Investigating Differences between Douglas-fir and Southern Yellow Pine Bonding Properties

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(ABSTRACT)

Differences in southern yellow pine (represented by *Pinus taeda*) and Douglas-fir (*Pseudotsuga menziesii*) mature and juvenile wood were examined in terms of density, chemical composition, surface energy, shear stress, % wood failure, and delamination. Density was measured using a QTRS density scanner. Loblolly pine contained a higher average density. Chemical composition was measured using the NREL standard for identifying the chemical composition of biomass. Southern yellow pine contained a higher % hemicellulose, lignin, and extractives. Douglas-fir had higher % cellulose than southern yellow pine. Surface energy was measured using the static sessile drop contact angle method and the acid/base approach. Southern yellow pine contained a lower average contact angle than Douglas-fir. Shear stress, % wood failure, and durability were measured using ASTM-D2559 with two adhesives, a one-part moisture cure polyurethane (PU), and a two-part ambient curing phenol-resorcinol-formaldehyde (PRF). Shear stress for southern yellow pine was affected the most by the type of growth regions at the bond (juvenile to mature wood) and the assembly times of the adhesives used. Douglas-fir shear stress was affected by the type of adhesive and the growth region at the bond. Delamination results demonstrated that when using PRF the southern yellow pine has less delamination statistically than Douglas-fir. Also, the growth region at the bond with both adhesives showed to impact delamination with juvenile to mature wood having less delamination than mature to mature wood.

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Chapter 1: Introduction

1.1. Defining the problem

Douglas-fir and southern yellow pine are two of the most used softwoods in wood composites. These two wood types look similar on the surface but contain different properties anatomically and chemically. The industry has stated that these two wood types have exhibited differences in strength durability and level of destruction for a given adhesive.

Knowledge of these two wood types individually is widely available in the literature, but little information is given on how these two wood types compare in terms of bonding. An understanding of how these two wood types differ in relation to bonding would allow increased knowledge for use in wood composites and could allow for increased understanding of the influence and optimization of adhesive use for both wood types.

1.2. Technical Objectives

The particular objective of this study was to characterize bonding variables between both wood types and determine how the variables influence durability and bond strength. Meeting these objectives will allow for a greater understanding of how these two wood types differ in terms of bonding characteristics and adhesive use. This will also provide insight on how bonding variables in the wood types impact the bond durability and strength.

Chapter 2: Literature Review

2.1 Introduction

Bonding properties that are significant in producing wood composites can be identified by reviewing scientific literature. The following review contains information about factors significant to bonding and theories of how to produce durable bonds.

2.2 Factors affecting bonding

Determining the factors that influence a satisfactory bond under various bonding conditions is enhanced by examining what causes a bond to fail. Different conditions should be used depending on the purpose of the material being created. Failure of a bond helps to know how to make a bond that is capable of being satisfactory under various conditions. Both the adhesives and adherends contain different properties that are relevant to making a durable bond. One of the most recognized models separates the wood and the adhesive into components [1]. These components are listed in order of wood interior, wood subsurface, interface, boundary layer, and then the adhesive only [1]. This model has been used by many researchers as a starting point when examining bonding failure [2, 3, 4, 5]. Another model states that wood and adhesive failure can be described in a similar, but different way, by examining the difference between both adherends, wood failure, the penetrated and unpenetrated wood interface, penetrated wood, the adhesive-wood interface, and the bulk adhesive [6]. More recently these two models were investigated to determine which said model is more applicable when discussing failure of wood bonds. It was determined that the model examining the adhesive components described first was more relevant to determining where failure occurs [7].

As stated above, understanding failure in wood adhesive bonds allows a greater understanding of bonding and how it can be improved. Wood adhesive bonds are much different than other adhesive bonds that take place between metals and plastics because wood is a porous material with high variability. This means that a certain piece of wood

bonded with the same conditions as another piece of wood may exhibit different properties in terms of bonding.

Theories that are most commonly used in understanding wood adhesive bonding include mechanical interlocking, electronic or electrostatic theory, adsorption or wetting theory, diffusion theory, chemical bonding theory, and the theory of weak boundary layers and interphases [8, 9]. Each of these theories incorporates a chemical and anatomical aspect of the wood and adhesive to different scales. It is also important to note that more than one of these theories may be applied at the same time. What theory is used is very dependent on the conditions and materials used.

Mechanical interlocking describes how an adhesive forms an interwoven bond with a porous material [10]. The electrostatic theory is the idea of different charges being attracted to each other. Adsorption or wetting theory in terms of wetting a wood surface deals with the idea that the adhesive should have a satisfactory wetting on the wood surface allowing it to spread in a favorable manner. Diffusion theory is the ability of the polymers in the adhesive to diffuse into the polymers of the wood. Chemical bonding theory is the formation of chemical bonds between the adhesive and the wood substrate. The theory of weak boundary layers is the concept of weak layers on the boundaries of the bond cause failure. Extensive study has been done on the influence of over drying of surfaces [12, 13].

Bonding of wood can be examined on the millimeter, the micrometer and the nanometer scales of bonding [11, 14, 15, 16]. Results from a study of the characteristics of wood adhesion in relation to using hydroxymethyl resorcinol as a primer is provided in Table 2.1 with a comparison of these adhesive interactions relative to a length scale [11]. The researchers stated that each of these theories could be categorized as theories of entanglement or interlocking and those theories based on charge interactions [11]. Also, the length scale of the theories listed in the table below can change depending on several factors such as the type of adhesive used, the composite being made, and the type of

wood being used. A phenol-formaldehyde adhesive was used to examine different anatomical and adhesive interactions when bonding with a softwood. The length scales differed in magnitudes from the molecular length of phenol-formaldehyde compared to the tracheid lumen diameter [14, 15]. Size of the composite being created can affect how large the view of the adhesive wood interaction scales. Large glulam beams being magnitudes in length scale different than viewing the how the adhesive interacts with the wood cell wall polymers [15, 16].

Table 2.1 Adhesion theories with their type of interaction and their respective length scale [11]. (Used with permission)

Adhesion Theory	Type of interaction	Length scale
Mechanical	interlocking or entanglement	0.01-2000 μm
Diffusion	interlocking or entanglement	10 nm-2 mm
Electrostatic	Charge	0.1-1μm
Covalent bonding	Charge	0.1-0.2 nm
Acid-base interaction	Charge	0.1-0.4 nm
Lifshiftz-van der Waals	Charge	0.5-1 nm

These bonding mechanisms shown above lead to the concept that wood and adhesive combinations are different for each adhesive, composite, and wood type that is used in bonding. Looking at the various scales of length shown above it is easy to see that many factors are in play when analyzing what makes a favorable bond.

2.3 Durable Wood Bonds

There are several important factors when evaluating a wood surface for bonding and creation of a durable wood bond. The factors that have been found to be the most important in affecting durable wood bonds are the ability to distribute stress with moisture change and how the adhesive chemistry and polymer properties contribute to moisture changes affects on the wood bondline [17]. The stress applied to a wood bond by the shrinkage and swelling of the wood can be overbearing on the bond. When analyzing wood undergoing moisture change it can be seen that the wood warps with water change. The type of warp is dependent on the orientation of the wood structure

itself. Using five epoxy adhesives demonstrated that the main points of failure were in the wood epoxy interphase regions knowing that epoxy is usually a durable moisture adhesive with other adherends [18]. Adhesive chemistry and polymer properties of adhesives were separated into two groups: *in-situ* polymerized and pre-polymerized adhesives based on the way the adhesive interacts with the cell wall and the adhesives chemistry [17]. The *in-situ* adhesives helped distribute stress away from the adhesive wood bondline whereas the pre-polymerized adhesives had longer polymer chains and allowed more flexibility at the bondline. The longer polymer chains with more flexibility allow for the stress from warping in the wood structure due to moisture change to be distributed through the adhesive rather than the adhesive wood interphase [17]. Adhesive chemistry and polymer properties demonstrate in theory that a durable bond can be achieved if favorable bonding to the wood surface is achieved. Hybrid poplar wood bonded with a phenol-formaldehyde and poly-vinyl-acetate adhesive demonstrated that bond strength and stiffness increased with the amount of the adhesive coverage on the surface of the wood substrate [29]. Delamination and shear strength was measured with a focus on surface preparation in several softwoods. The largest factor influencing delamination and bond strength was from the time gap between surfacing till bonding and the effect of surfacing on the damage to the wood surface [19]. In a separate study, it was shown that different surfacing effects on several softwoods provided no definite effect on the tensile shear strength and wood failure percentage using polyurethane and phenol-resorcinol-formaldehyde [20]. Overall there is no one adhesive or joint that will provide satisfactory durability to weathering in all scenarios [3].

2.4 Douglas-fir and Southern Yellow Pine

2.4.1 Anatomy

Douglas-fir and southern yellow pine are both resinous softwoods. Softwood anatomy consists of a majority of longitudinal tracheids. The size of tracheids differs with earlywood to latewood and in relation to adhesion theories these factors can affect the degree of mechanical interlock and the weak boundary layer. The amount of void space

in earlywood and latewood tracheids allows for the adhesive to form a mechanical interlock in the porous structure of wood. Mechanical interlocking's contributions to bond quality are dependent on the space available which can vary depending on the tracheid's volume in earlywood to latewood. Weak boundary layer theory is also affected by the anatomical features such as tracheid diameter because with a smaller cell wall thickness in earlywood, the mechanical properties of the tracheid are less favorable than mature wood and this then forms a weak point in the failure of a bond affecting bond quality.

The tracheid length can differ slightly in earlywood to latewood but there is no real conclusion of whether or not it is consistently getting larger or smaller as the tree ages or from earlywood to latewood in mature trees [21]. Mature Douglas-fir earlywood tracheids measured from multiple samples and 35 trees had an average length of 3.56mm with a radial diameter of 41.2 micrometers [22]. Loblolly pine earlywood and latewood tracheid length measured from 18 different trees with an average of 47 measurements are summarized into mean values in Table 2.2 [21]. Tracheid diameter can be correlated to the thickness of the cell wall of tracheids which can then be related to the density because tracheids comprise most of the cells in softwoods. When comparing the two wood types, you can see that the average length of the tracheids is longer, and the tracheids have a wider diameter in southern yellow pine than in Douglas-fir. In relation to mechanical interlocking, one might think that a larger volume in the tracheids would provide more surface area on the cell wall for the adhesive to solidify and provide a favorable earlywood mechanical interlock. On the other hand, with a larger volume in earlywood tracheids the cell wall is smaller and this would lead to the concept of the weak boundary layer theory where a failure would be more likely to occur.

Table 2.2 Loblolly pine tracheid length and diameter from earlywood and latewood in mature and juvenile wood [21].

Growth Region	Earlywood (mm)	Latewood (mm)	Radial Diameter Earlywood (μm)	Radial Diameter Latewood (μm)
Juvenile	2.99	3.14	43.8	26.3
Mature	4.16	4.14	46.8	27.5

2.4.2 Chemical Composition

Woody material consists of three major chemical components that are cellulose, hemicellulose, and lignin. These three chemical components combined in different combinations make up the cellular structure of the wood. Chemically the base units of these components provide a surface upon which the adhesive can make a chemical bond or diffuse through if the molecular weight of the adhesive is small enough. In relation to adhesion, this could affect the diffusion, chemical bonding, acid-base interaction, and wettability. Douglas-fir and loblolly pine have their chemical compositions shown in Table 1.5 below [23]. Data from this chart was collected by the USDA, Forest Service, and Forest Products Laboratory from 1927 to 1968.

Table 2.3 Chemical compositions of Douglas-fir and loblolly pine [23].

Wood Type	Glucose (%)	Xylose (%)	Galactose (%)	Arabinose (%)	Mannose (%)	Lignin (%)
Douglas-fir	44	2.8	4.7	2.7	11	32
Loblolly Pine	45	6.8	2.3	1.7	11	28

When comparing between these two wood types, loblolly pine contains 1 percent more glucose and about 0.6 percent more hemicellulose. Hemicellulose total percentage was calculated by summing up the four hemicelluloses listed above to make a total. However, there is more lignin in Douglas-fir than in loblolly pine. The composition is important because in bonding of wood, the cellulose content might be the major component, but the hemicellulose content is the main site of interaction. The concept of cellulose not being the major component on the surface of the wood is thought true because hydrogen bonding has greater access to hemicellulose after surfacing [41,42]. Hydrogen bonding is believed to be one of the central mechanisms of secondary bonding because many of the major adhesives used are water-based and water is contained in the cell wall of wood allowing for interaction between the water of the adhesive and wood to occur. When looking at Douglas-fir and loblolly pine their percentages seem very similar, but the chemical composition of trees changes with the location of wood obtained from the tree, different ages of the tree, and different geographical areas.

Extractives play a large role in the bonding of woody material. Extractives are natural products produced by trees during the formation of heartwood and are thought to be produced by the tree as a mechanism to defend the tree. The extractives vary between wood types as well as the quantity produced in each tree. Extractives can affect the wettability of the wood by being a chemically unfavorable bonding site. Extractives mitigating to the surface and blocking the adhesive from flowing into cells also impacts bonding. The amount of extractives recovered from wood is also dependent on the extraction method and where the wood is obtained. Southern yellow pine was found to have 4% extractives in one board using ethanol-toluene (8hours), ethanol (8 hours), and distilled water (2 hours) [25]. Loblolly pine has been found to have an average of 2.5% extractives content on average based on an oven-dry basis when using ether (8 hours) to remove the compounds [26]. Douglas-fir was found to have 3.85% extractive content on an oven-dry basis using acetone extraction for two days [27]. When comparing these two wood types, there seems to be some deviation of percent extractives in the method used and where the tree was obtained. The tree type with the higher % extractives, will, in theory, have an unfavorable experience when bonding if the proper precautions such as surfacing prior to bonding are not taken.

2.5 Phenol-Resorcinol-Formaldehyde (PRF) and Polyurethane (PU)

2.5.1 Phenol-Resorcinol-Formaldehyde

Phenol-resorcinol-formaldehyde adhesives were first introduced to help lower the cost of ambient-curing resorcinol adhesives. There are three different major phenol-resorcinol-formaldehyde polymers that are formulated. One is a phenol-formaldehyde reacted with resorcinol and then mixed with a hardener just prior to bonding. Another is where phenol-formaldehyde is mixed with a resorcinol hardener just prior to bonding. The last type is phenol-formaldehyde reacted with resorcinol that is then mixed with a phenol-formaldehyde adhesive just prior to bonding [28]. PRF is well known in the literature to produce bonds that are favorable for weathering durability, wood failure, and bond strength in wood composites depending on the application [28, 37, 54]. A theory

how phenol-resorcinol-formaldehyde contributes to favorable wet and dry properties is proposed in the literature [17]. The theory states that phenol-resorcinol-formaldehyde infiltrates the cell wall under the diffusion theory of adhesion, and a degree of high crosslinking occurs making the adhesive very rigid [17]. These adhesives help control the shrinking and swelling of the wood due to water at the bondline and reduce the stresses related to moisture change at the bondline. Also, phenol-resorcinol-formaldehyde exhibits absorption of water similar to wood allowing it not to have a large difference in swelling which was recorded as high as 18% weight gain from water [52].

2.5.2 Polyurethane

Polyurethane adhesives usually are a one-or two-part adhesive depending on the application needed for adhesion. The one-part polyurethane moisture cure adhesives are used for average room temperature/humidity curing because the adhesive reacts with moisture in the air to allow for crosslinking to occur. One-part moisture cure polyurethanes typically consist of two phases. A soft phase and a hard phase. The soft phase is a flexible component and the hard phase is made to react with moisture by crosslinking. The two-part adhesives have an isocyanate portion and an isocyanate-reactive portion that need to be mixed prior to bonding. Portions of polyurethane exposed to air form a thick layer to help with moisture diffusion that is the primary mechanism of curing. Factors like humidity have an affect on the curing of polyurethane since there is moisture in the air. Ten polyurethanes now commercially available were cured at lower than recommended moisture content and tested in shear strength [48]. These ten polyurethanes demonstrated below specified results by the manufacturer. Oak, oriental beech, and Scotch pine bonded with a moisture cure polyurethane then tested for shear strength after submerging in boiling water then cold water in the BS EN 205 standard demonstrated severe loss in strength of oak [49]. Four one-part polyurethanes bonded to Douglas-fir and yellow-poplar in a modified version ASTM-D2559 exhibited low levels of wood failure and low resistance to delamination [36]**.** Recently three one-part moisture cure polyurethanes with different mass ratios of hard-to-soft segments tested in double

cantilever beam fracture specimen showed that the largest ratio of hard to soft segment demonstrated critical fracture energy similar to the other formulations in mode one fracture but the least amount of adhesive penetration [50]. Polyurethane one-part adhesives have been seen to have favorable shear strength and wood failure but not under wet conditions. Previously discussed was the theory describing adhesive weathering durability explaining how adhesive models deal with durability in wood by stating that polyurethane belongs in the group of pre-polymerized adhesives [17]. Polyurethane has a long polymer chain which is very flexible and allows the stress from the wood shrinking and swelling at the bondline due to water to be distributed on the bulk adhesive as opposed to the bondline [17]. Testing of two one-part polyurethanes and phenol-resorcinol-formaldehyde cured resins in tensile strength after soaking showed similar results that polyurethane is a flexible material compared with the *in-situ* adhesives mentioned in the theory discussed above with the strain at failure being around 25% for the polyurethanes and 2.5% for phenol-resorcinol-formaldehyde [51].

2.6 Summary

There are many factors that affect bonding and what comprises a durable bond but there is not much research that incorporates more than one of these factors when looking at what influences bonding properties. Douglas-fir and southern yellow pine properties as stated above differ for many reasons. For example, where the adherends are taken from within the tree, the geographic location of the tree, and tree age. Adhesives polyurethane and phenol-resorcinol-formaldehyde exhibit different properties when dry and wet but it is important to note that their adhesive properties with wood are very dependent on the formulation of the adhesive, environmental conditions, and several factors of the wood type variability [4].

Chapter 3: Materials and Methods

3.1. Materials

3.1.1. Wood Types

Two loblolly pine *(Pinus taeda)* trees harvested from the Reynolds Homestead Forest Resources Research Center (FRRC) in Critz, Virginia, were chosen to represent southern yellow pine (Figure 3.1). The particular trees were selected based on their diameter breast height (dbh), trunk straightness, and general health. The selected trees were felled, delimbed, and bucked to 2.44 meters. There were 8 stem bolts total with the dbh ranging from 0.20-0.36 meters. Both trees were planted around the 1970's by Virginia Tech students and had received no prior history of silvicultural practices. The only non-natural occurrence was a prescribed fire in 2002 which allowed for higher moisture holding soil layers to occur in the soil profile. After bucking of sections, the logs were end coated twice with clear Waxlor to prevent extreme moisture loss as well as end checks and splits. The tree bolts were then transported to the Brooks Center in Blacksburg, Virginia, where they were again end coated with clear Waxlor. The tree bolts were stored for 8-14 days with cutting starting on the 8^{th} day and finishing on the 14^{th} day.

Figure 3.1 Loblolly pine logs felled from Critz, Virginia being prepared to be sawed

Raw material for the Douglas-fir (*Pseudotsuga menziesii*) was harvested from McDonald-Dunn research forest in Benton County, Oregon, which is managed by the Oregon State University (OSU) College of Forestry. This tree was removed as part of a planned thinning operation in an almost pure stand of Douglas-fir trees. Douglas-fir trees growing in this are under natural conditions and are second- or third-growth Douglas-fir forests. The single tree approximately 47 years of age was cut into nine 2.44 meter logs shown in Figure 3.2. The logs were transported by truck from Corvallis, Oregon, to the Brooks Center in Blacksburg, Virginia. The logs were storied outside for 7 days with a tarp covering them until completely sawn. The end coating used was Waxlor clear end sealant and to help prevent moisture loss which causes large end checks and splits.

Figure 3.2 Douglas-fir tree felled from Oregon cut into nine equal sections.

3.1.2. Adhesives

A two-part phenol-resorcinol-formaldehyde adhesive was received from Hexion. One-part is a phenol-resorcinol known as Cascophen LT-5210 and is listed by the manufacturer to have a 55% solids content. The other part is a para-formaldehyde known as Cascoset FM-7400. The polyurethane adhesive was Purbond HB E202 received from Henkel and exhibited a 100% solids content. This adhesive is a one-part, moisture reactive adhesive, used in the manufacturing of glulam beams.

3.2 Methods

3.2.1 Sample Preparation

3.2.1.1 Preparing Boards

Materials were sawed using the Timber King portable sawmill bandsaw. The tree bolts of both wood types were cut with an emphasis on getting the highest grade. There was also an emphasis on optimizing juvenile wood and mature wood from tree bolts. Tree bolts were placed on the portable sawmill and the piths were measured from their height off the ground. Piths were measured from their height off the ground to help

reduce the grain angle due to the tapering of the tree. The tree bolt was sawed until there was a visibly clear 0.17 meter wide section of clear wood. Boards were then cut to a thickness of 31.75 millimeters. After all sections on the tree bolt were cut they were stacked and held together to be edged. Following the edging was done the boards were stacked and stickered. The boards were placed 25.4-50.8 millimeters apart with stickers being placed every 0.30 meters. Boards were stacked for the day and/or the following days until all the boards were cut. A cover was placed over the top of the boards to reduce the amount of moisture received from precipitation and the effects of sunlight.

