layers that debonded after the first cycle of ASTM D2559. Results from these specimens were not considered in further statistical analyses because these outlier values could skew results and undermine statistical analyses. For all other specimens, the total delamination values (sum of measurements from both end-grain surfaces and all bond lines) allowed by the standard for softwoods is 5 percent, with not more than 1 percent delamination in each measured bond line. All PRF combinations were less than the 5 percent delamination

Table 4.—Surface free energy of southern yellow pine (SYP) and Douglas-fir (DF) mature and juvenile wood.

	Surface energy, γ_L (mJ/m^2)	Dispersive, γ_L^D (mJ/m^2)	Polar, γ_L^P (mJ/m^2)	Acid, γ_L^+ (mJ/m^2)	Base, γ_L^- (mJ/m^2)
SYP juvenile	54.51	44.87	9.638	1.584	14.66
DF juvenile	42.81	38.33	4.476	0.6213	8.061
SYP mature	54.92	44.95	9.967	0.8818	28.17
DF mature	39.36	39.05	0.3106	4.98E-03	4.843

MIRABILE AND ZINK-SHARP

Table 6.—Results of ASTM International shear strength testing.[a]

| | Mature-to-mature | | | | Juvenile-to-mature | | | |
| | PUR | | PRF | | PUR | | PRF | |
Assembly time	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir
Average shear stress (kPa)								
Min.–min.	**13,353**	**10,241**	**11,878**	**11,004**	11,464	11,014	**11,791**	**10,870**
Min.–max.	10,964	10,866	11,278	11,548	10,474	11,256	11,146	10,450
Max.–max.	**10,551**	**11,607**	11,743	11,838	11,697	11,052	11,269	10,766
Maximum shear stress (kPa)								
Min.–min.	16,965	12,870	13,615	12,774	12,929	14,006	15,040	13,135
Min.–max.	12,925	12,937	13,831	13,551	13,524	14,637	14,111	13,406
Max.–max.	11,905	14,269	13,701	15,347	13,336	13,170	12,526	12,876
Minimum shear stress (kPa)								
Min.–min.	8,807	5,148	7,782	9,810	8,857	8,330	9,322	8,310
Min.–max.	9,373	7,856	9,106	9,934	7,506	7,666	8,510	8,155
Max.–max.	9,298	8,857	8,518	9,244	9,997	9,039	8,375	9,650
SD								
Min.–min.	2,191	2,077	1,472	820	979	1,678	1,484	1,272
Min.–max.	1,050	1,255	1,196	775	1,514	1,866	1,424	1,312
Max.–max.	1,120	697	1,432	1,535	1,046	1,290	962	1,099
No. of samples								
Min.–min.	20	22	19	19	21	19	22	20
Min.–max.	20	22	20	20	22	20	20	19
Max.-max.	19	21	19	19	19	21	20	21

[a] Values shown in bold are statistically different within the pairs of data. PUR = polyurethane; PRF = phenol-resorcinol-formaldehyde; min. = minimum; max. = maximum.

Table 7.—Percent wood failure results after shear strength testing.[a]

| | Mature-to-mature | | | | Juvenile-to-mature | | | |
| | PUR | | PRF | | PUR | | PRF | |
Assembly time	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir
Average (%)								
Min.–min.	81.0	76.6	77.4	76.3	82.9	88.2	84.8	77.5
Min.–max.	75.5	80.9	87.3	82.0	79.1	81.8	86.0	79.7
Max.–max	83.2	85.5	80.3	80.3	79.0	79.8	83.3	79.8
Maximum (%)								
Min.–min.	95	95	95	95	95	95	95	95
Min.–max.	95	95	100	95	95	100	95	95
Max.–max.	100	95	100	95	100	95	95	95
Minimum (%)								
Min.–min.	30	15	20	20	50	50	20	45
Min.–max.	20	50	60	25	50	25	65	60
Max.–max.	65	65	25	45	60	65	60	60
SD (%)								
Min.–min.	17.1	21.2	18.0	16.8	12.9	11.0	17.0	13.8
Min.–max.	19.6	12.1	11.8	15.3	11.7	19.1	8.7	10.9
Max.–max.	10.4	7.4	19.0	12.7	12.5	10.4	13.0	9.4
No. of samples								
Min.–min.	20	22	19	19	21	19	22	20
Min.–max.	20	22	20	20	22	20	20	19
Max.–max.	19	21	19	19	19	21	20	21

[a] PUR = polyurethane; PRF = phenol-resorcinol-formaldehyde; min. = minimum; max. = maximum.