The southern yellow pine boards were dried at mild temperatures for high grade southern yellow pine boards at a thickness of 31.75 millimeters with the temperatures reaching a maximum of 85˚C and the process lasting 6 days as shown in Table 3.1. Boards were loaded into the kiln with 25.4-50.8 millimeters spacing between them and stacked 1 meter in width allowing for a higher stack and more airflow to circulate through them. Following the end of the kiln drying a residual drying stress test was completed and the boards were conditioned in a conditioning chamber at an EMC of 12%. The drying was done in the SII kiln located in the Thomas M. Brooks Forest Products Center at Virginia Tech.

Table 3.1 Drying schedule for high grade southern yellow pine boards.

Steps	Time (hours)	Drybulb start	Drybulb end	Wetbulb start	Wetbulb end	Fanspeed Start	Fanspeed end
1	24	65.6 (°C)	71.1 (°C)	61.7 (°C)	65.6 (°C)	65 (%)	65 (%)
2	24	71.1 (°C)	71.1 (°C)	65.6 (°C)	62.8 (°C)	65 (%)	65 (%)
3	48	71.1 (°C)	76.7 (°C)	62.8 (°C)	65.6 (°C)	65 (%)	65 (%)
4	48	76.7 (°C)	85.0 (°C)	65.6 (°C)	54.4 (°C)	70 (%)	70 (%)

The Douglas-fir boards were dried at mild temperatures for high grade Douglas-fir boards at a thickness of 31.75 millimeters. This process lasted 6 days and reached a maximum temperature of 82.2˚C. Boards were loaded into the kiln with 25.4-50.8 millimeters spacing between them and stacked 1 meter in width allowing for a higher stack and more airflow to circulate through them. Then a residual drying stress test was

completed and the boards were conditioned in a conditioning chamber at an EMC of 12%. The drying was done in the SII kiln located in the Thomas M. Brooks Forest Products Center at Virginia Tech. Table 3.2 shows the drying schedule of the Douglas-fir boards.

Table 3.2 Drying schedule for high grade Douglas-fir boards.

Steps	Time (hours)	Drybulb start	Drybulb end	Wetbulb start	Wetbulb end	Fanspeed Start	Fanspeed end
1	24	65.6 (°C)	71.1 (°C)	61.7 (°C)	65.6 (°C)	65 (%)	65 (%)
2	24	71.1 (°C)	71.1 (°C)	65.6 (°C)	62.8 (°C)	65 (%)	65 (%)
3	48	71.1 (°C)	76.7 (°C)	62.8 (°C)	65.6 (°C)	65 (%)	65 (%)
4	48	76.7 (°C)	82.2 (°C)	65.6 (°C)	54.4 (°C)	70 (%)	70 (%)

3.2.1.2 Surface Analysis

Mature and juvenile specimens were prepared at 19.05 millimeters in width by 19.05 millimeters in height and 25.4 millimeters in length at the same tree height of 4.88-7.32 meters from the base of the trees to limit variation from height. The top and bottom surfaces were the tangential-longitudinal surface. Six mature and six juvenile wood blocks were placed in a flask. The flask was filled with HPLC grade water and a pressure vacuum applied to the glass nozzle on the flask for one and a half hours or until all air bubbling ceased. Two days later after all wood blocks had been saturated they were taken to the Leica (SM2500) microtome for surfacing. The longitudinal-tangential surface was surfaced with an emphasis on earlywood due to the degree of difficulty in surfacing latewood. Each block was labeled with a letter as well as an arrow pointing to the newly surfaced side. Each sample was placed in a newly cleaned glass container. The glass containers were then placed in a desiccator with a P205 container to absorb the moisture released during drying. The desiccator was attached to a vacuum pump till to 0.02 mm Hg measured using a mercury manometer. When 0.02 mm Hg is reached the vacuum was disconnected from the desiccator using a valve and nitrogen was pumped into the desiccator to allow for a clean atmosphere inside the desiccator and on the

microtomed specimen surfaces. This process was repeated three more times then the desiccator was disconnected from the vacuum. The P205 was changed twice a day for five days. The weight of the wood blocks was recorded to determine the moisture content. After the weight reached a constant, the specimen remained in the desiccator for 6 hours and then was weighed again. If <2% or no changes in weight occurred, then the contact angle analysis was completed. This process was repeated twice for both wood types for a total of 12 samples of mature and juvenile wood for each species.

3.2.1.3 Compositional Analysis

Test specimens of both juvenile and mature wood were taken from each respective height and wood type. Sections were milled using a large scale Wiley mill. The mill used a 1.2mm mesh which allowed fine particles to be produced. These particles were sealed in zip lock bags labeled with the wood type, tree height, and growth region.

3.2.1.4 Density Scans

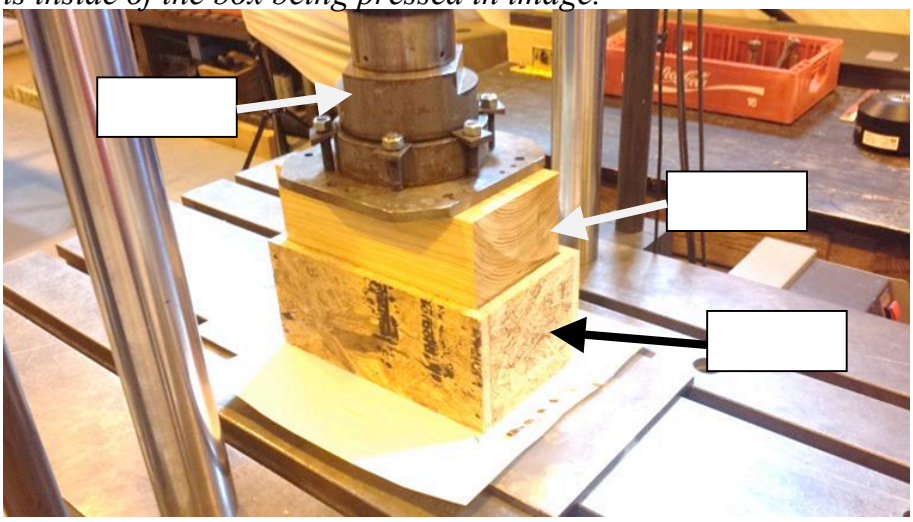
The density specimens were cut from the cross-section of the boards not used in ASTM-D2559. Specimens were 1.59 millimeters in longitudinal thickness, approximately 152 millimeters in radial length, and between 25.4-50.8 millimeters in tangential height and were taken at the end of a tree bolt from different locations according to height. Samples from these heights included juvenile, mature, and transitional wood. These segments were turned into strips using a bandsaw then stored in the conditioning chamber at 12% moisture content.

3.2.1.5 ASTM-D2559/D-905

Material was cut into mature and juvenile sections. Boards of both growth types were cut after drying to 305 millimeters in longitudinal length using the radial arm saw. These pieces then were cut to the radial width of 159 millimeters using the table saw. The specimens were then made to a final tangential thickness of 24 millimeters using the joiner and planer. Wood laminates of both wood types were made uniformly from all lumber. The tangential thicknesses of laminates were 24 millimeters and needed to be at a

final tangential thickness of 19 millimeters but to make sure the surfaces were fresh, surfacing was not done until right before bonding. The laminates were surfaced on both sides using a planer which had fresh blades to allow for the best surface. After surfacing the laminates to a uniform tangential thickness of 19 millimeters, they were then brought to the lab for applying the adhesive within an hour. A box was built 3.2 millimeters larger in both width and length than the laminates to put the final layups in. This was done to keep the laminates from sliding around during the pressing. Nonstick paper was applied to the inside walls of the box to limit the adhesive from bonding to the platen or box. The platen was made of bonded pieces of wood and was the exact dimension of the top of the box. The height of the platen was 152 millimeters larger than the height of the box to allow full pressure to be applied. An image of the press set up can be seen in Figure 3.3. Pressing time and pressure varied with adhesive.

Figure 3.3 Fixture used for pressing of bonded assemblies. Layup is inside of the box being pressed in image.



The phenol resorcinol formaldehyde required 24 hours pressing time and a pressure of 1.20MPa for a maximum pressure of $5.95x10^3$kg to cure. The polyurethane was allowed two hours pressing time and a pressure of 1.38MPa for a maximum pressure of $6.80x10^3$kg to cure. Both curing times were 100% increased times from the

manufacture's recommendations to allow more than sufficient time to cure. Mature and juvenile loblolly pine specimens tested in Compression perpendicular to the grain strength for mature and juvenile is from 7.54 to 7.04 MPa [60]. The pressure required to bond for both adhesives is minimal compared to the compression perpendicular to the grain strength of wood. Only half of the samples required by the ASTM standard [30] were made due to the requirement of knots in the wood to be less than 3 millimeters in diameter and the knots in the wood being used in this study were often much larger.

The phenol-resorcinol-formaldehyde adhesive was mixed with a 2.6-to-1 ratio of phenol-resorcinol resin to paraformaldehyde hardener at room temperature (23ºC). The mix was then stirred at a rate of 500 rpms for one minute and allowed to sit five minutes before the application process started. Applying the phenol-resorcinol-formaldehyde adhesive was done using a paint roller and several Bestt Liebco Tru-pro 178 millimeter roller covers. Laminates were weighed and the balance tared, then the laminates were aligned in the proper alternating grain order and ready for spreading of the adhesive. After the initial 5 minutes of waiting for the adhesive to settle after mixing it was spread in 4 rolls with a motion of rolling twice in longitudinal direction upwards and twice downwards. After that the sample was weighed again and 4 more rolls were applied to reach 8 rolls of the adhesive on the surface of the laminate. The final weight needed to be over 4.79×10^{-6} MPa based on the requirements from the adhesive manufacturer and the final weight was recorded. The minimum open and minimum closed times for the phenol-resorcinol-formaldehyde were as soon as possible and 5 minutes, respectively. The maximum open and closed times were 1 minute open and 20 minutes closed, respectively. The viscosity of the PRF adhesive was tested after mixing and settling for 5 minutes under the exact same conditions as the mixing stated above at room temperature (25ºC). The shear rate went from 0.1 to 500 (1/s) over a time period of 1400 seconds and can be seen in Appendix I.

Polyurethane adhesive was applied to the wood surfaces in a similar way by spreading using the same brand of rollers and using 12 rolls to apply the adhesive in total because the adhesive was much more viscous and harder to spread. The final weight of

the adhesive on the surface was over $1.76x10^{-6}$ MPa based on the requirements from the adhesive manufacturer and the final weight was recorded. The minimum open and closed times were as soon as possible and 10 minutes, respectively. The maximum open and closed times were 1 minute and 15 minutes, respectively. The polyurethane adhesive viscosity was tested under the shear rates of 1 to 1000 (1/s) at room temperature (25ºC) for a time period of 1400 seconds and can be seen in Appendix J.

Laminates were bonded mature to mature wood bonded together and juvenile to mature wood bonded together using both adhesives and following the procedures listed in ASTM-D2559 [30].

3.2.2 Specimen Testing

3.2.2.1 Surface Analysis

The static sessile drop method and three liquids were used for analyzing the surface energy of mature and juvenile Douglas-fir and southern yellow pine wood. The instrument used was a goniometer called the Dynamic Contact Angle Analyzer by First Ten Angstroms and the longitudinal-tangential surface was used for investigation. The three liquids were diiodomethane, formamide, and water. The block was placed on the sample stage of the instrument with a camera recording the images of the droplet under a 10 second period at 1 image every 0.1 seconds for a total of 100 images. The acid-base approach was used to determine the surface energy because it has been seen as the most informative approach to understanding surface energy in relation to adhesive wetting [58]. The three liquids above were used because the model needs two polar and one non polar liquid used for testing. Only three liquids were used because of time constraints. Each liquid was tested on every sample.

3.2.2.2 Compositional Analysis

Extractive content was measured by doing an acetone extraction at room temperature. This was done by adding 20mL of acetone to 20mL of the dried milled material in a testtube and shaking it for 10 minutes on the high setting of the vortex

shaker. The sample was held stationary for 5 minutes, and then 10 more minutes of shaking occurred. The samples were then allowed to sit stationary for 24 hours. These samples were then put into a centrifuge at 5000 rpms and run for 30 minutes. Samples were then decanted and washed with water using the same procedure listed for the centrifuge above. The washing with water was done twice to help remove any acetone residue. Following centrifuging, the samples were placed into an oven at 100˚C until weight changed less than 2%. The initial weight was then subtracted from the final weight to calculate the % extractives. This was done for samples at each height, wood growth region, and wood type.

Compositional analysis was done using extracted free wood listed above in the NREL procedure for determining the composition of structural carbohydrates and lignin in biomass [33]. The procedure was run using a Metrohm Ion Chromatography (IC) installed with a pulsed amperometric detector (PAD), Metrohm Inc., USA. The carbohydrates were separated using a Hamilton RCX-30 column using DI water as the eluent and 350 mmol/L NAOH as the post reaction. The eluent was run with a flow rate of 1 mL/min, with the Hamilton RCX-30 column at a temperature of 32 degrees Celsius. Post reaction NAOH was run at a flow rate of 0.43 mL/min after column separation to help identify the carbohydrates in the PAD at a temperature of 35 degrees Celsius. Linear calibration curves were processed to receive an R squared value of 99.9%. The concentrations were then calculated according to the NREL standard [57]. All samples were run in duplicates.

3.2.2.3 Density Scans

Density was measured using the QTRS-01X densitometer. The samples were placed in a holder which then is placed in the instrument. The instrument releases an X-ray beam which is passed through the wood specimen then to the detector. The readings from the detector then determine the density based on sample densities which were recorded for 3 different regions in both wood types using the wax immersion method. Density scans were run for 3 samples from each wood type, growth region, and height

region. Measurements received were averaged across the samples to give a final density for each sample.

3.2.2.4 ASTM-D2559 [30]

The procedure was run exactly as listed in the standard at the Georgia Pacific research and development facility in Decatur, GA. Samples were run in a random order. The delamination along the bondline was measured using electronic calipers.

An average of delamination was measured and used to represent each specific combination tested.

3.2.2.5 ASTM-D905 [31,32]

The procedure was run exactly as listed in the standard. Samples were run in a random order.

Testing was done using a 10,000lb United load frame. The specimen's bond area was measured using electronic calipers to the nearest 0.05 inches. The blocks were tested to failure and the % wood failure visually estimated by applying a grid visually to the surface of specimen after testing and measured to the nearest 5%. An average was taken and represented each different combination tested.

3.2.2.6 Statistical Analysis

The statistical analysis method differed with the experiment. The ASTM-D2559/ASTM-D905 used a nested factorial model. The factors included species, growth region used at bondline, adhesive, and assembly time. The nested factor was the assembly time which differed for each adhesive. The other experiments were statistically compared using a two sample t-test. Statistical data shown in the results includes Tukey's honestly significant difference (HSD) test for a pairwise comparison of treatment groups. Tukey's HSD is known as a rather conservative test if the sample sizes differ. If an effects p-value was less than 0.05, it meant the treatment group likely had an effect on the test. With a value less than 0.05 it can be concluded that there was less than a 5 percent chance that data being studied are not different. Parameters mentioned in effect tests below are the

number of parameters (Nparm), degrees of freedom (DF), the sum of squares, and F-ratio. Nparm is the number of parameters being tested. If using a variable that has a continuous set of numbers, Nparm is one. Nparm for a nominal or ordinal effect is one less than its number of levels. DF is the independent variable factors of each effect. The sum of squares is the squared sums of the difference between the response variable and the sample mean. The F-ratio is used to determine if the effect is significant or not on the response variable. If the effect being tested was significant, then Tukey's HSD was also run and listed below. If the effect was not significant Tukey's test was not run.

Chapter 4: Results

4.1 Introduction

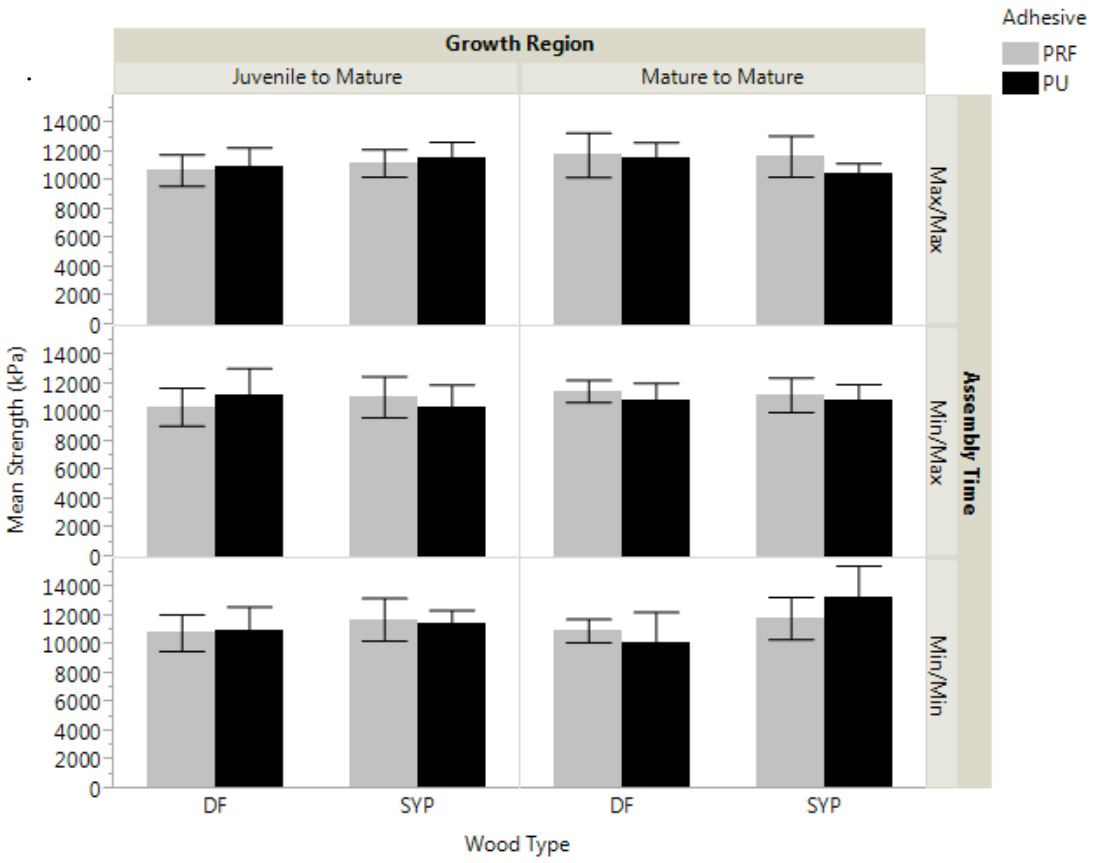
Southern yellow pine and Douglas-fir trees were used in various experiments to determine their chemical/mechanical properties in relation to delamination.

4.2 ASTM-D2559

4.2.1 ASTM-D905 Shear by Compression Loading [31]

Shear block tests following the modified ASTM-D2559 standard [30] using the alternative two-ply assembly. An average of 20 shear stress tests was conducted for each species, assembly time, growth region, and adhesive combination. Shear blocks were conditioned to 12% moisture content and tested more than 2 weeks after conditioning. The average shear strength results are shown in Figure 4.2. A sample image of juvenile to mature and mature to mature bonds can also be seen in Figure 4.1.

Figure 4.1 Image of shear stress specimen showing juvenile to mature (left) and mature to mature bonds (right).



Shear strength values are over the required minimum stated in the ASTM-D2559 requirements for solid wood shear strengths at 12% moisture content. Results demonstrate that the highest mean shear stress was southern yellow pine using the polyurethane adhesive with a minimum open and closed assembly time. The lowest mean shear stress was Douglas-fir under the exact same conditions as the southern yellow pine stated above. Tukeys HSD (honest square differences) was used to determine which groups were statistically different. The statistical analysis was run with a separation of species to determine what the most significant factors were for each species. Douglas-fir statistical analysis can be seen in Table 4.1. Douglas-fir mean strength was most affected by the adhesive type in combination with the growth region at the bond. Southern yellow pine statistical data can be seen in Table 4.2 and it shows that mean strength statistically

Figure 4.2 Shear strength of both wood types using different adhesives, assembly times, and growth regions at the bondline. (Standard deviation

was most affected by the growth region at the bond in combination with the assembly time of the adhesives.

Table 4.1 Statistical data for Douglas-fir ASTM-D905 shear strength

Effects Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Adhesive	1	1	7183.84	0.1750	0.6761
Growth region at bond	1	1	100544.83	2.4496	0.1189
Adhesive* Growth region at bond	1	1	302255.68	7.3640	0.0072*
Assembly[Adhesive]	4	4	281265.46	1.7131	0.1479
Growth region at bond *Assembly[Adhesive]	4	4	328940.62	2.0035	0.0948

Tukeys HSD Adhesive* growth region at the bond

Level			Shear Strength (kPa)
PRF, Mature to mature	A		11463
PU, Juvenile to mature	A	B	11107
PU, Mature to mature	A	B	10901
PRF, Juvenile to mature		B	10695

Levels not connected by same letter are significantly different.

Table 4.2 Statistical data for southern yellow pine ASTM-D905 shear strength

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Adhesive	1	1	12785.4	0.3367	0.5623
Growth region at bond	1	1	130215.9	3.4297	0.0653
Adhesive* Growth region at bond	1	1	10243.0	0.2698	0.6040
Assembly[Adhesive]	4	4	1510448.5	9.9457	<.0001*
Growth region at bond *Assembly[Adhesive]	4	4	973445.9	6.4098	<.0001*

Tukeys HSD Assembly [Adhesive]

Level				Shear Strength (kPa)
[PU]Min/Min	A			12408
[PRF]Min/Min	A	B		11834
[PRF]Max/Max		B	C	11506
[PRF]Min/Max		B	C	11212
[PU]Max/Max		B	C	11123
[PU]Min/Max			C	10719

Levels not connected by same letter are significantly different

Tukeys HSD Growth region at bond*Assembly [Adhesive]

Level				Shear Strength (kPa)
[PU]Mature to mature, Min/Min	A			13353
[PRF]Mature to mature, Min/Min		B		11878
[PRF]Juvenile to mature, Min/Min		B	C	11791
[PRF]Mature to mature, Max/Max		B	C	11743
[PU]Juvenile to mature, Max/Max		B	C	11696
[PU]Juvenile to mature, Min/Min		B	C	11464
[PRF]Mature to mature, Min/Max		B	C	11278
[PRF]Juvenile to mature, Max/Max		B	C	11269
[PRF]Juvenile to mature, Min/Max		B	C	11146
[PU]Mature to mature, Min/Max		B	C	10964
[PU]Mature to mature, Max/Max		B	C	10551
[PU]Juvenile to mature, Min/Max			C	10474

Levels not connected by same letter are significantly different

Percent wood failure is shown in Figure 4.3. Wood failure was calculated visually using ASTM-D5226 [32]

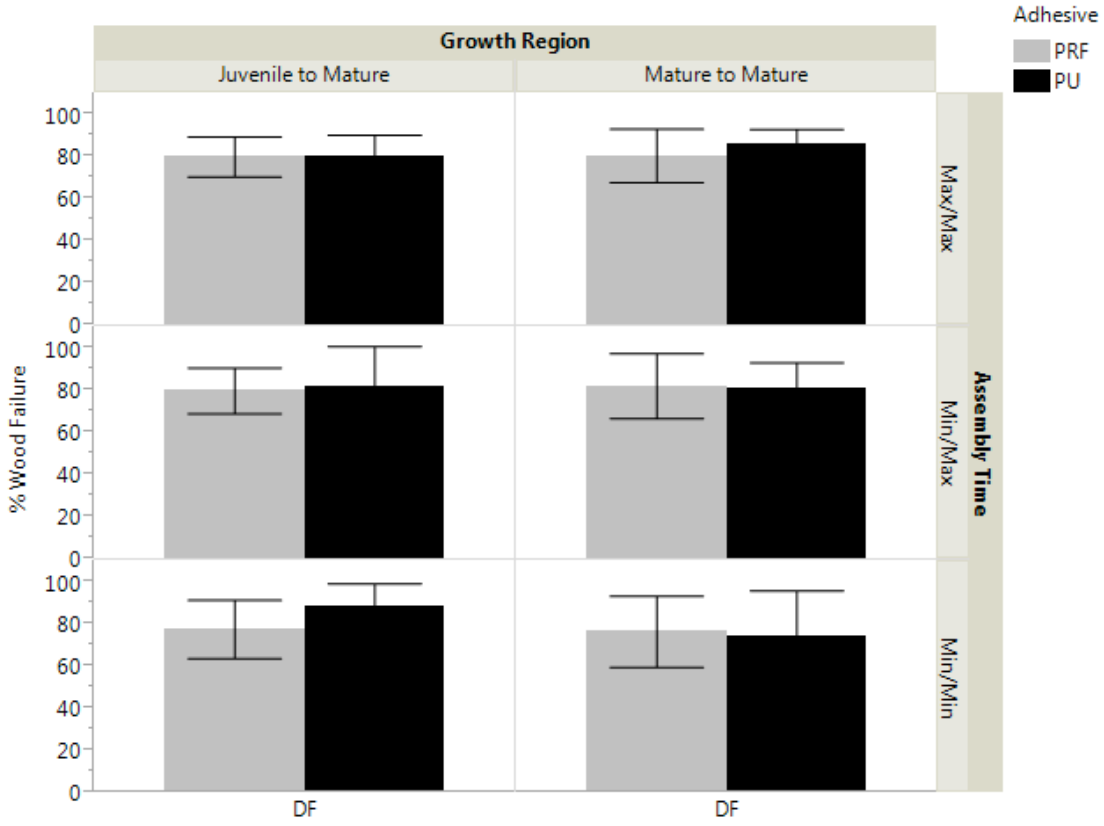


Figure 4.3 Percent Wood failure results of both wood types (Standard deviation inside graph)

All percent wood failure results are above the minimum requirements in ASTM-D2559 which requires 75% wood failure. Results statistically were separated by wood type to help determine the differences among wood types. Douglas-fir percent wood failure statistics in Table 4.3 showed Douglas-fir was affected by the growth region at the bond in combination with the assembly time for each adhesive. Southern yellow pine percent wood failure statistics shown in Table 4.4 demonstrate that southern yellow pine statistically was not affected by any main factor or interaction of factors.

Table 4.3 % Wood failure statistical data for Douglas-fir

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Adhesive	1	1	379.7553	1.9547	0.1634
Growth region at bond	1	1	86.2358	0.4439	0.5059
Adhesive*Growth region at bond	1	1	179.1831	0.9223	0.3379
Assembly[Adhesive]	4	4	384.5782	0.4949	0.7395
Growth region at bond*Assembly[Adhesive]	4	4	2051.1899	2.6395	0.0347*

Tukeys HSD for Douglas-fir Growth region at bond*Assembly (adhesive)

Level		% Wood failure
[PU]Juvenile to mature, Min/Min	A	88.15
[PU]Mature to mature, Max/Max	A	85.47
[PRF]Mature to mature, Min/Max	A	82.00
[PU]Juvenile to mature, Min/Max	A	81.75
[PU]Mature to mature, Min/Max	A	80.91
[PRF]Mature to mature, Max/Max	A	80.26
[PRF]Juvenile to mature, Max/Max	A	79.76
[PU]Juvenile to mature, Max/Max	A	79.76
[PRF] Juvenile to mature, Min/Max	A	79.73
[PRF] Juvenile to mature, Min/Min	A	77.50
[PRF] Mature to mature, Min/Min	A	76.31
[PU] Mature to mature, Min/Min	A	75.54

Levels not connected by same letter are significantly different.

Table 4.4 % Wood failure statistical data for southern yellow pine

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Adhesive	1	1	562.1507	2.5976	0.1084
Growth region at bond	1	1	179.8115	0.8309	0.3630
Adhesive*Growth region at bond	1	1	104.2764	0.4818	0.4883
Assembly[Adhesive]	4	4	1235.7904	1.4276	0.2256
Growth region at bond*Assembly[Adhesive]	4	4	707.8904	0.8178	0.5150

4.2.2 ASTM-D2559 Resistance to Delamination During Accelerated Exposure [30]

Delamination tests were conducted using a modified ASTM-D2559 [30]. An image of a specimen right after drying and ready to be measured for the amount of delamination can be seen in Figure 4.4. There were 3 specimens used for species, assembly time, growth region, and adhesive combination. The results showed that there was significant delamination in the PU compared to the PRF. The data is shown in Figure 4.5. The group of southern yellow pine bonded with juvenile to mature wood using the PRF adhesive and a minimum open and closed assembly time debonded completely after first cycle of ASTM-D2559. The results from this group were not added in the total

results because it would lead to an outlier in the statistical analysis and skewed results in total.

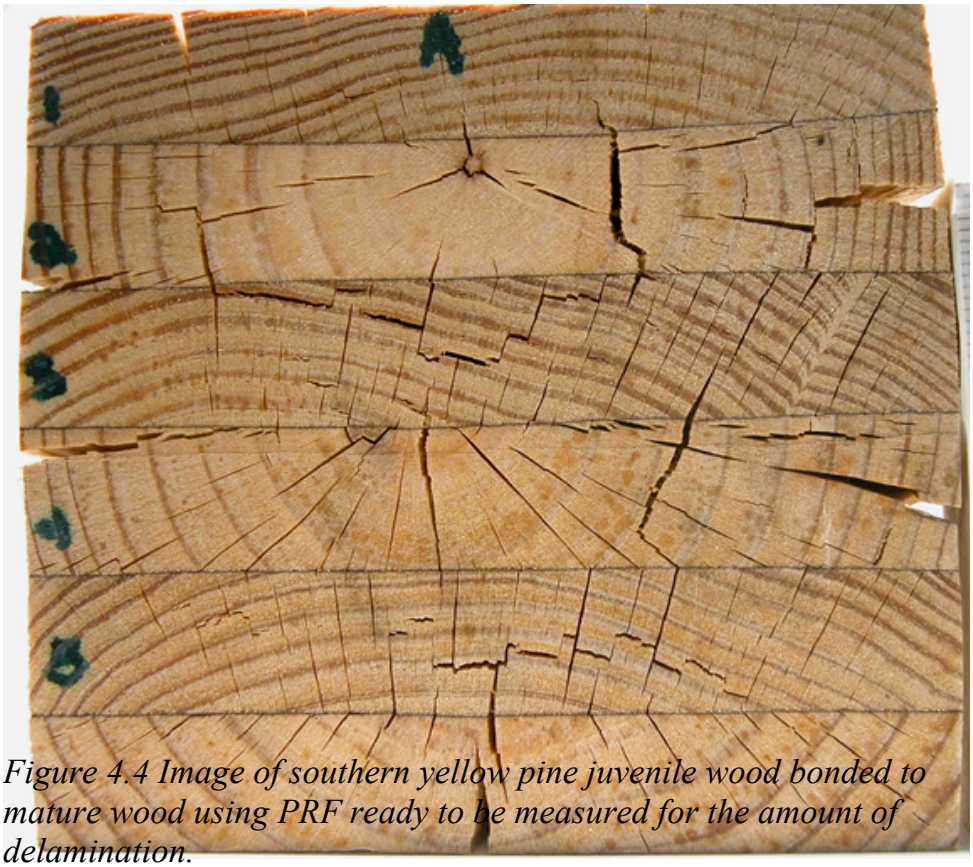


Figure 4.4 Image of southern yellow pine juvenile wood bonded to mature wood using PRF ready to be measured for the amount of delamination.

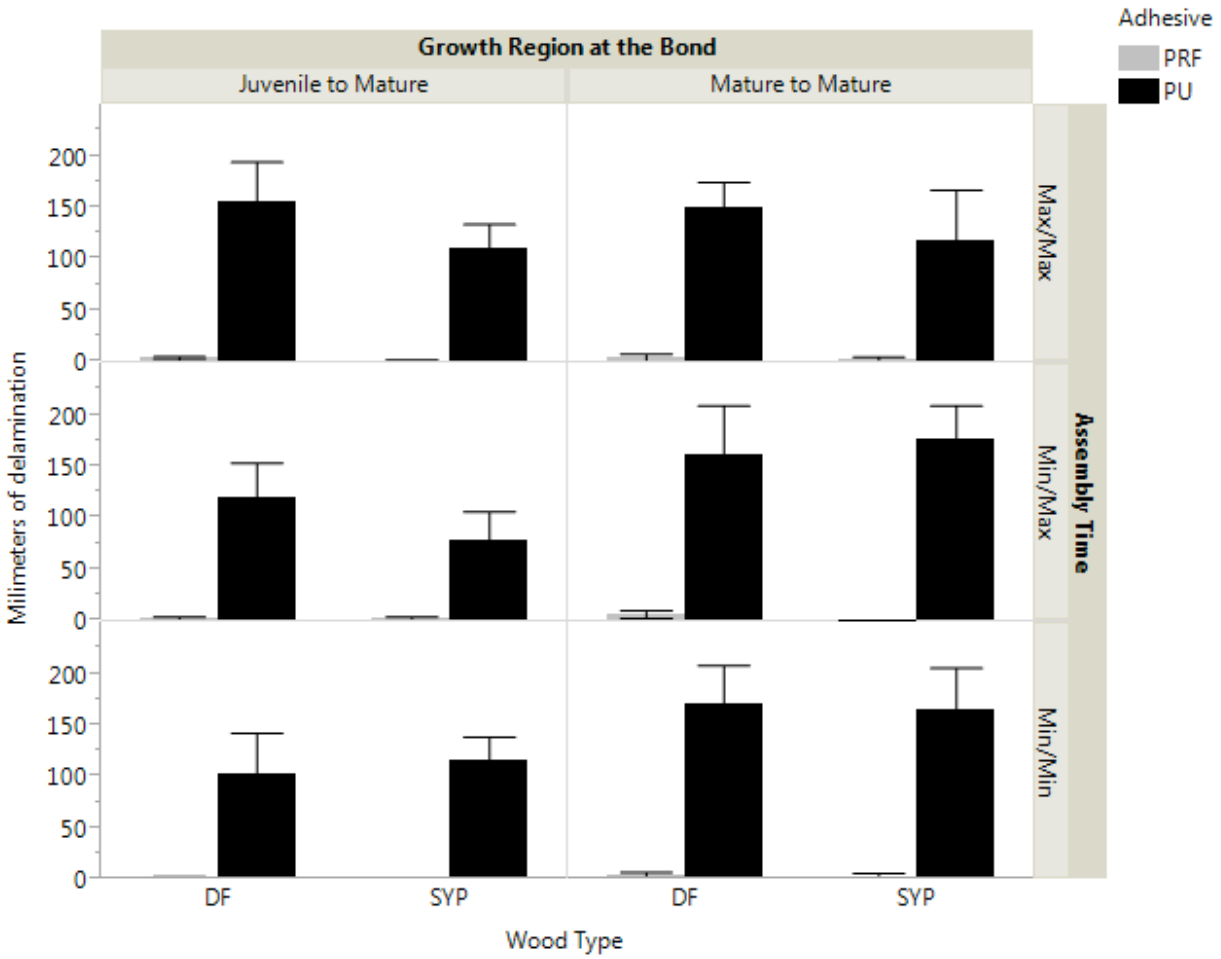


Figure 4.5 Results of both wood types from ASTM-D2559 (Standard deviation inside bars)

The total allowable delamination values allowed for softwoods is 5% with not more than 1% delamination in each measured bondline. All PRF combinations were under the 5% delamination requirement whereas the PU values for delamination were all over the allowable limit. For a better understanding, the statistics were run with a separation in adhesive to help determine the differences between wood types. The statistical results for PRF are shown in Table 4.5 and Table 4.6 for PU. PRF delamination was affected by the wood type being used as well as the growth region of the laminate at the bond. The PU delamination was affected by only the growth region of the laminate at the bondline.

Table 4.5 Statistical data for visual delamination of PRF

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Species	1	1	58.174400	7.8476	0.0070*
Growth region at bond	1	1	25.168893	3.3952	0.0707
Species*Growth region at bond	1	1	12.600467	1.6998	0.1977

Tukeys HSD of Species

Level			Delamination (mm)
DF	A		3.35
SYP		B	1.33

Levels not connected by same letter are significantly different.

Table 4.6 Statistical data for visual delamination of PU

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Species	1	1	4796.042	3.0451	0.0856
Growth region at bond	1	1	31635.083	20.0855	<.0001*
Species*Growth region at bond	1	1	1309.235	0.8312	0.3652

Tukeys HSD of Growth region at the bond

Level			Delamination (mm)
Mature to mature	A		157
Juvenile to mature		B	114

Levels not connected by same letter are significantly different.

4.3 Surface Analysis

Douglas-fir and southern yellow pine growth regions were investigated by measuring the contact angle of three test liquids on the tangential-longitudinal earlywood surface. Contact angle is used commonly to measure the surface energy. Earliest interpretation of how contact angle relates to a measure of surface energy was from Young [62]. Interfacial tension of the liquid being used and the vapor of the air multiplied with the cosine of the contact angle is equivalent to the interfacial tension of the solid surface and the vapor subtracted by the interfacial tension of the solid surface interaction with the liquid [62]. Further research demonstrated that knowing the acid-base, dispersive, and polar portions of a minimum of three liquids makes it possible to determine the acid-base, dispersive, and polar portions of the surface in question [63].

Different growth regions were used in this study as well to determine the surface energy components. Initial images used for analysis were taken at 0.3 seconds to have a uniform reading on all specimen used. Vibration of droplets can occur when initial

contact of liquid to specimen surface happens and at 0.3 seconds no vibration occurred. Images were taken every 0.1 seconds for 10 seconds. Contact angle data averages are shown in Table 4.7.

Table 4.7 Average contact angle (degrees) for each liquid on each wood type and growth region.

Southern yellow pine

Liquid	Water		Diiodomethane		Formamide	
Wood	Juvenile	Mature	Juvenile	Mature	Juvenile	Mature
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	0.09	0.07	0.17	0.09	0.09	0.12

Douglas-fir

Liquid	Water		Diiodomethane		Formamide	
Wood	Juvenile	Mature	Juvenile	Mature	Juvenile	Mature
Average(˚)	73.9	87.0	43.8	42.3	60.3	67.8
Std.(˚)	9.68	10.6	6.38	5.54	11.2	9.22
C.O.V.	0.13	0.12	0.15	0.13	0.19	0.14

The surface energy was calculated using the liquid surface energy values for each of the three tested liquids posted in the literature shown in Table 4.8 [61, 63]. Surface energy was calculated using the acid/base approach on the FTA 32 software and the Drop Shape Analysis Software V. 2.0. [63]. The surface free energy of both wood types is shown below in Table 4.10. A recent study shows a rather different approach to examining contact angle. Instead of reporting the surface energy as a function of the initial contact angle, the authors examine the time dependency of the droplet on the surface of the wood specimen as the liquid used changes from the initial to the equilibrium contact angle [46]. The K-value represents the constant decreasing rate of the liquid on the surface over time until it reaches an equilibrium and is referred to as the "Intrinsic relative constant contact angle decreasing rate" [46]. Wood is a porous material and the change in the contact angle represents not only wetting but penetration of liquid into wood's porous structure. Therefore, the K-value represents a constant value which can be used to interpret favorable or unfavorable wetting by examining how fast a liquid

decreases constantly or for purposes of this research, spreading on a wood surface. The larger a K-value, the higher the amount of spreading that occurs for the liquid droplet to reach its equilibrium state in which no more spreading occurs. An example can be seen in Figure 4.6 [46]. The equation used to calculate K-value is shown in Equation 1 [46]. The variables listed are θ_i, θ_e, K, and t. θ_i represents the initial contact angle at the start of contact between the liquid and surface. θ_e indicates the equilibrium contact angle, or also known as when the spreading ceases, or in some cases the end of the acquisition period. The variable t is the time of the whole period in which contact angle is being analyzed. Using the data calculated for southern pine and Douglas-fir, the K-value was calculated using the software program Origin and a non-linear model based on the equation below to fit the contact angle data as it starts at 0.3 seconds until it approaches the end of the acquisition period of 10 seconds. The tables for these calculated surface energies and K-values can be seen in Tables 4.9, 4.10, and 4.11.

$$\theta = \frac{\theta_i \theta_e}{\theta_i + (\theta_e - \theta_i)\exp[K\left(\frac{\theta_e}{\theta_e - \theta_i}\right)t]} \qquad \textit{(Equation 1)[46]}$$

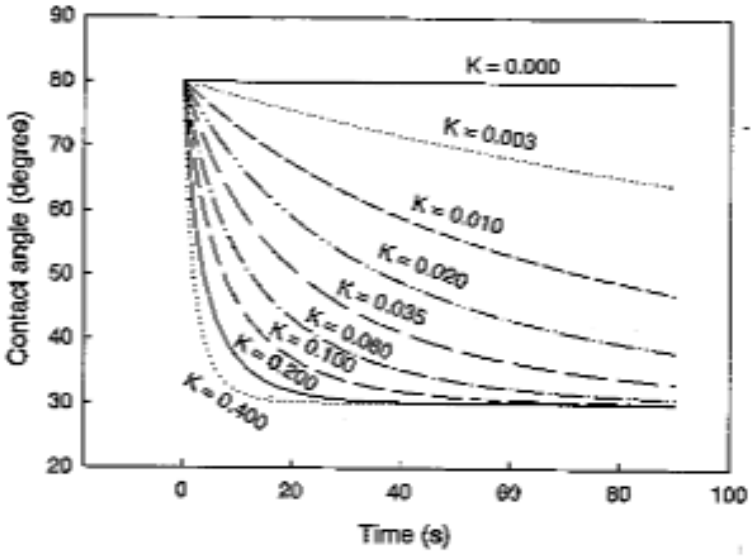


Figure 4.6 Different K-values and how K-value would differ starting at the initial contact angle of 80° until it reaches equilibrium at 30° [46]. (Used with permission)

Table 4.8 Surface energy values for the 3 test liquids used to calculate surface energy [61].