Table 8.—ASTM 2559 delamination test results.[a]

Assembly time	Mature-to-mature				Juvenile-to-mature			
	PUR		PRF		PUR		PRF	
	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir	Southern yellow pine	Douglas-fir
Average (mm)								
Min.–min.	165.39	170.38	2.74	3.54	115.41	97.44	—	1.36
Min.–max.	175.53	161.00	**0.00**	**6.06**	77.65	119.00	1.45	1.73
Max.–max.	116.76	149.90	1.83	3.54	**110.92**	**155.76**	**0.67**	**3.27**
Maximum (mm)								
Min.–min.	222.11	222.63	7.58	8.57	138.16	150.62	—	2.86
Min.–max.	210.35	239.36	0.00	9.97	114.41	151.87	4.60	4.30
Max.–max.	209.07	196.13	5.91	8.65	125.31	216.64	2.68	4.52
Minimum (mm)								
Min.–min.	129.55	126.54	0.00	0.00	87.71	41.47	—	0.00
Min.–max.	139.98	87.74	0.00	0.00	45.85	73.09	0.00	0.00
Max.–max.	61.73	128.45	0.00	0.00	80.06	114.50	0.00	0.00
SD								
Min.–min.	40.52	37.85	3.22	3.61	23.40	44.59	—	1.58
Min.–max.	33.64	48.01	0.00	3.79	28.28	33.30	2.25	1.97
Max.–max.	50.40	24.56	2.86	3.98	22.80	38.69	1.34	1.72
Total no. of measurements								
Min.–min.	6	6	6	4	6	4	—	4
Min.–max.	6	6	6	6	6	4	6	6
Max.–max.	6	6	6	6	6	6	4	6

[a] ASTM International 2014. Values shown in bold are statistically different within the adhesive paired data. PUR = polyurethane; PRF = phenol-resorcinol-formaldehyde; min. = minimum; max. = maximum; — = no results because of debonding of layers within specimens after first cycle of testing.

requirements (except the pine juvenile wood to mature wood that had debonded layers); however, all values for the PUR assemblies were greater than the 5 percent limits. PRF-bonded pine specimens using minimum open and maximum closed times resulted in zero delamination, but the Douglas-fir PRF average value was the highest at that same assembly time combination.

Discussion

Research objectives for this study were to characterize bonding variables for two wood types and attempt to describe how the anatomical and chemical structural properties influenced bond durability and strength when bonded with the same adhesive. Aspects studied were various properties of the two wood types, two wood growth regions, two adhesive types, and three assembly times for each adhesive. Statistical analyses were used to compare the two wood types bonded with two adhesives and three assembly times with each other. As mentioned, the two growth regions (mature bonded to mature and juvenile bonded to mature) were considered separate specimen types and were not compared with one another.

Wood properties

With regard to wood anatomy and chemical content, major findings are that overall average density values were statistically different for the two wood types studied and that density and chemical content were found to be fairly consistent along the axis of the trees. Other research has indicated a gradual reduction in density from base to crown (Gartner et al. 2002). A higher density at the base of trees can be due to compaction over time from the crown weight and a higher percentage of latewood within individual growth rings at the base to provide mechanical resistance to cantilever bending from wind and snow loads. However, in the three trees we studied, there were no detectable trends in density variation from base to higher sections in the trees. The trees used in our study were growing within a forest setting and were not open growth without neighboring trees. Neither stand had been exposed to consistent winds or snow loading, so development of density gradients along the stem axis had not occurred in these trees because of mechanical property requirements. Extractive, carbohydrate, and lignin content also did not exhibit variation with height within the trees. As with density variations, changes in composition along the tree axis were expected; however, the trees we studied were very consistent in chemical composition along the tree axis. Many factors enter into wood cell wall formation and it is not unusual for individual trees to exhibit patterns different from established trends for physical and chemical properties.

Trends in contact angle and surface energy measurements were very clear for the two wood types. Contact angles were statistically different for all combinations of liquids, growth regions, and wood types and consistently lower for all three liquids and both growth regions studied on the loblolly pine specimens. Surface energies were correspondingly higher. Lower contact angles and higher surface energies on the loblolly pine specimens are thought to provide better surfaces for wettability with adhesives. Factors that affect contact angle include the temperature of surroundings, temperature of the specimen, relative humidity, wood grain surface, earlywood versus latewood, extractives, surface energy, and speed of droplet dispensing. All specimens were

tested at room temperature and, although no relative humidity control was provided, observation of the relative humidity in the test room indicated fairly steady levels during the testing. All surfaces were prepared using the same methods and all were earlywood, tangential surfaces. Droplet application was carefully monitored and was as consistent as possible with the application instrument.

Time-dependent wetting (K values) measured with initial and equilibrium contact angles was less consistent when comparing the two wood types. Higher K values indicate faster achievement of an equilibrium contact angle. Water and methylene iodide exhibited higher initial contact angles and K values for the Douglas-fir specimens; however, the formamide exhibited higher initial contact angles in the Douglas-fir but lower K values than the loblolly pine specimens. Taken together, these results indicate that initially the loblolly pine exhibited the better wetting properties with all three liquids, but the time-dependent behavior was different and slightly faster for Douglas-fir with water and methylene iodide. Spread and penetration of the polar liquids, water and methylene iodide, on the Douglas-fir was more favorable, but spread of the nonpolar liquid, formamide, was less favorable on the Douglas-fir specimens. Time-dependent behavior of liquids on surfaces may have influenced spread and penetration of the adhesives used in this study, particularly with the PUR moisture-cure adhesive and could be indirectly related to differences observed with the various assembly time and wood type interactions as described below.

Bond strength, percent wood failure, and delamination due to accelerated weathering

Considering shear strength and percent wood failure, the southern yellow pine specimens exhibited the higher shear strength averages in general but especially at the minimum open and closed assembly times with the PUR adhesive. Pine specimens also exhibited acceptable percent wood failure values for all test combinations. However, it should be noted that except for the minimum assembly times, most of the shear strength values shown in Table 6 were statistically similar when comparing the two wood types and the two adhesives. It was determined statistically that the southern yellow pine specimens were affected the most by assembly time. The highest overall average values were for the minimum open and closed assembly times and the PUR adhesive. This means that for southern yellow pine bonding with either the PUR or the PRF adhesive, assembly time is critical for maximum shear strength development. Longer open and closed assembly times were found to produce lower average shear strength values in this study. Factors in the pine specimens that likely contributed to high shear strengths were higher mature wood density, higher surface energies, lower initial contact angles, and higher percentages of hemicelluloses with more hydroxyl bonding sites. Higher wood density leads to higher mechanical properties in wood in general because of high quantities of cell wall material to resist fracture and withstand high loading. Any negative impact on formation of mechanical interlocking due to higher density resulting from small lumina was likely overcome by some other adhesion factor such as the higher surface energy found for the pine specimens and the higher percentage of hydroxyl bonding sites. Higher surface energy values should be favorable for more rapid adhesive spread and more uniform coverage with fewer gaps because higher-energy surfaces would result in greater attractive forces at the surface to draw the adhesive across and into the wood cell structure. Values for percent wood failure in the southern yellow pine specimens were all within the acceptable levels and appeared to not be statistically affected by any test variables, which provided evidence that high-integrity bonds were formed with both the PUR and PRF adhesives, all assembly times, and both growth regions present in the pine specimens.