	Surface Energy	Dispersive	Polar	Acid	Base
	γ_L (mJ/m2)	γ_L^D (mJ/m2)	γ_L^P (mJ/m2)	γ_L^+ (mJ/m2)	γ_L^- (mJ/m2)
Formamide	58.0	39.0	19.0	2.3	39.6
Water	72.8	21.8	51.0	25.5	25.5
Diiodomethane	50.8	50.8	0.00	0.00	0.00

Table 4.9 Surface free energy of Douglas-fir (DF) and southern yellow pine (SYP) mature and juvenile wood.

	Surface Energy	Dispersive	Polar	Acid	Base
	γ_L (mJ/m2)	γ_L^D (mJ/m2)	γ_L^P (mJ/m2)	γ_L^+ (mJ/m2)	γ_L^- (mJ/m2)
DF Juvenile	42.8	38.3	4.48	0.621	8.06
DF Mature	39.4	39.1	0.311	4.98E-03	4.84
SYP Juvenile	54.5	44.9	9.64	1.58	14.7
SYP Mature	54.9	45.0	9.97	0.882	28.2

Table 4.10 K-value calculation of Douglas-fir juvenile and mature wood and its 3 test liquids used to conduct contact angle.

Water	Intial Contact Angle (˚)	K-value (1/s)	Model Fit R2
Juvenile	72.7	0.170	98%
Mature	83.8	0.123	99%
Diiodomethane	Intial Contact Angle (˚)	K-value (1/s)	Model Fit R2
Juvenile	42.5	0.0151	98%
Mature	41.1	0.0216	98%
Formamide	Intial Contact Angle (˚)	K-value (1/s)	Model Fit R2
Juvenile	49.3	0.569	82%
Mature	61.6	0.538	98%

Table 4.11 K-value calculation of southern yellow pine juvenile and mature wood and its 3 test liquids used to conduct contact angle.

Water	Intial Contact Angle (˚)	K-value (1/s)	Model Fit R2
Juvenile	55.6	0.262	99%
Mature	43.4	0.306	99%
Diiodomethane	Intial Contact Angle (˚)	K-value (1/s)	Model Fit R2
Juvenile	28.4	0.129	95%
Mature	28.2	0.073	98%
Formamide	Intial Contact Angle (˚)	K-value (1/s)	Model Fit R2
Juvenile	23.8	1.82	98%
Mature	22.5	1.52	99%

A t-test was run in different combinations to see the statistical differences between contact angle from both species and growth regions. The p-value of each test is shown in Table 4.12. The p-value describes the chance that the null hypothesis is correct or in other terms that the sample averages are actually similar. With a value less than 0.05 or 5% it can be deduced that the samples must be different in average if less than a 5% chance exists that they are the same.

Table 4.12 P-value of different t-tests run with the different contact angles to determine the difference between wood type and growth region with p-values less than 0.05 bolded.

	Mature to Mature	Mature to Juvenile (DF)	Mature to Juvenile (SYP)	Juvenile to Juvenile
Water	**0.000**	**0.001**	**0.000**	**0.000**
Formamide	**0.000**	0.102	0.056	**0.000**
Diiodomethane	**0.000**	0.409	0.372	**0.000**

The significant difference between groups is important because a difference in surface energy can lead to a difference in how each treatment group can be wetted when an adhesive is applied to the surface. This ultimately influences bond quality in a favorable or unfavorable way. Douglas-fir contained a higher contact angle statistically than southern yellow pine in water, formamide, and diiodomethane. With a higher contact angle the Douglas-fir will have a less favorable spreading of liquids than does the southern yellow pine. A lower contact angle leads to a more favorable bond quality in southern yellow pine and a higher surface free energy.

4.4 Compositional Analysis

Chemical composition of Douglas-fir and southern yellow pine was investigated using the NREL procedure for determining structural carbohydrates and lignin in biomass [33]. Average percentages for each major component of both wood types and different growth regions are listed in Table 4.13 and Table 4.14.

Table 4.13 Douglas-fir chemical composition of mature and juvenile wood on a percent basis using NREL standard for determine chemical composition of biomass. Standard deviation is in parenthesis.

Mature Douglas-fir								
Height (m.)	% Extractives	% Lignin	% Arabinose	% Galactose	% Glucose	% Xylose	% Mannose	Total %
0 to 2.4	1.35	25.6(0.94)	0.81(0.02)	1.74(0.05)	45.6(1.35)	3.35(0.07)	14.9(0.50)	93.4
2.4 to 4.9	0.77	24.9(0.60)	0.89(0.03)	1.69(0.03)	45.6(0.80)	3.31(0.02)	14.4(0.28)	91.7
4.9 to 7.3	2.06	25.9(0.29)	0.89(0.02)	1.73(0.01)	45.2(0.83)	3.54(0.10)	14.4(0.12)	93.9
7.3 to 9.8	1.05	26.0(0.45)	0.91(0.01)	1.75(0.01)	46.3(0.30)	3.63(0.01)	13.9(0.01)	93.6
9.8 to 12.2	1.09	27.3(0.48)	0.98(0.02)	1.81(0.03)	45.5(0.34)	3.83(0.01)	13.8(0.08)	94.4
12.2 to 14.6	1.64	27.2(0.24)	1.00(0.02)	1.91(0.02)	45.3(1.07)	3.91(0.07)	13.7(0.33)	94.8
14.6 to 17.1	1.22	26.5(0.19)	0.91(0.01)	1.68(0.06)	45.7(1.70)	3.17(0.12)	13.4(0.50)	92.6
17.1 to 19.5	1.32	29.3(0.36)	0.80(0.02)	2.61(0.03)	43.7(0.63)	3.43(0.07)	12.3(0.24)	93.6
Average	**1.31**	**26.6**	**0.91**	**1.77**	**45.6**	**3.59**	**14.2**	**93.6**

Juvenile Douglas-fir								
Height (m.)	% Extractives	% Lignin	% Arabinose	% Galactose	% Glucose	% Xylose	% Mannose	Total %
0 to 2.4	3.30	31.6(0.26)	0.56(0.02)	3.16(0.33)	41.9(0.25)	4.76(0.01)	13.2(0.07)	98.5
2.4 to 4.9	3.44	31.4(0.11)	0.50(0.01)	2.84(0.01	42.8(0.67)	4.52(0.05)	13.1(0.17)	98.7
4.9 to 7.3	3.00	30.9(0.04)	0.54(0.03)	2.78(0.05)	43.4(0.06)	4.24(0.01)	13.3(0.01)	98.2
7.3 to 9.8	2.28	31.1(0.43)	0.65(0.05)	2.91(0.12)	42.2(0.41)	4.72(0.01)	13.3(0.09)	97.3
9.8 to 12.2	3.21	30.7(0.49)	0.62(0.01)	2.72(0.09)	43.2(0.09)	4.42(0.03)	13.4(0.09)	98.4
12.2 to 14.6	2.42	30.2(0.09)	0.74(0.02)	2.30(0.04)	43.0(0.07)	4.33(0.02)	13.3(0.05)	96.3
14.6 to 17.1	3.00	30.3(0.43)	0.86(0.05)	2.99(0.12)	41.8(0.80)	4.65(0.01)	13.5(0.03)	97.2
17.1 to 19.5	1.52	27.5(0.67)	1.08(0.01)	2.65(0.03)	40.6(0.39)	4.56(0.16)	12.9(0.02)	90.9
19.5 to 21.9	3.32	28.5(0.31)	1.00(0.18)	2.91(0.05)	39.3(0.02)	4.16(0.02)	12.1(0.01)	91.3
Average	**2.83**	**30.2**	**0.60**	**2.79**	**42.7**	**4.50**	**13.3**	**97.9**

Table 4.14 Southern yellow pine chemical composition of mature and juvenile wood on a percent basis using NREL standard for determine chemical composition of biomass. Standard deviation is in parenthesis.

Mature southern yellow pine								
Height (m.)	% Extractives	% Lignin	% Arabinose	% Galactose	% Glucose	% Xylose	% Mannose	Total %
0 to 2.4	3.52	28.6(0.38)	1.21(0.02)	1.53(0.02)	43.3(0.37)	6.42(0.02)	11.2(0.03)	95.9
2.4 to 4.9	2.91	32.3(0.16)	1.23(0.03)	3.64(0.04)	38.1(0.69)	7.45(0.03)	9.6(0.08)	95.4
4.9 to 7.3	3.29	28.8(0.61)	1.17(0.02)	1.85(0.69)	43.4(0.99)	6.27(0.12)	10.7(0.39)	95.5
7.3 to 9.8	3.26	30.1(0.65)	0.94(0.16)	2.34(0.39)	37.5(0.62)	6.08(0.01)	9.48(1.6)	89.7
9.8 to 12.2	3.88	32.3(0.15)	1.02(0.05)	3.62(0.21)	40.4(1.88)	6.41(0.24)	9.40(0.36)	97.1
12.2 to 14.6	3.87	30.6(0.07)	1.17(0.04)	2.78(0.09)	42.7(1.23)	7.20(0.27)	10.0(0.32)	98.4
0 to 2.4	3.89	27.7(0.78)	1.01(0.11)	2.01(0.25)	40.9(0.48)	5.97(0.68)	11.3(1.28)	92.9
2.4 to 4.9	3.71	27.5(0.14)	1.31(0.02)	1.56(0.04)	46.0(0.60)	6.53(0.11)	11.0(0.17)	97.7
Average	**3.54**	**29.7**	**1.13**	**2.42**	**41.5**	**6.54**	**10.3**	**95.3**

Juvenile southern yellow pine								
Height (m.)	% Extractives	% Lignin	% Arabinose	% Galactose	% Glucose	% Xylose	% Mannose	Total %
0 to 2.4	5.89	32.2(0.84)	1.20(0.02)	3.57(0.01)	38.6(0.56)	7.86(0.16)	9.21(0.16)	98.6
2.4 to 4.9	5.75	31.5(0.02)	1.33(0.01)	2.57(0.18)	38.5(0.08)	7.77(0.09)	9.47(0.07)	97.0
4.9 to 7.3	6.02	31.8(0.82)	1.32(0.02)	3.37(0.04)	39.3(0.61)	7.51(0.14)	10.1(0.22)	99.5
7.3 to 9.8	6.17	31.0(0.11)	2.10(0.01)	3.61(0.05)	40.0(0.71)	7.15(0.03)	9.02(0.07)	99.1
9.8 to 12.2	5.78	30.4(0.47)	1.32(0.01)	2.01(0.02)	41.1(0.29)	8.23(0.02)	10.7(0.01)	99.6
12.2 to 14.6	4.05	30.4(0.25)	1.11(0.22)	2.09(0.44)	36.1(1.59)	6.92(1.43)	9.02(1.89)	89.7
0 to 2.4	4.27	29.5(0.73)	1.41(0.02)	3.51(0.04)	40.4(0.81)	7.28(0.03)	11.1(0.14)	97.5
2.4 to 4.9	4.18	30.6(0.96)	1.39(0.06)	4.05(0.06)	39.3(0.37)	7.25(0.11)	9.68(0.10)	96.5
Average	**5.26**	**30.9**	**1.40**	**3.10**	**39.2**	**7.49**	**9.80**	**97.2**

Compositional analysis data was run through different t-tests to determine differences between wood type and growth region. The results are shown in Table 4.15. This table shows that the majority of components are statistically significantly different. These components are important when it comes to bonding with some components being more favorable than others.

Table 4.15 P-value of different t-tests run to determine the difference between wood type and growth region with P-values less than 0.05 bolded.

Components	Mature to Mature	Mature to Juvenile (DF)	Mature to Juvenile (SYP)	Juvenile to Juvenile
Extractives	**0.000**	**0.000**	**0.001**	**0.000**
Lignin	**0.000**	**0.000**	**0.037**	0.114
Arabinose	**0.000**	**0.004**	**0.004**	**0.000**
Galactose	**0.025**	**0.000**	**0.027**	0.190
Glucose	**0.001**	**0.000**	**0.035**	**0.000**
Xylose	**0.000**	**0.000**	**0.000**	**0.000**
Mannose	**0.000**	**0.004**	0.101	**0.000**

Hemicellulose has been linked to having the most hydroxyl bonding sites which is one of the main secondary bonding mechanisms followed by cellulose then lignin [42]. When comparing between both species there is more hemicellulose in southern yellow pine than in Douglas-fir. This was calculated by adding all the components of hemicellulose then comparing them statistically. Douglas-fir had more cellulose than southern yellow pine statistically. Continuing, there was more lignin found in southern yellow pine than in Douglas-fir statistically. Finally, in the case of extractives there were more extractives in southern yellow pine than Douglas-fir. Extractive content has been well shown in the literature to have a negative impact on bond quality.

4.5 Density

Density was measured in Douglas-fir and southern yellow pine at different growth regions. The data can be seen graphically in Figure 4.7. The density differed statistically between both wood types in mature, juvenile, and transitional wood. Density is used in the literature to help estimate mechanical properties [34, 35]. When discussing these two wood types mature and juvenile wood density is statistically higher in southern yellow pine than in Douglas-fir, as found in Table 4.16. This is consistent with the results from the shear by compression loading with the southern yellow pine having higher shear stress values than the Douglas-fir on average.

Table 4.16 Statistical data for density comparisons using a 2 sample t-test.

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Mature growth region	1	1	2112445.6	377.0421	<.0001*

T-test of mature versus mature wood density

Level			Density Kg/M^3
SYP Mature	A		714
DF Mature		B	613

Levels not connected by same letter are significantly different.

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Juvenile growth region	1	1	190214.21	33.4303	<.0001*

T-test of juvenile versus juvenile wood density

Level			Density Kg/M^3
DF Juvenile	A		486
SYP Juvenile		B	459

Levels not connected by same letter are significantly different.

Effect Tests

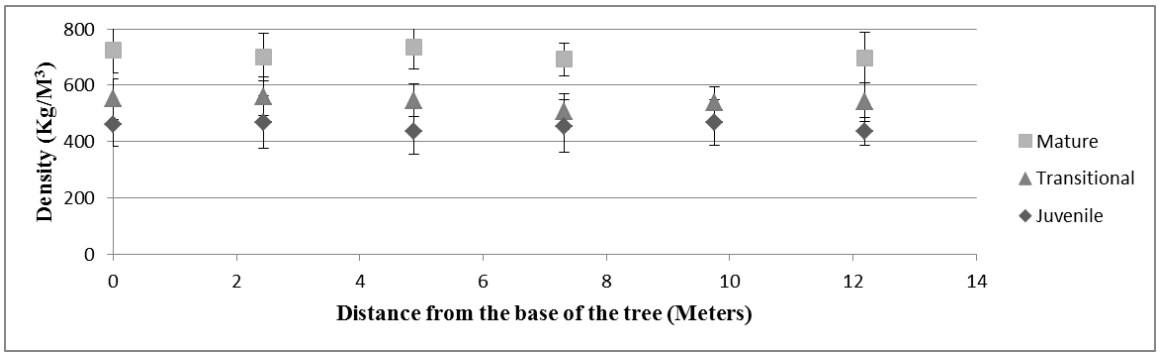
Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Transitional growth region	1	1	427305.10	77.8062	<.0001*

T-test of transitional versus transitional wood density

Level			Density Kg/M^3
DF Transitional	A		581
SYP Transitional		B	544

Levels not connected by same letter are significantly differ

Southern yellow pine



Douglas-fir

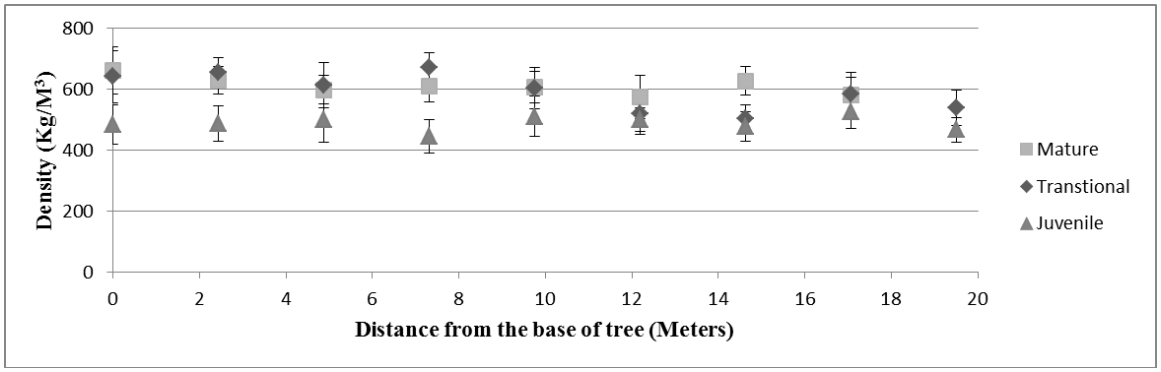


Figure 4.7 Graphical comparison of density at different height regions and different growth regions within each wood type. (Standard deviation shown on symbol.)

Chapter 5: Discussion

Douglas-fir has a lower density, lower surface free energy, and fewer hydroxyl bonding sites than southern yellow pine of the trees compared in this study. The amount of delamination can be related to all these factors. Density, surface free energy, and the chemical composition is known to affect the degree of penetration where less dense wood, higher surface free energy, and higher % hemicellulose wood could result in less delamination.

Generally lower density woods have more numerous and larger cell lumens into which an adhesive can penetrate. Higher surface energy allows more favorable spreading of the liquid adhesive across the wood surface because a liquids surface tension will want the liquid to retain its shape and if the surface energy is higher it causes the liquid to increase its surface area. Higher surface energy allows the adhesive to spread at a faster rate and allows fewer gaps to be found between the adhesive and the wood surface allowing for a stronger bond to potentially form. Chemical composition also plays a role in the amount of hydroxyl bonding sites available which, in turn, influences the amount of bonding. Covalent bonds are the strongest forces by far and have a potential to form but there is no evidence.

There also are some secondary bonding mechanisms which are involved including van der Waal's forces, London forces, and hydrogen bonding. Hydrogen bonding forces are the strongest of these forces. Salehuddin and group found that the different chemical constituents of wood contributed differently to the bonding in wood related to hydrogen bonding [42]. With lignin having the least amount of contribution to hydrogen bonding, then cellulose, and finally with hemicellulose having the most sites available for hydrogen bonding.

The amount of the chemical constituent on the surface differs based on mechanical preparation beforehand. For example, planing of wood surfaces prior to bonding causes the surface to be fractured. Lignin and hemicellulose have a lower mechanical value and

therefore fracture before cellulose [41]. To determine the contribution the amount of each chemical substituent in the cell wall needs to be taken into account.

The optimal degree of penetration is not known for each adhesive and wood combination but it is known that adequate penetration can be linked to optimal performance of wood adhesion interaction and bond performance. Although adhesive penetration was not measured in this study it is important to note its effect on wood composites. Results from this study showed that there was significantly less delamination in the juvenile wood as compared to the mature wood for both adhesives. Density of juvenile wood is less than that of mature wood. A lower wood density could have contributed to the adhesive penetrating further into the wood substrate of juvenile wood than mature wood; because juvenile wood has much more earlywood than latewood this is bound to be a contributing factor.

Penetration is discussed further with the contribution of the adhesive and wood interphase to resistance to delamination below. Juvenile wood in general has a higher % of extractives as shown in Table 4.13, 4.14 in the results as well as higher % lignin and lower % cellulose on average compared to mature wood. Hemicellulose is considered the major contributor to hydrogen bonding and was relatively the same numerically in total percentage for the samples in this study.

Extractives affect the ability of the adhesive to spread and penetrate into the cells of the wood substrate's surface. It is well known that removal of wood extractives generally can decrease the contact angle [45]. Lower delamination can only mean that some factors are more influential than others in the terms of bond quality. The lower density of juvenile wood seems to have had more of a contribution than the bonding sites available from the wood chemical constituents in relation to the amount of delamination. Also, the surface energy based off the delamination results seemed too contribute more than other factors to the resistance of delamination in juvenile wood to mature wood with a positive trend. With further investigation in this area by examining the K-value, the southern yellow pine had a similar K-value between the juvenile and mature wood. A similar K-value in southern yellow pine juvenile and mature wood means the liquid

reached equilibrium state around the same time. Douglas-fir had a lower K-value for juvenile wood than mature wood. This means that the rate decrease in the liquid to its equilibrium state of the juvenile wood was higher than the mature wood of Douglas-fir. Also, southern yellow pine having a higher overall K-value means liquids spread at a higher rate on southern yellow pine than Douglas-fir. When looking at the surface energy in Table 4.9 it can be seen that the polar component of mature Douglas-fir was smaller than the polar component of the juvenile wood of Douglas-fir. There is a high chance that fewer polar types of bonding occurred in the mature Douglas-fir woods surface than in the juvenile wood Douglas-fir surface. Southern yellow pine exhibited a higher surface energy and therefore would have more favorable properties than Douglas-fir in relation to wettability and bonding properties.

Differences between the juvenile wood and the mature wood include a lower density, but relatively the same amount of hemicellulose in percent available for hydroxyl bonding sites. Juvenile wood exhibited higher or similar surface free energy and less delamination than mature wood. Little is known about how specific extractives interact with adhesives. Results in this study showed that there were higher percent extractives in the juvenile wood as compared to mature wood. Extractives are known to have a negative impact but due to the difference of these extractives compared to the amount of delamination they seemed to not play as major of a role when the wood surfaces used for bonding are surfaced properly.