Douglas-fir specimens exhibited generally lower average shear strength values than the southern yellow pine (Table 6) for both adhesives despite having some properties that could have led to more favorable bonding (e.g., lower mature wood density, higher K values, and lower extractives percentage) and potentially higher shear strengths. However, it should be noted again that most of the shear strength values shown in Table 6 were statistically similar when comparing the two wood types and the two adhesives. Therefore the better density, time-dependent wetting, and extractive characteristics were not found to produce statistically superior bonding in the Douglas-fir specimens. When looking at statistical analyses of the interactions and the impacts of the various test variables, it was found that the pine specimens were sensitive to assembly times, but Douglas-fir specimens were more influenced by the interaction of the adhesive with the growth region at the bond line than the influence of assembly times alone. This means that Douglas-fir bonding with either the PUR or the PRF adhesive will be affected by whether or not the substrate is composed of juvenile wood, mature wood, or some combination and it is not as sensitive to assembly time as the pine specimens. Regarding percent wood failure, as with the pine specimens, no statistically significant differences were found for percent wood failure results across the various factors for Douglas-fir (Table 7). All values were above acceptable limits determined by ASTM standards, indicating reasonable bonding for the Douglas-fir with the two adhesives when considering percent wood failure requirements. High or acceptable percent wood failure values are supposed to be an indication of good adhesive bond quality because the failures are within the wood bulk material rather than within the adhesive bond lines. However, the percent wood failure analysis in this study was not found to be a particularly sensitive test for identifying potential differences between the two wood types and their interactions with the adhesives or assembly times.

Specimens subjected to extreme moisture, pressure, and temperature conditions as prescribed by the ASTM standard exhibited large differences in performance on the basis of adhesive type but not wood type. Much greater delamination and unacceptably high values were measured for the PUR adhesive assemblies compared with the PRF for both wood types. Delamination measurements from the PUR adhesive (Table 8) at several hundred millimeters were all above the 5 percent limits, but with the same combination of bonding factors, delamination measurements for the PRF assemblies were acceptable at only tens of millimeters and, in many cases, no measurable delamination was evident on the surfaces. Delamination has been found to be affected to a high degree by the ability of a wood and adhesive combination to distribute stresses (Frihart 2009). Shrinking and swelling of the bonded assemblies due to moisture content changes create strains and strain distributions that

result in stresses at the bond line that have potential to result in delamination. Previous research has shown that PRF adhesives compared with PUR show less strain at the bond line and a higher degree of penetration into the wood structure (Gindl et al. 2001). PRF has been said to displace water in the cell wall of woody tissue and mirror the shrink and swell properties of the wood (Frihart 2009). PUR, on the other hand, has a higher molecular weight that cannot penetrate the cell wall structure, but it is a more flexible adhesive that allows stresses to be distributed through the adhesive itself rather than the interphase of the wood and adhesive. PUR adhesives are ordinarily formulated to be used for normal room-temperature and humidity conditions. They are prepolymerized adhesives that have polyether or polyester segments joined together with di-isocyanates, they are not highly or irreversibly cross-linked, and they have proteins that are rigid when dry but flexible as water content increases due to internal hydrogen bond plasticization (Custodio et al. 2009, Frihart 2009). PRF adhesives polymerize in situ, can infiltrate into cell walls before curing, and are relatively rigid polymers and highly cross-linked after curing (Frihart 2009). Despite rigidity and the potential to form inflexible or brittle bonds, PRF adhesives are considered the most moisture-durable wood adhesives because of their ability to infiltrate wood cell walls and decrease the shrink and swell due to moisture changes (Frihart 2009).

The high degree of delamination measured in this study with the PUR adhesives for all combinations of wood variables likely reflects the extremes of the test regime, the lower degree of cross-linking, and the lack of cell wall penetration and stabilization with this adhesive. Under ordinary indoor conditions, PUR adhesives are reported to provide good strength and durability even under damp conditions, but poor resistance to delamination with PUR-bonded assemblies tested with severe cyclic delamination tests has also been reported by others (Frihart 2009). Testing bond durability in the manner of ASTM D2559 does not require external force, but extreme swelling and shrinking forces that develop during the various cycles are sufficient to cause bond and bulk material failure. The test involves cycles of vacuum water soaking followed by oven-drying and a water boil in the second cycle. In Vick and Okkonen (2000), Douglas-fir specimens were bonded with four different formulations of a one-part moisture-cure PUR and a resorcinol-formaldehyde adhesive. When the specimens were tested dry, they exhibited very similar strengths for the two adhesive systems, but after undergoing different wet cycles, much different results were obtained. The four PUR-bonded assemblies showed a dramatic decrease in percent wood failure to around an average of 38 percent, whereas the resorcinol-formaldehyde specimens maintained a wood failure of 98 percent.