Douglas-fir mature wood on the other hand had a lower density than southern yellow pine but had more delamination in PRF than southern yellow pine. These differences in delamination could also be linked to the difference in the surface free energy and the difference in chemical composition. High surface free energy allows the adhesive to spread more favorably allowing less area for air pockets or improper wetting of the wood surface. Also this results in a more favorable degree of penetration. Based on the data from this study Douglas-fir had a lower surface free energy than that of southern yellow pine which means that southern yellow pine should have a higher wettability or more favorable spread of adhesive.

Chemical composition of Douglas-fir contained a higher amount of cellulose statistically than southern yellow pine but less hemicellulose and lignin. As a result, the southern yellow pine should have more hydrogen bonding than that of Douglas-fir. Delamination is known to be most affected by the ability of a wood and adhesive combination to distribute stress [17].

Wood shrinking and swelling and the adhesive shrinking and swelling to a different degree causes the strain difference to result in high stresses at the bondline and delamination to occur. PRF has been thought to displace the water in the cell wall and affect the woody tissue near the bondline causing it to shrink and swell similar to the adhesive [17]. PU on the other hand has a higher molecular weight that cannot penetrate the cell wall but being a more flexible adhesive allows these high stresses to be distributed through the adhesive itself rather than the interphase of the wood and adhesive.

When analyzing the data for the amount of delamination it should not go unnoticed that because of the degree of curvature in early rings of juvenile wood tangential to tangential bonds are not all possible. The curvature of rings can be seen in Figure 4.4 and shows that some of the bond joints are actually the radial section bonded to the tangential section. The bonding of two different orientations could impact the results because wood in the radial section generally tends to shrink and swell about half as much as the tangential section. When the juvenile to mature wood bonds are swelling there should theoretically be less stress on the adhesive wood interface because the radial side is not stressing the interface as much as the tangential side. Another factor that is important to note is the degree of penetration for the radial surface compared to the tangential. In a study testing the contact angle of southern yellow pine with water it was reported that the radial section had a lower initial contact angle than the tangential section [59]. Lower initial contact angles could mean that the surface wets better but it is very dependent on the adhesive chemistry and the anatomy of the wood being used.

PRF and PU had significantly different levels of delamination. PRF had less delamination than the PU. PU having a significantly higher amount of delamination could

have resulted from the degree of penetration. Literature has shown that PRF compared to PU shows less strain at this bondline with a higher degree of penetration. The effect was found to be more profound in PRF than in PU [40]. There was a statistical difference in PRF between these two species with Douglas-fir having a higher amount of delamination than the southern yellow pine. As stated above the difference in delamination is thought to be linked to the lower density, lower surface energy, and less % hemicellulose in Douglas-fir than southern yellow pine.

When describing the differences between % wood failure and shear strength it is important to note that dealing with the wood dry is much different than the effects of moisture involved as well. Percent wood failure is displayed in the results section with a separation between the two wood types to help determine the difference between them. Douglas-fir had an interaction of factors which were statistically significant in affecting the % wood failure which were the assembly time used and the growth region used at the bond. Further investigation showed that each of these factors was statistically similar in their numerical distribution to each other. Meaning that this interaction affected the amount of wood failure but there was no statistical difference between the groups. Southern yellow pine had no statistically significant factors impacting the amount of wood failure.

In relation to the differences between these two wood types Douglas-fir has shown that it is more sensitive to the effect of the adhesive's assembly time as well as the growth region used at the bond when in combination whereas southern yellow pine was not. Shear strength of both wood types was separated as well to help determine more in depth information about the differences between both. Douglas-fir shear strength was found to be affected by the interaction of the adhesive used and the growth region at the bondline.

The adhesive being used and the growth region at the bondline affecting the shear strength is a very reasonable conclusion when discussing shear strength and not discussing the effects of water. A less dense material generally tends to have a lower mechanical strength than the adhesive bond which is formed. The results section showed

this as well with Tukey's HSD showing PRF bonded with mature wood being higher in shear strength statistically than the PRF bonded with juvenile to mature wood. Also, PU and PRF were shown to be statistically similar in shear strength.

Southern yellow pine shear strength was statistically affected by the assembly time of the adhesives and the interaction of the growth region at the bondline and the assembly time of the adhesive used. Tukey's HSD showed that the PU bonding mature to mature wood was significantly higher in shear strength than PU bonding mature to juvenile wood. Another reasonable conclusion because the density of juvenile wood is less than mature wood because when stressing the bond the adhesive should form a stronger bond than the wood itself and because juvenile wood has less favorable mechanical properties compared to mature wood it should theoretically fracture first. Shear stress and % wood failure are completely different than delamination though because shear strength and % wood failure are for relatively dry wood and act drastically different when having to deal with the stress at the bondline from shrinkage and swelling. This was also shown by Vick and others when testing the shear strength of wet and dry blocks using polyurethane and a modified version of ASTM-D905 [36].

Industry advisors on this project noted that southern yellow pine was harder to bond and provided below test value specifications compared to Douglas-fir when testing wood composites for weathering durability and shear strength using the same adhesive. Research above is only from two trees of southern yellow pine and one tree of Douglas-fir which is a very small population size but showed that southern yellow pine performed better than Douglas-fir in weathering durability and shear strength.

Chapter 6: Summary and Conclusions

6.1. Summary

The objective of this study was to identify differences in bonding characteristics between southern yellow pine and Douglas-fir using the same adhesive. Southern yellow pine was found to have less delamination in ASTM-D2559 testing as compared to Douglas-fir using the PRF adhesive. Delamination was found to be similar between both wood types using the PU adhesive. ASTM-D905 shear stress statistical data demonstrated that using PU with southern yellow pine mature wood in a minimum open and closed assembly time was different than PU in Douglas-fir mature wood using a minimum open and closed assembly time. The % wood failure was found to be similar between both wood species and adhesives. Surface energy was shown to be different between the two wood types as well with Douglas-fir having a lower surface energy than southern yellow pine. Compositional analysis data showed that there was more hemicellulose, extractives, and lignin in southern yellow pine than Douglas-fir. Douglas-fir had a higher amount of cellulose as compared with southern yellow pine. Finally, density scans demonstrated that southern yellow pine had a higher average density than Douglas-fir but similar juvenile wood density.

6.2. Conclusions

Southern yellow pine in terms of bonding performance in durability has shown less delamination than Douglas-fir using the PRF adhesive. Similar results statistically were demonstrated in both wood types using the PU adhesive in terms of delamination. Finally juvenile wood bonded to mature wood showed less delamination in both adhesives.

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Appendix A: Contact Angle Results Graph

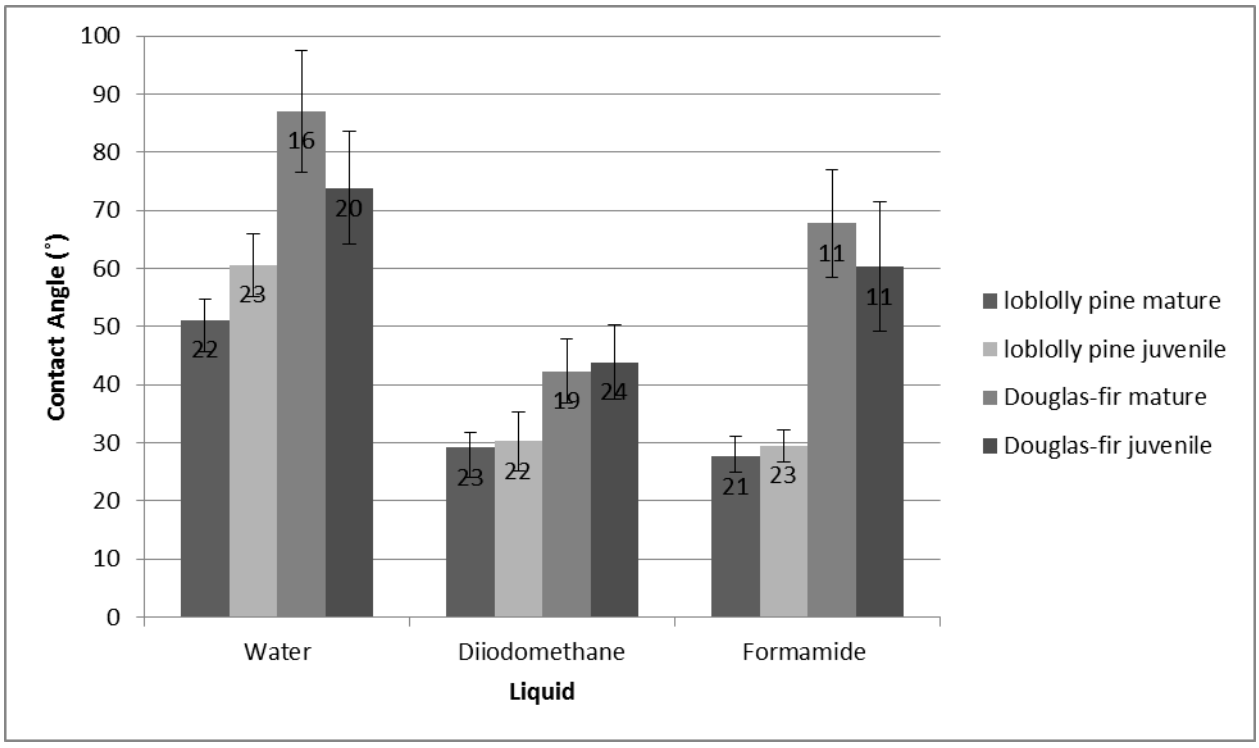

Figure A.1 Initial contact angle summary (number inside bar is samples size)

Appendix B: Statistics for Contact Angle

Douglas-fir water

Two-Sample T-Test and CI: Mature, Juvenile

Two-sample T for Mature vs Juvenile

	N	Mean	StDev	SE Mean
Mature	16	87.0	10.6	2.6
Juvenile	20	73.85	9.68	2.2

Difference = μ (Mature) - μ (Juvenile)
Estimate for difference: 13.18
95% CI for difference: (6.21, 20.16)
T-Test of difference = 0 (vs ≠): T-Value = 3.86 P-Value = 0.001 DF = 30

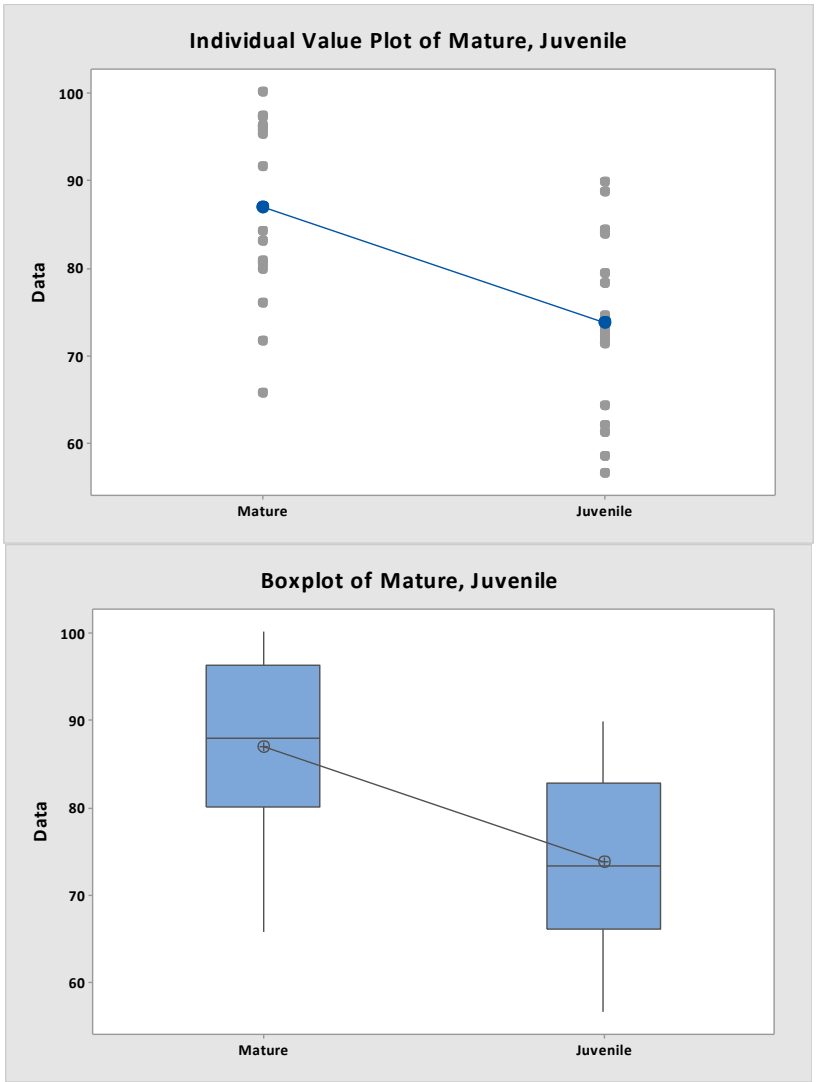

Figure B.1 Data distribution and box plot of contact angle for Douglas-fir using water

Douglas-fir formamide

Two-Sample T-Test and CI: Mature, Juvenile

Two-sample T for Mature vs Juvenile

	N	Mean	StDev	SE Mean
Mature	11	67.76	9.22	2.8
Juvenile	11	60.3	11.2	3.4

Difference = μ (Mature) - μ (Juvenile)
Estimate for difference: 7.51
95% CI for difference: (-1.62, 16.64)
T-Test of difference = 0 (vs ≠): T-Value = 1.72 P-Value = 0.102 DF = 19

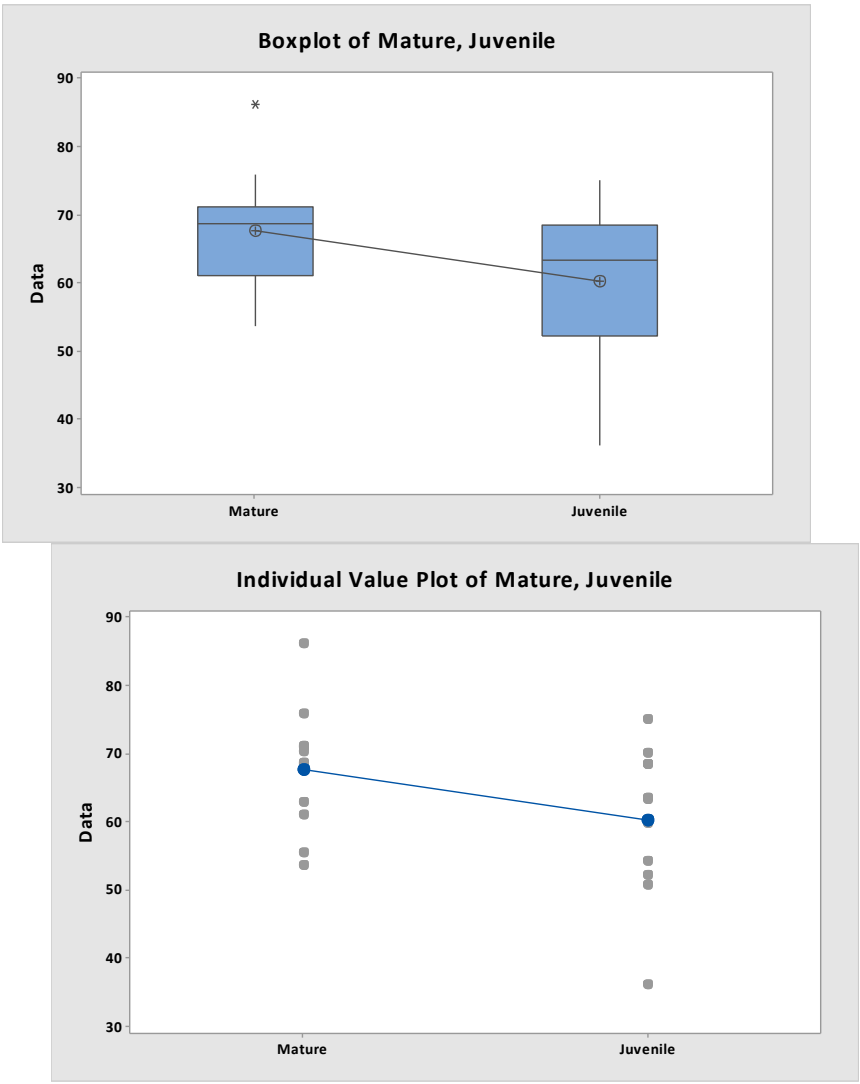

Figure B.2 Data distribution and box plot of contact angle for Douglas-fir using formamide

Douglas-fir diiodomethane

Two-Sample T-Test and CI: Mature, Juvenile

Two-sample T for Mature vs Juvenile

	N	Mean	StDev	SE Mean
Mature	19	42.29	5.54	1.3
Juvenile	24	43.81	6.38	1.3

Difference = μ (Mature) - μ (Juvenile)
Estimate for difference: -1.52
95% CI for difference: (-5.20, 2.16)
T-Test of difference = 0 (vs ≠): T-Value = -0.83 P-Value = 0.409 DF = 40

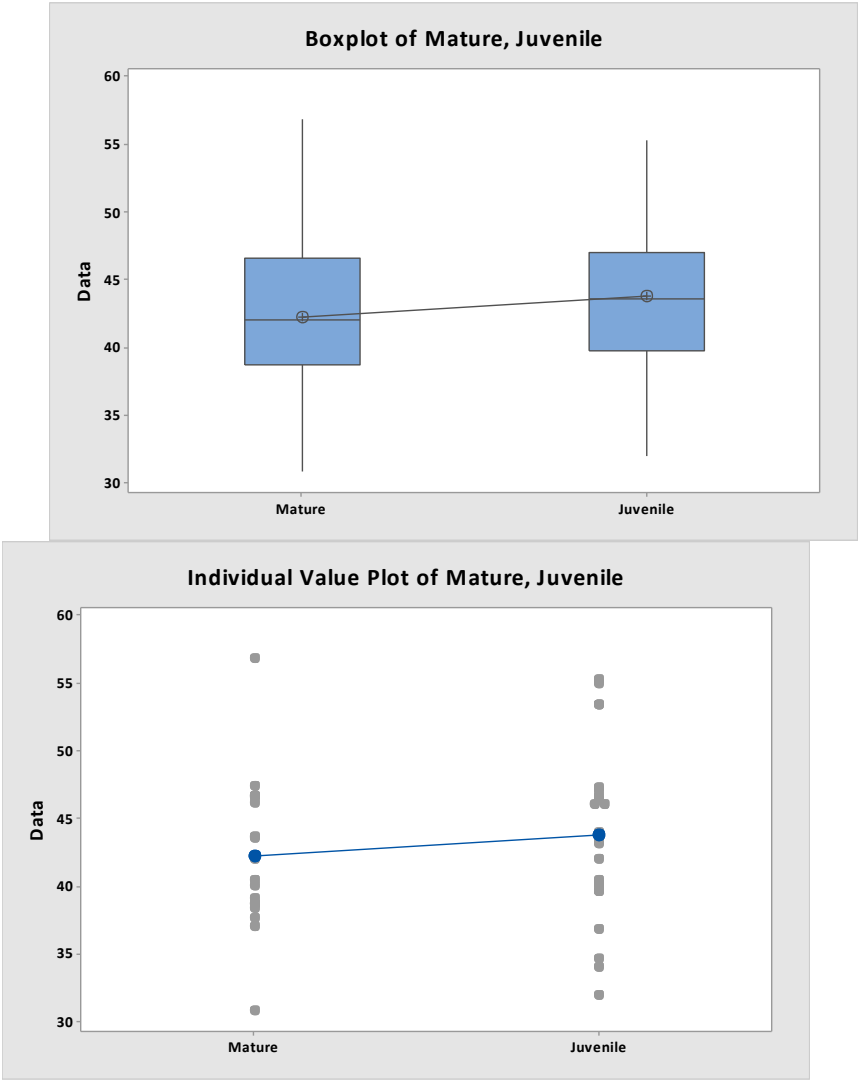

Figure B.3 Data distribution and box plot of contact angle for Douglas-fir using diiodomethane

Loblolly pine water

Two-Sample T-Test and CI: Mature, Juvenile

Two-sample T for Mature vs Juvenile

	N	Mean	StDev	SE Mean
Mature	22	51.08	3.73	0.79
Juvenile	22	60.61	5.38	1.1

Difference = μ (Mature) - μ (Juvenile)
Estimate for difference: -9.53
95% CI for difference: (-12.36, -6.70)
T-Test of difference = 0 (vs ≠): T-Value = -6.83 P-Value = 0.000 DF = 37