Despite evidence that high-integrity bonds were formed at all combinations studied per the dry shear strength and percent wood failure testing, one group of the pine, PRF, minimum open and closed assembly time specimens had layers that were completely debonded after the first cycle of the ASTM D2559 weathering test. Examination of the debonded layers and the bonding surfaces did not reveal any obvious problems or spotty bonding that lead to this particular behavior and several layers remained intact after the first cycle; however, visual observation of the percent wood failure on two debonded layers showed very small amounts and shallow wood failure (about 10%) on the surfaces. It is possible to speculate that this group of southern yellow pine specimens did not develop sufficient wet strength at the minimum open and closed assembly times with the PRF adhesive, but reasons for the debonding were undeterminable at the time of testing. Complete debonding at the minimum open and closed assembly times for the pine specimens bonded with the PRF adhesive might mean a strong sensitivity to assembly time for this combination of bonding factors, but additional exploration is needed to confirm this speculation.

Statistical analyses within an adhesive type but across the two woods revealed that many of the overall average values for delamination were not different from one another except in three cases—the minimum open and maximum closed assembly times bonded with the PRF adhesive and the two assemblies bonded with maximum open and closed assembly times and the PUR adhesive. Where these statistical differences were noted, the Douglas-fir specimens exhibited higher delamination than the pine specimens. Greater delamination in the Douglas-fir specimens for these assembly times and adhesive combinations may have resulted from a sensitivity to interactions between the adhesive and assembly time with the Douglas-fir specimens and time-dependent spreading and penetration of the adhesives. It was found previously in our work that Douglas-fir exhibited time-dependent wetting (K values) that showed more rapid spreading of polar liquids on the Douglas-fir specimens and slower spreading rates for the nonpolar liquid. Potential for more rapid spreading and penetration of the adhesives for the Douglas-fir specimens, especially at the maximum open and closed assembly times with the PUR adhesive, may have contributed to any differences in delamination between the two wood types.

Summary and Conclusions

ASTM shear-strength testing demonstrated that maximum average dry shear strengths were developed with the pine specimens bonded with the PUR adhesive at minimum open and closed assembly times. In contrast, the lowest average shear strength was developed with the Douglas-fir specimens bonded with the same PUR adhesive and the same minimum open and closed assembly times. However, most all other average shear strengths were statistically similar and not affected by the adhesive or assembly times studied. Percent wood failure values were all above 75 percent, which is within acceptable limits and were found to be statistically similar across all variables studied, and both adhesives provided similar percent wood failure results on both wood types. Very high delamination measurements were found for the PUR adhesive assemblies for both wood types and all assembly times. In contrast, very small delamination values were measured for all specimens bonded with the PRF adhesive. However, it was determined that many of the averaged delamination values were statistically similar and no outstanding statistical differences could be found between the Douglas-fir and pine specimens.

Although the number of trees was limited in this study, results indicated that southern yellow pine specimens developed generally higher dry shear strength values and lower delamination due to accelerated weathering tests, particularly with the PRF adhesive. Similar and extremely high delamination was measured for both wood types with the PUR adhesive, so no significant differences in bonding

MIRABILE AND ZINK-SHARP

properties of the two wood types were observed with this adhesive. Both wood types and adhesives exhibited favorable bonding as measured with dry shear strength and percent wood failure. Expectations that the southern yellow pine specimens might provide less favorable bonding when tested in extreme weathering conditions were not confirmed with the wood bonding factors, adhesives, and assembly times tested in this study.

Acknowledgments

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