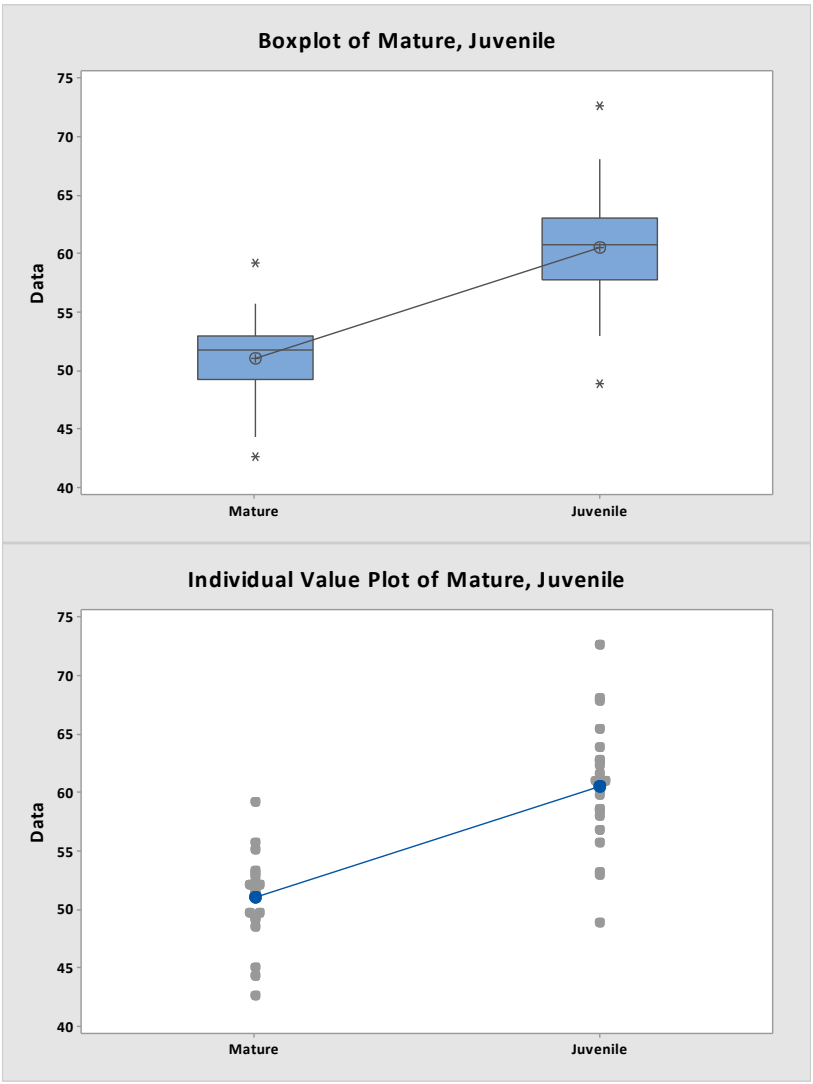

Figure B.4 Data distribution and box plot of contact angle for Douglas-fir using water

Loblolly pine formamide

Two-Sample T-Test and CI: Mature, Juvenile

Two-sample T for Mature vs Juvenile

	N	Mean	StDev	SE Mean
Mature	21	27.60	3.41	0.74
Juvenile	23	29.44	2.72	0.57

Difference = μ (Mature) - μ (Juvenile)
Estimate for difference: -1.842
95% CI for difference: (-3.737, 0.053)
T-Test of difference = 0 (vs ≠): T-Value = -1.97 P-Value = 0.056 DF = 38

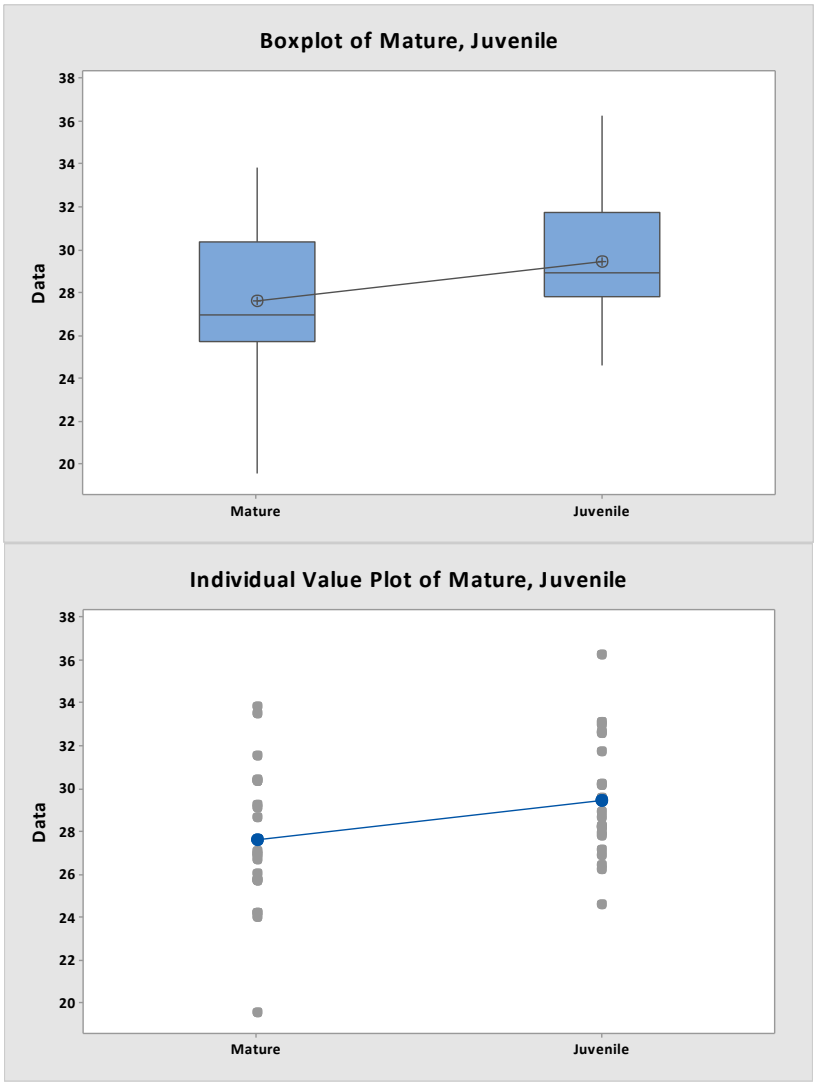

Figure B.5 Data distribution and box plot of contact angle for Douglas-fir using water

Loblolly pine diiodomethane

Two-Sample T-Test and CI: Mature, Juvenile

Two-sample T for Mature vs Juvenile

	N	Mean	StDev	SE Mean
Mature	23	29.16	2.67	0.56
Juvenile	22	30.26	5.06	1.1

Difference = μ (Mature) - μ (Juvenile)
Estimate for difference: -1.10
95% CI for difference: (-3.58, 1.38)
T-Test of difference = 0 (vs ≠): T-Value = -0.91 P-Value = 0.372 DF = 31

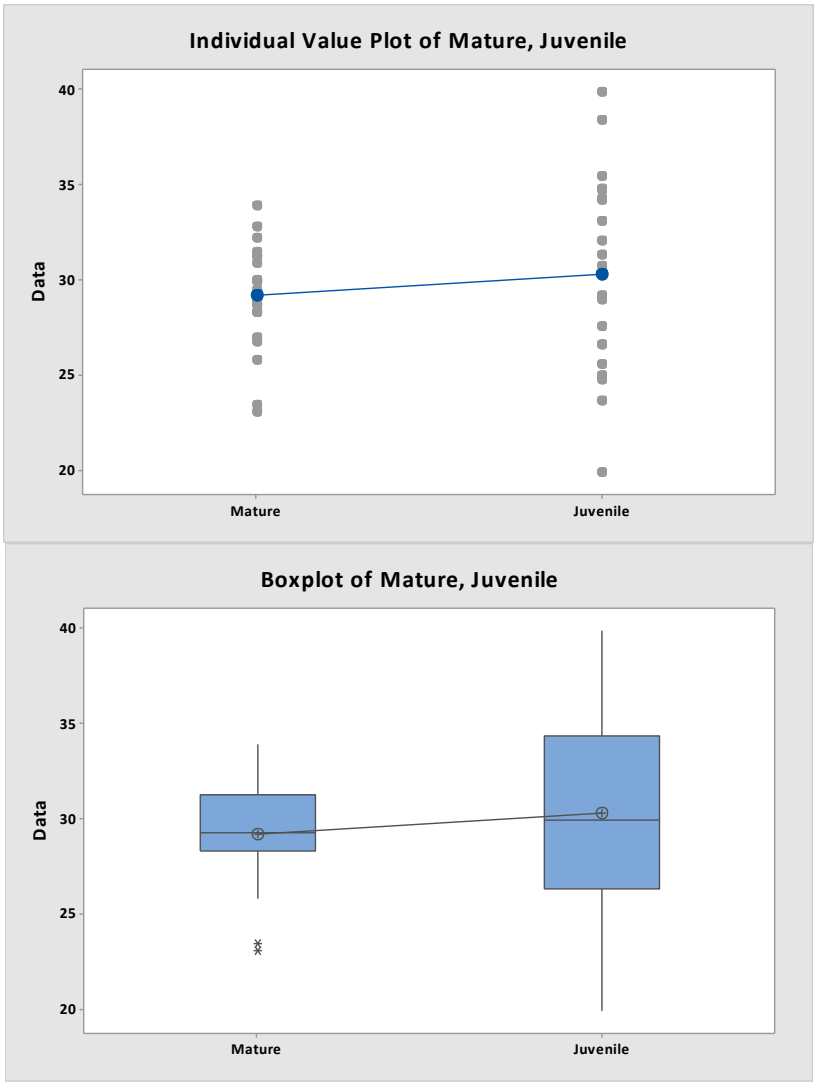

Figure B.6 Data distribution and box plot of contact angle for Douglas-fir using diiodomethane

Appendix C: Statistics for Extractives

Mature extractives

Two-Sample T-Test and CI: Mature lb, Mature df

Two-sample T for Mature lb vs Mature df

	N	Mean	StDev	SE Mean
Mature lb	8	3.542	0.362	0.13
Mature df	8	1.312	0.395	0.14

Difference = μ (Mature lb) - μ (Mature df)
Estimate for difference: 2.230
95% CI for difference: (1.820, 2.639)
T-Test of difference = 0 (vs ≠): T-Value = 11.77 P-Value = 0.000 DF = 13

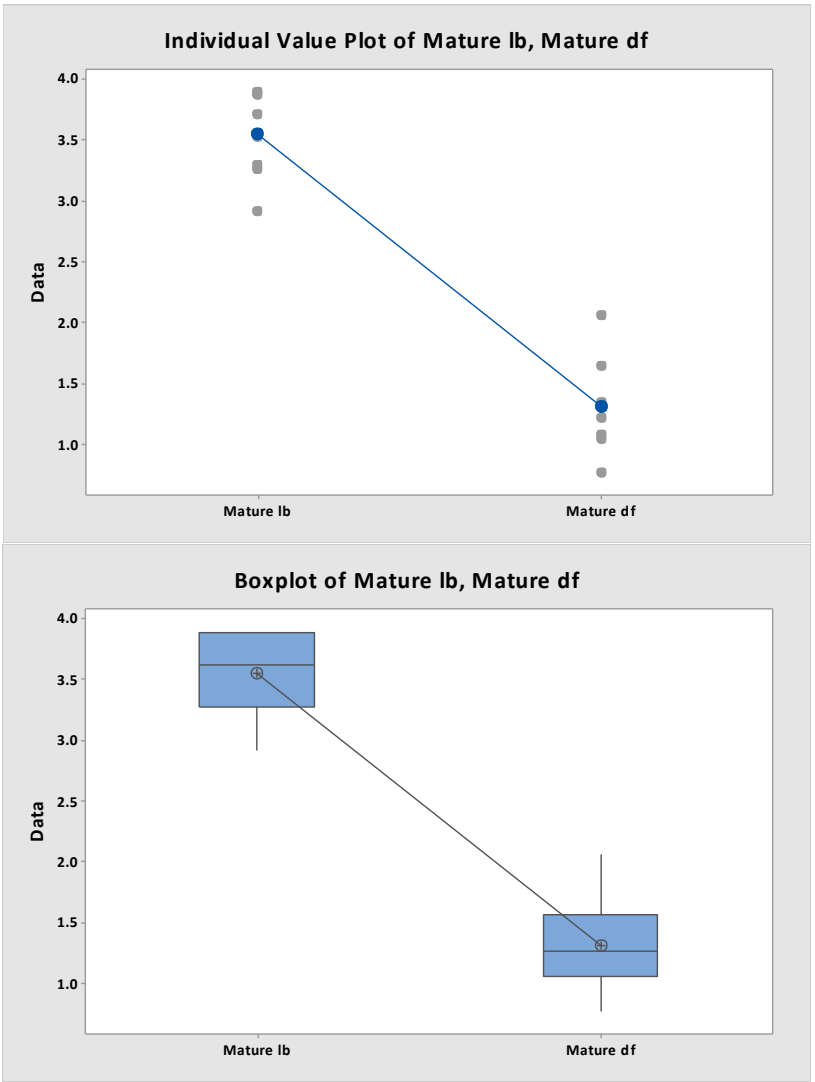

Figure C.1 Data distribution and box plot of extractives in mature loblolly pine and Douglas-fir

Juvenile extractives

Two-Sample T-Test and CI: Juvenile lb, Juvenile df

Two-sample T for Juvenile lb vs Juvenile df

	N	Mean	StDev	SE Mean
Juvenile lb	8	5.263	0.921	0.33
Juvenile df	9	2.831	0.633	0.21

Difference = μ (Juvenile lb) - μ (Juvenile df)
Estimate for difference: 2.432
95% CI for difference: (1.587, 3.277)
T-Test of difference = 0 (vs ≠): T-Value = 6.27 P-Value = 0.000 DF = 12

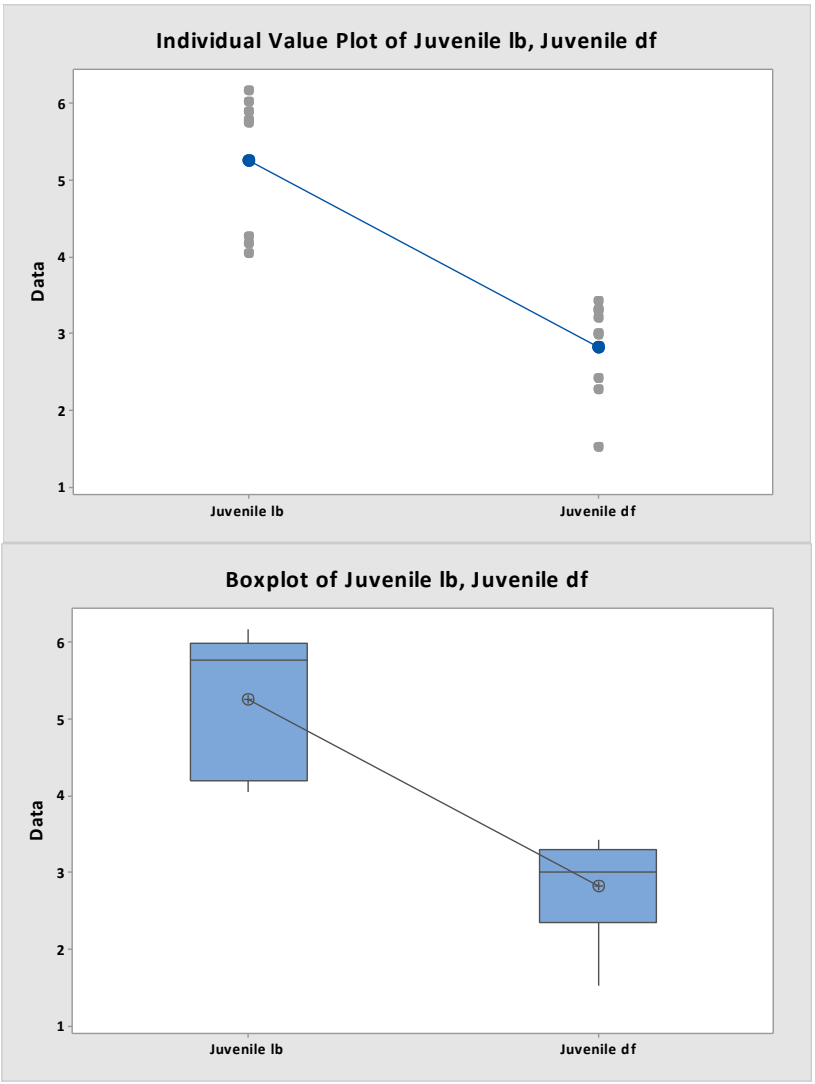

Figure C.2 Data distribution and box plot of extractives in juvenile loblolly pine and Douglas-fir

Total extractives

Two-Sample T-Test and CI: lb, df

Two-sample T for lb vs df

	N	Mean	StDev	SE Mean
lb	16	4.40	1.12	0.28
df	17	2.117	0.938	0.23

Difference = μ (lb) - μ (df)
Estimate for difference: 2.286
95% CI for difference: (1.550, 3.023)
T-Test of difference = 0 (vs ≠): T-Value = 6.35 P-Value = 0.000 DF = 29

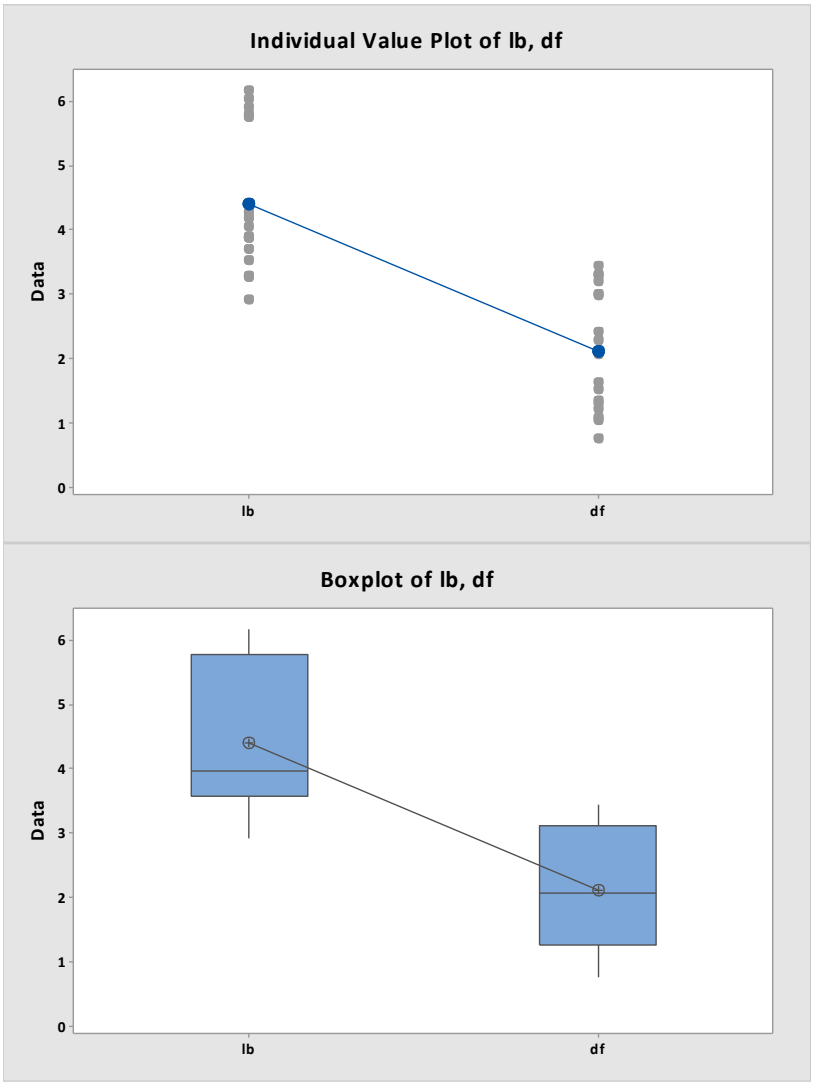

Figure C.3 Data distribution and box plot of total extractives in loblolly pine and Douglas-fir

Appendix D: Compositional Analysis Statistics

Total lignin

Two-Sample T-Test and CI: lb, df

Two-sample T for lb vs df

	N	Mean	StDev	SE Mean
lb	16	30.37	1.56	0.39
df	17	28.57	2.30	0.56

Difference = μ (lb) - μ (df)
Estimate for difference: 1.798
95% CI for difference: (0.404, 3.192)
T-Test of difference = 0 (vs ≠): T-Value = 2.64 P-Value = 0.013 DF = 28

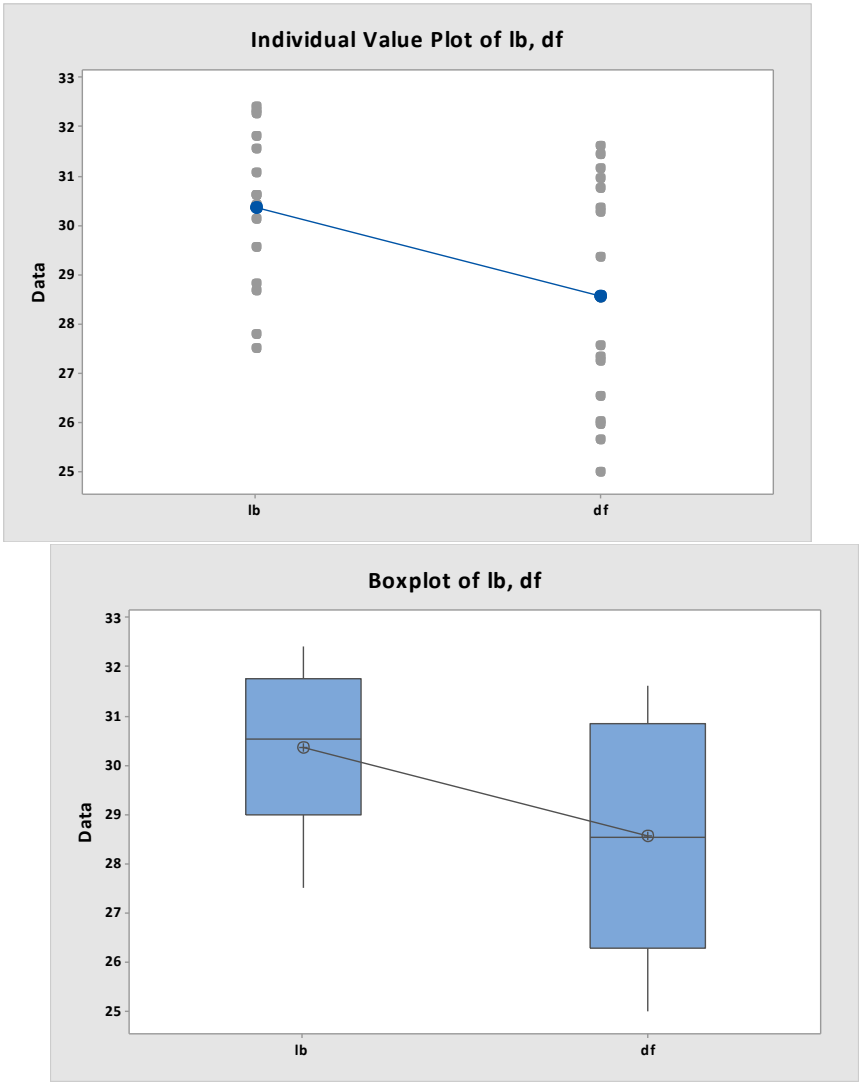

Figure D.1 Data distribution and box plot of total lignin in loblolly pine and Douglas-fi

Total arabinan

Two-sample T for lb vs df

	N	Mean	StDev	SE Mean
lb	16	1.266	0.262	0.066
df	17	0.807	0.178	0.043

Difference = μ (lb) - μ (df)
Estimate for difference: 0.4590
95% CI for difference: (0.2975, 0.6205)
T-Test of difference = 0 (vs ≠): T-Value = 5.84 P-Value = 0.000 DF = 26

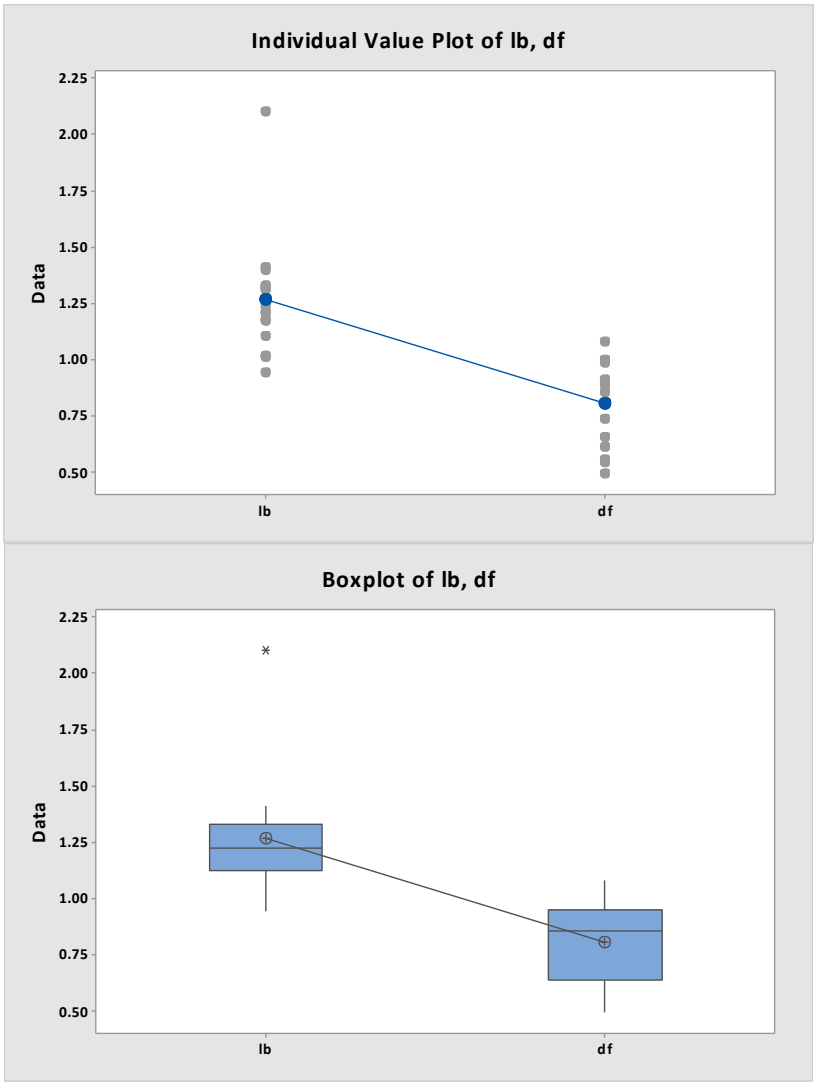

Figure D.2 Data distribution and box plot of total arabinan in loblolly pine and Douglas-fir

Total galactan

Two-Sample T-Test and CI: lb, df

Two-sample T for lb vs df

	N	Mean	StDev	SE Mean
lb	16	2.756	0.858	0.21
df	17	2.365	0.554	0.13

Difference = μ (lb) - μ (df)
Estimate for difference: 0.392
95% CI for difference: (-0.130, 0.913)
T-Test of difference = 0 (vs ≠): T-Value = 1.55 P-Value = 0.134 DF = 25

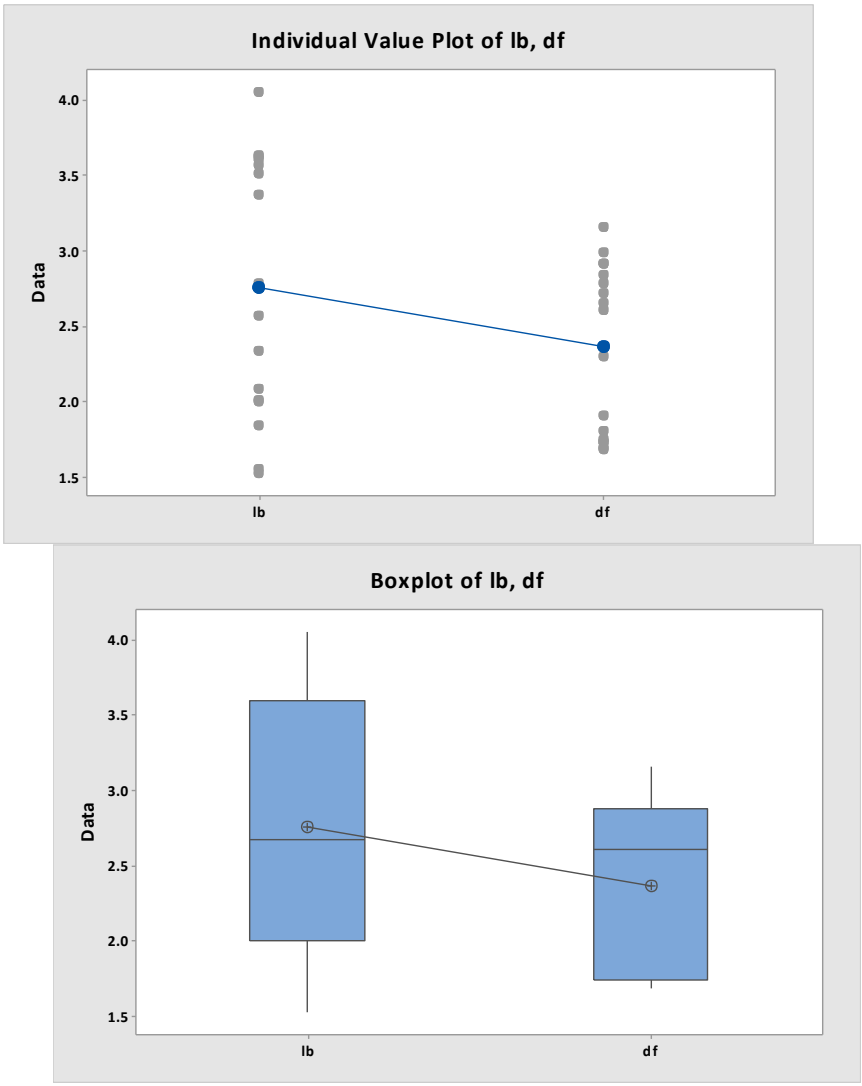

Figure D.3 Data distribution and box plot of total galactan in loblolly pine and Douglas-fir

Total glucan

Two-Sample T-Test and CI: lb, df

Two-sample T for lb vs df

	N	Mean	StDev	SE Mean
lb	16	40.40	2.53	0.63
df	17	43.64	2.03	0.49

Difference = μ (lb) - μ (df)
Estimate for difference: -3.241
95% CI for difference: (-4.882, -1.600)
T-Test of difference = 0 (vs ≠): T-Value = -4.05 P-Value = 0.000 DF = 28

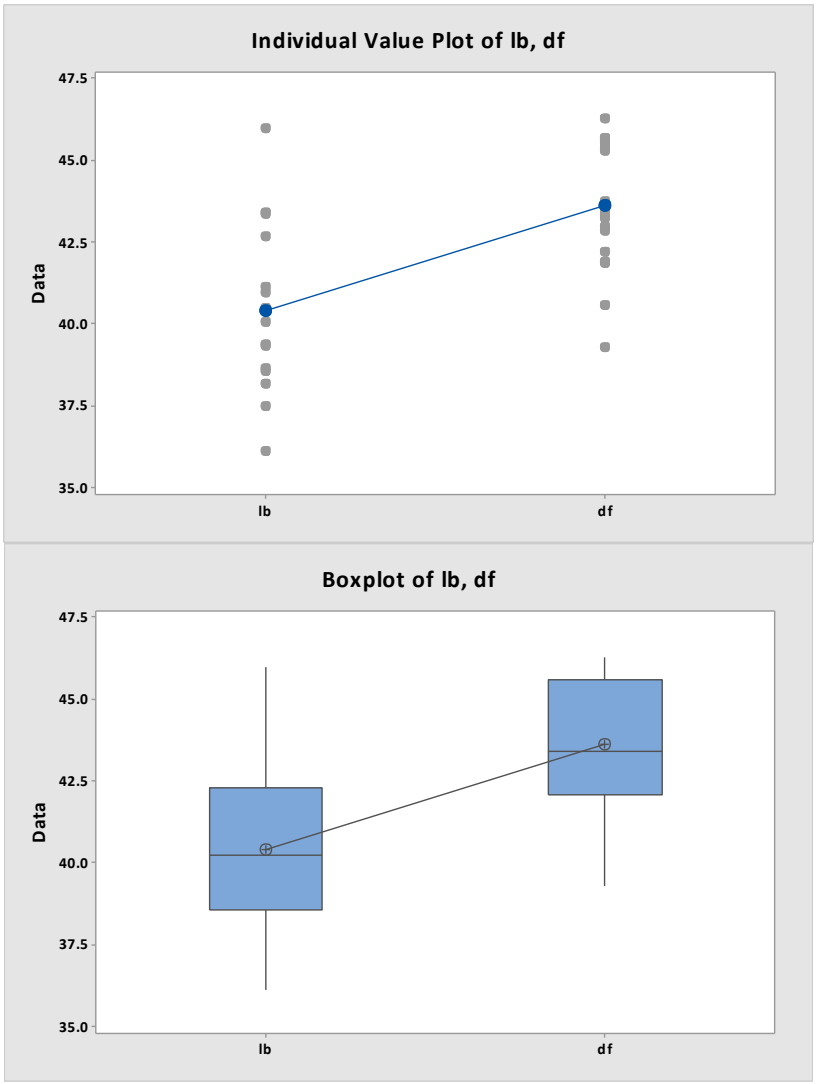

Figure D.4 Data distribution and box plot of total glucan in loblolly pine and Douglas-fir

Total xylan

Two-Sample T-Test and CI: lb, df

Two-sample T for lb vs df

	N	Mean	StDev	SE Mean
lb	16	7.017	0.676	0.17
df	17	4.031	0.545	0.13

Difference = μ (lb) - μ (df)
Estimate for difference: 2.986
95% CI for difference: (2.547, 3.426)
T-Test of difference = 0 (vs ≠): T-Value = 13.92 P-Value = 0.000 DF = 28

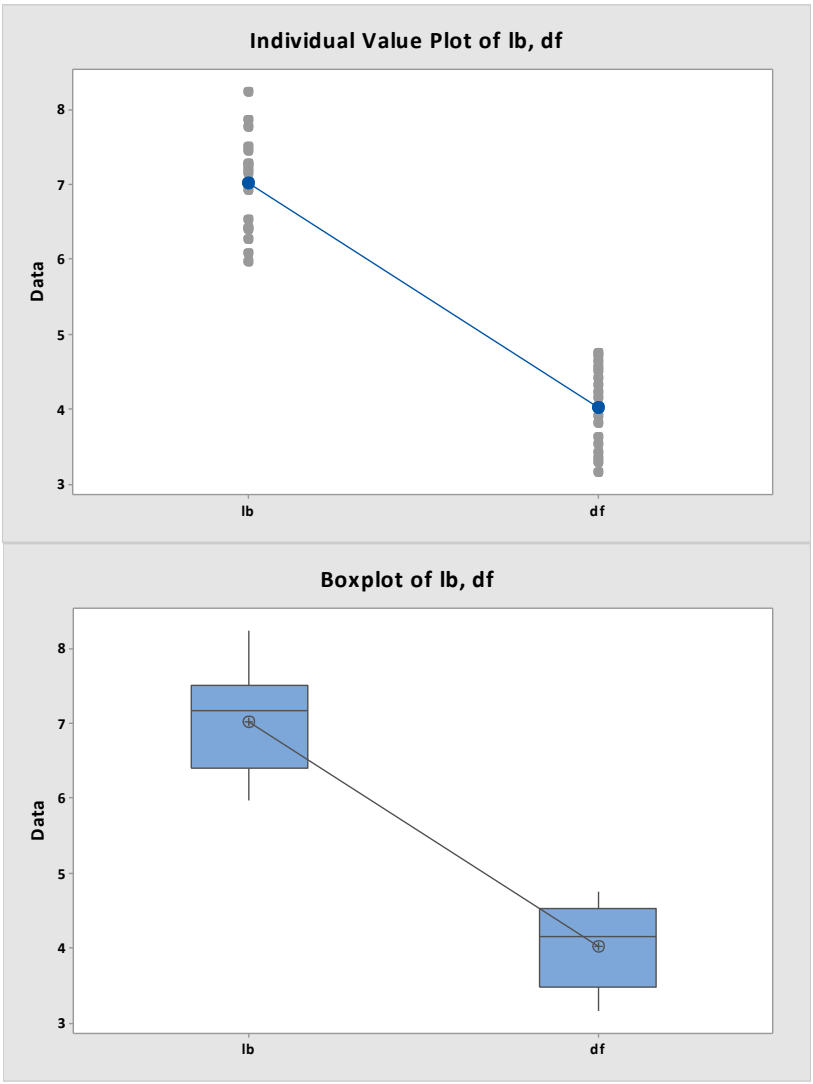

Figure D.5 Data distribution and box plot of total xylan in loblolly pine and Douglas-fir

Total mannan

Two-Sample T-Test and CI: lb, df

Two-sample T for lb vs df

	N	Mean	StDev	SE Mean
lb	16	10.087	0.838	0.21
df	17	13.508	0.693	0.17

Difference = μ (lb) - μ (df)
Estimate for difference: -3.422
95% CI for difference: (-3.971, -2.872)
T-Test of difference = 0 (vs ≠): T-Value = -12.74 P-Value = 0.000 DF = 29

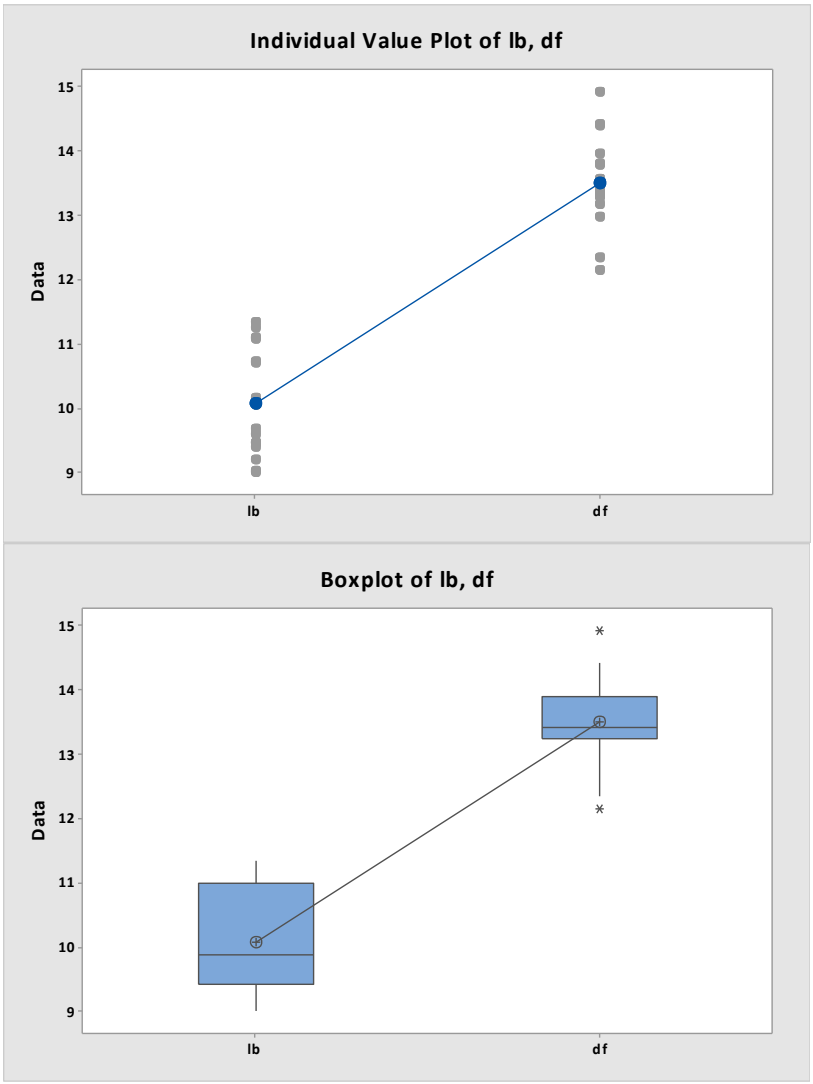

Figure D.6 Data distribution and box plot of total mannan in loblolly pine and Douglas-fir

Appendix E: Statistics for % Wood Failure

% Wood failure

Response % wood failure Species=DF

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	11	3041.696	276.518	1.4233
Error	231	44878.880	194.281	**Prob > F**
C. Total	242	47920.576		0.1632

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Adhesive	1	1	379.7553	1.9547	0.1634
Growth region	1	1	86.2358	0.4439	0.5059
Adhesive*Growth region	1	1	179.1831	0.9223	0.3379
Assembly time[Adhesive]	4	4	384.5782	0.4949	0.7395
Growth region*Assembly time[Adhesive]	4	4	2051.1899	2.6395	0.0347*

Response % wood failure Species=SYP

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	11	2777.767	252.524	1.1669
Error	229	49558.332	216.412	**Prob > F**
C. Total	240	52336.100		0.3112

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Adhesive	1	1	562.1507	2.5976	0.1084
Growth region	1	1	179.8115	0.8309	0.3630
Adhesive*Growth region	1	1	104.2764	0.4818	0.4883
Assembly time[Adhesive]	4	4	1235.7904	1.4276	0.2256
Growth region*Assembly time[Adhesive]	4	4	707.8904	0.8178	0.5150

Appendix F: Statistics for Shear Strength

Shear strength

Response kPa Species=DF

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	11	1020914	92810.4	2.2612
Error	231	9481453	41045.3	**Prob > F**
C. Total	242	10502367		0.0124*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Adhesive	1	1	7183.84	0.1750	0.6761
Growth region	1	1	100544.83	2.4496	0.1189
Adhesive*Growth region	1	1	302255.68	7.3640	0.0072*
Assembly time[Adhesive]	4	4	281265.46	1.7131	0.1479
Growth region*Assembly time[Adhesive]	4	4	328940.62	2.0035	0.0948

Response kPa Species=SYP

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	11	2636430	239675	6.3127
Error	229	8694500	37967	**Prob > F**
C. Total	240	11330929		<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Adhesive	1	1	12785.4	0.3367	0.5623
Growth region	1	1	130215.9	3.4297	0.0653
Adhesive*Growth region	1	1	10243.0	0.2698	0.6040
Assembly time[Adhesive]	4	4	1510448.5	9.9457	<.0001*
Growth region*Assembly time[Adhesive]	4	4	973445.9	6.4098	<.0001*

Appendix G: ASTM-D905 Results Table

Table G.1 Average stress and % wood failure of all effects for both wood types

Factors	Species	southern yellow pine											
	Growth	Mature						Juvenile					
	Adhesive	PU			PRF			PU			PRF		
	Assembly*	Min/Min	Min/Max	Max/Max	Min/Min	Min/Max	Max/Max	Min/Min	Min/Max	Max/Max	Min/Min	Min/Max	Max/Max
Stress(psi)	Max	2460	1875	1727	1975	2006	1987	1875	1961	1934	2181	2047	1817
	Min	1277	1359	1285	1129	1321	1235	1285	1089	1450	1352	1234	1400
	Average	1937	1590	1530	1723	1636	1703	1663	1519	1696	1710	1617	1634
	Stdev	317.7	152.3	101.1	213.5	173.4	207.7	142.0	219.6	151.7	215.2	206.5	139.5
(%)wood failure	Max	95.00	95.00	100.00	95.00	100.00	100.00	95.00	95.00	100.00	95.00	95.00	95.00
	Min	30.00	20.00	65.00	20.00	60.00	25.00	50.00	50.00	60.00	20.00	65.00	60.00
	Average	81.00	75.50	83.16	77.37	87.25	80.26	82.86	79.09	78.95	84.77	86.00	83.25
	Stdev	17.14	19.59	10.44	17.98	11.75	19.04	12.90	11.71	12.54	17.01	8.68	13.01
	# of samples	20.00	20.00	19.00	19.00	20.00	19.00	21.00	22.00	19.00	22.00	20.00	20.00

Factors	Species	Douglas-fir											
	Growth	Mature						Juvenile					
	Adhesive	PU			PRF			PU			PRF		
	Assembly*	Min/Min	Min/Max	Max/Max	Min/Min	Min/Max	Max/Max	Min/Min	Min/Max	Max/Max	Min/Min	Min/Max	Max/Max
Stress(psi)	Max	1866	1876	2069	1853	1965	2226	2031	2123	1910	1905	1944	1867
	Min	747	1139	1348	1423	1441	1341	1208	1112	1311	1205	1183	1215
	Average	1485	1574	1683	1596	1675	1717	1597	1633	1603	1577	1516	1561
	Stdev	301.3	181.9	162.4	118.9	112.5	222.7	243.4	270.7	187.1	184.6	190.4	159.4
(%)wood failure	Max	95.00	95.00	95.00	95.00	95.00	95.00	95.00	100.00	95.00	95.00	95.00	95.00
	Min	15.00	50.00	65.00	20.00	25.00	45.00	50.00	25.00	65.00	45.00	60.00	60.00
	Average	76.55	80.91	85.48	76.32	82.00	80.26	88.16	81.75	79.76	77.50	79.74	79.76
	Stdev	21.21	12.11	7.40	16.82	15.34	12.74	10.96	19.08	10.43	13.81	10.86	9.42
	# of samples	22.00	22.00	21.00	19.00	20.00	19.00	19.00	20.00	21.00	20.00	19.00	21.00

Appendix H: Table of Results for Delamination

Table H.1 Results from ASTM-D2559

Wood Type	Assembly Time	Adhesive	Growth Region at Bondline	Delamination (mm)
DF	Max/Max	PU	Juvenile to Mature	217
DF	Max/Max	PU	Juvenile to Mature	115
DF	Min/Min	PU	Mature to Mature	194
DF	Min/Min	PU	Mature to Mature	127
SYP	Max/Max	PU	Juvenile to Mature	142
SYP	Max/Max	PU	Juvenile to Mature	108
SYP	Min/Max	PU	Mature to Mature	195
SYP	Min/Max	PU	Mature to Mature	180
DF	Min/Max	PU	Mature to Mature	162
DF	Min/Max	PU	Mature to Mature	239
DF	Min/Min	PU	Mature to Mature	193
DF	Min/Min	PU	Mature to Mature	223
SYP	Max/Max	PU	Juvenile to Mature	125
SYP	Max/Max	PU	Juvenile to Mature	80.1
SYP	Min/Max	PU	Juvenile to Mature	56.0
SYP	Min/Max	PU	Juvenile to Mature	57.6
SYP	Min/Min	PU	Mature to Mature	211
SYP	Min/Min	PU	Mature to Mature	144
SYP	Min/Min	PU	Juvenile to Mature	87.8
SYP	Min/Min	PU	Juvenile to Mature	87.7
DF	Min/Max	PU	Mature to Mature	156
DF	Min/Max	PU	Mature to Mature	158
DF	Min/Min	PU	Mature to Mature	147
DF	Min/Min	PU	Mature to Mature	140
SYP	Max/Max	PU	Mature to Mature	112
SYP	Max/Max	PU	Mature to Mature	117
SYP	Min/Max	PU	Juvenile to Mature	114
SYP	Min/Max	PU	Juvenile to Mature	45.9
SYP	Max/Max	PU	Mature to Mature	61.7
SYP	Max/Max	PU	Mature to Mature	83.1
SYP	Min/Min	PU	Mature to Mature	130
SYP	Min/Min	PU	Mature to Mature	134
SYP	Min/Min	PU	Juvenile to Mature	112
SYP	Min/Min	PU	Juvenile to Mature	138
SYP	Min/Max	PRF	Juvenile to Mature	0.00
SYP	Min/Max	PRF	Juvenile to Mature	0.00

SYP	Min/Max	PRF	Juvenile to Mature	4.09
SYP	Min/Max	PRF	Juvenile to Mature	0.00
SYP	Min/Max	PRF	Juvenile to Mature	0.00
SYP	Min/Max	PRF	Juvenile to Mature	4.60
SYP	Max/Max	PRF	Mature to Mature	0.00
SYP	Max/Max	PRF	Mature to Mature	0.00
DF	Max/Max	PRF	Mature to Mature	5.76
DF	Max/Max	PRF	Mature to Mature	0.00
DF	Min/Max	PRF	Mature to Mature	9.73
DF	Min/Max	PRF	Mature to Mature	6.94
SYP	Min/Max	PRF	Mature to Mature	0.00
SYP	Min/Max	PRF	Mature to Mature	0.00
SYP	Min/Min	PRF	Mature to Mature	0.00
SYP	Min/Min	PRF	Mature to Mature	7.58
DF	Min/Min	PRF	Mature to Mature	8.57
DF	Min/Min	PRF	Mature to Mature	3.03
DF	Max/Max	PRF	Mature to Mature	0.00
DF	Max/Max	PRF	Mature to Mature	6.82
DF	Min/Max	PRF	Mature to Mature	6.03
DF	Min/Max	PRF	Mature to Mature	0.00
SYP	Min/Max	PRF	Mature to Mature	0.00
SYP	Min/Max	PRF	Mature to Mature	0.00
SYP	Min/Min	PRF	Mature to Mature	0.00
SYP	Min/Min	PRF	Mature to Mature	4.81
DF	Min/Max	PRF	Mature to Mature	9.97
DF	Min/Max	PRF	Mature to Mature	3.71
SYP	Min/Max	PRF	Mature to Mature	0.00
SYP	Min/Max	PRF	Mature to Mature	0.00
DF	Max/Max	PU	Juvenile to Mature	132
DF	Max/Max	PU	Juvenile to Mature	151
DF	Max/Max	PU	Mature to Mature	196
DF	Max/Max	PU	Mature to Mature	128
SYP	Min/Max	PU	Juvenile to Mature	103
SYP	Min/Max	PU	Juvenile to Mature	89.2
SYP	Max/Max	PU	Mature to Mature	209
SYP	Max/Max	PU	Mature to Mature	118
DF	Min/Min	PRF	Mature to Mature	0.00
DF	Min/Min	PRF	Mature to Mature	2.56
SYP	Max/Max	PRF	Mature to Mature	0.00
SYP	Max/Max	PRF	Mature to Mature	5.11
SYP	Min/Max	PU	Mature to Mature	128

SYP	Min/Max	PU	Mature to Mature	210
DF	Max/Max	PRF	Mature to Mature	0.00
DF	Max/Max	PRF	Mature to Mature	8.65
SYP	Min/Min	PRF	Mature to Mature	4.05
SYP	Min/Min	PRF	Mature to Mature	0.00
DF	Min/Min	PRF	Juvenile to Mature	2.86
DF	Min/Min	PRF	Juvenile to Mature	0.00
SYP	Max/Max	PRF	Juvenile to Mature	0.00
SYP	Max/Max	PRF	Juvenile to Mature	2.68
SYP	Min/Min	PU	Juvenile to Mature	136
SYP	Min/Min	PU	Juvenile to Mature	131
DF	Min/Max	PU	Mature to Mature	164
DF	Min/Max	PU	Mature to Mature	87.7
DF	Max/Max	PRF	Juvenile to Mature	2.77
DF	Max/Max	PRF	Juvenile to Mature	4.02
DF	Min/Min	PRF	Juvenile to Mature	2.60
DF	Min/Min	PRF	Juvenile to Mature	0.00
DF	Max/Max	PRF	Juvenile to Mature	3.91
DF	Max/Max	PRF	Juvenile to Mature	0.00
DF	Min/Max	PRF	Juvenile to Mature	3.49
DF	Min/Max	PRF	Juvenile to Mature	0.00
SYP	Max/Max	PRF	Juvenile to Mature	0.00
SYP	Max/Max	PRF	Juvenile to Mature	0.00
SYP	Min/Min	PU	Mature to Mature	222
SYP	Min/Min	PU	Mature to Mature	152
DF	Min/Max	PU	Juvenile to Mature	152
DF	Min/Max	PU	Juvenile to Mature	127
DF	Min/Max	PRF	Juvenile to Mature	2.58
DF	Min/Max	PRF	Juvenile to Mature	0.00
DF	Max/Max	PRF	Juvenile to Mature	4.52
DF	Max/Max	PRF	Juvenile to Mature	4.42
DF	Max/Max	PU	Juvenile to Mature	187
DF	Max/Max	PU	Juvenile to Mature	134
DF	Max/Max	PU	Mature to Mature	155
DF	Max/Max	PU	Mature to Mature	143
DF	Min/Min	PU	Juvenile to Mature	97.9
DF	Min/Min	PU	Juvenile to Mature	41.5
SYP	Max/Max	PU	Juvenile to Mature	90.9
SYP	Max/Max	PU	Juvenile to Mature	120
SYP	Max/Max	PRF	Mature to Mature	5.91
SYP	Max/Max	PRF	Mature to Mature	0.00

DF	Min/Max	PU	Juvenile to Mature	128
DF	Min/Max	PU	Juvenile to Mature	73.1
DF	Min/Max	PRF	Juvenile to Mature	0.00
DF	Min/Max	PRF	Juvenile to Mature	4.30
DF	Min/Min	PU	Juvenile to Mature	143
DF	Min/Min	PU	Juvenile to Mature	77.9
DF	Min/Min	PU	Juvenile to Mature	151
DF	Min/Min	PU	Juvenile to Mature	100
DF	Max/Max	PU	Mature to Mature	145
DF	Max/Max	PU	Mature to Mature	132
SYP	Min/Max	PU	Mature to Mature	199
SYP	Min/Max	PU	Mature to Mature	140

Appendix I: Viscosity Data for Phenol-Resorcinol-Formaldehyde

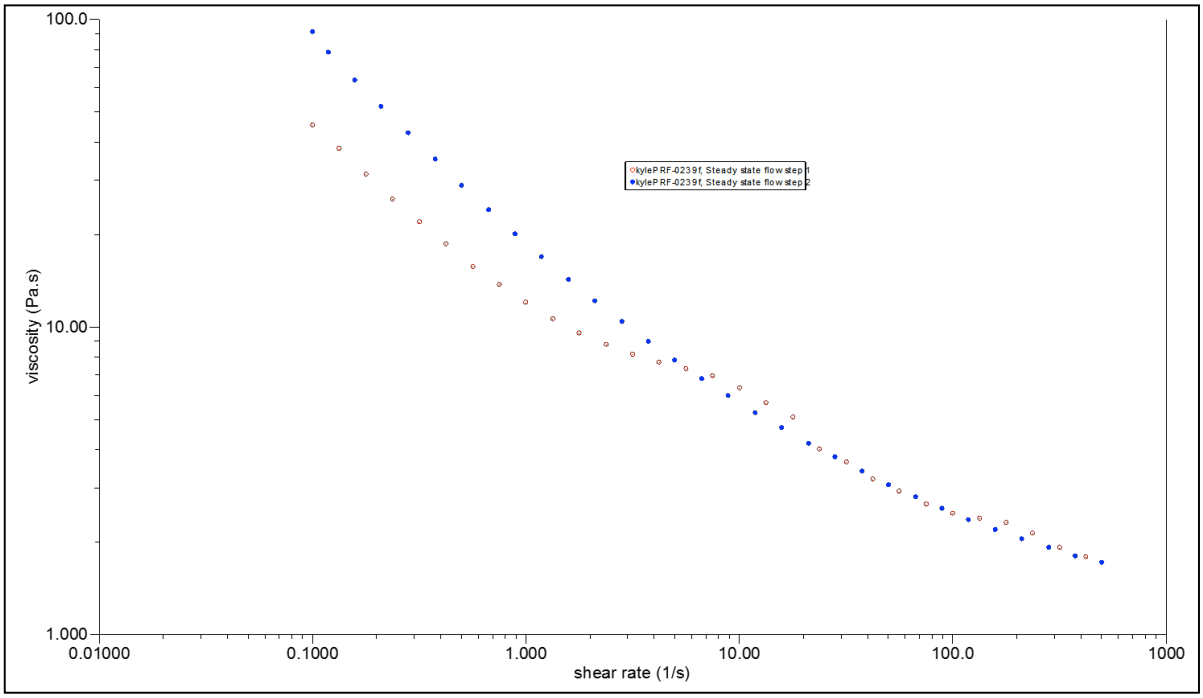

Figure I.1 Graphical representation of the viscosity of PRF tested at different shear rates using same steps performed before bonding as listed in methods.

Table I.1 Data from testing the viscosity of PRF adhesive shown above
Data from testing the viscosity of PRF adhesive shown above

Shear Stress	Shear Rate	Viscosity	Time	Temperature	Normal Stress
Pa	1/s	Pa.s	s	°C	Pa
4.52	0.10	45.3	61.91	25	254
5.06	0.13	37.9	107.8	25	264
5.57	0.18	31.4	153.9	25	265
6.18	0.24	26.1	199.7	25	258
6.92	0.32	21.9	245.8	25	251
7.79	0.42	18.5	291.7	25	231
8.81	0.56	15.7	336.8	25	238
10.3	0.75	13.7	382.7	25	260
12.0	1.00	12.0	428.8	25	271
14.2	1.33	10.6	474.7	25	290
16.9	1.78	9.52	520.6	25	301
20.8	2.37	8.75	565.9	25	300
25.7	3.16	8.13	611.9	25	313
32.3	4.22	7.67	657.6	25	332
41.0	5.62	7.30	702.6	25	324
51.8	7.50	6.90	747.8	25	339

63.2	10.0	6.32	793.8	25	362
75.1	13.3	5.63	839.9	25	365
90.1	17.8	5.07	885.9	25	391
94.7	23.7	3.99	941.8	25	370
115	31.6	3.63	987.6	25	397
134	42.2	3.18	1033	25	412
164	56.2	2.91	1079	25	420
198	75.0	2.64	1125	25	431
247	100	2.47	1171	25	448
318	133	2.38	1216	25	457
411	178	2.31	1261	25	473
506	237	2.13	1307	25	475
604	316	1.91	1353	25	481
751	422	1.78	1398	25	485
855	500	1.71	1443	25	504

Appendix J: Viscosity Data for Polyurethane

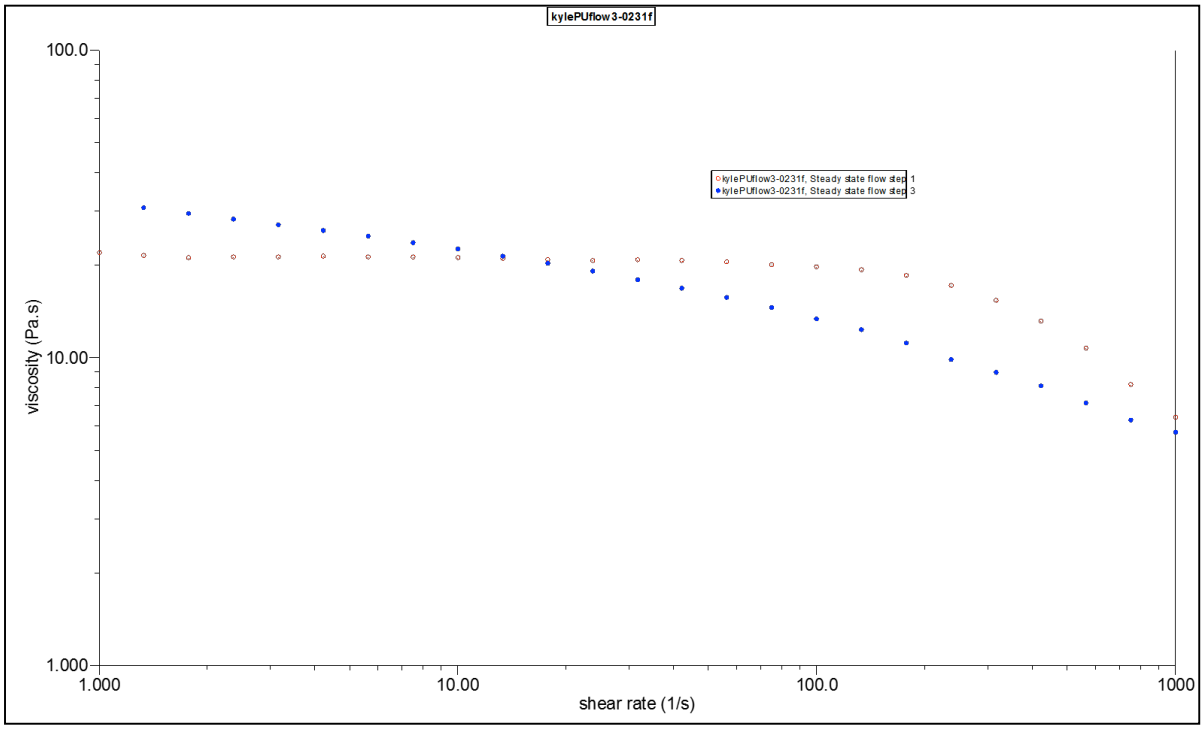

Figure J.1 Graphical representation of the viscosity of PU tested at different shear rates

Table J.1 Data from testing the viscosity of PU adhesive shown above
Data from testing the viscosity of PU adhesive shown above

Shear Stress	Shear Rate	Viscosity	Time	Temperature
Pa	1/s	Pa.s	s	°C
21.86	1.000	21.85	41.28	25
28.57	1.332	21.44	86.56	25
37.59	1.778	21.14	132.3	25
50.26	2.370	21.21	177.4	25
67.15	3.159	21.26	223.3	25
89.68	4.216	21.27	268.3	25
119.4	5.622	21.24	313.2	25
158.7	7.495	21.18	358.6	25
211.2	10.00	21.12	404.2	25
279.5	13.33	20.97	449.3	25
368.9	17.78	20.75	494.4	25
490.2	23.71	20.68	540.6	25
655.1	31.62	20.72	586.6	25

869.1	42.16	20.61	632.3	25
1146	56.22	20.39	677.3	25
1503	74.97	20.05	722.4	25
1969	100.0	19.69	768.4	25
2567	133.3	19.26	813.3	25
3280	177.8	18.45	858.4	25
4054	237.0	17.10	904.5	25
4840	316.1	15.31	950.2	25
5535	421.6	13.13	995.5	25
6027	562.1	10.72	1041	25
6124	749.8	8.168	1096	25
6386	1000	6.387	1142	25
5713	1000	5.714	41.16	25
4683	749.7	6.247	86.34	25
3994	562.1	7.106	132.2	25
3411	421.5	8.092	177.2	25
2825	316.1	8.936	222.4	25
2333	237.1	9.842	268.3	25
1981	177.8	11.15	314.3	25
1638	133.3	12.29	360.1	25
1332	100.0	13.33	405.1	25
1086	74.97	14.49	450.2	25
878.3	56.21	15.62	495.2	25
707.5	42.15	16.78	541.2	25
566.4	31.61	17.92	586.4	25
452.5	23.70	19.09	632.1	25
359.1	17.78	20.20	677.2	25
284.7	13.33	21.36	722.4	25
224.8	10.00	22.49	768.1	25
177.0	7.497	23.61	813.3	25
139.0	5.622	24.72	859.3	25
108.8	4.214	25.82	905.4	25
85.20	3.160	26.96	951.1	25
66.63	2.369	28.12	997.1	25
52.20	1.778	29.37	1042	25
40.87	1.331	30.71	1088	25
32.08	0.999	32.12	1134	25