



## AN ABSTRACT OF THE THESIS OF

Christopher P. Gabrielli for the degree of  
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Title: Chemical Modification of Wood: Dimensional Stabilization of Viscoelastic  
Thermal Compressed Wood.

Abstract approved:

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Frederick A. Kamke

The tendency of wood to shrink and swell with changing moisture content remains as one of the most significant challenges to using wood in its many applications. Viscoelastic Thermal Compression (VTC) has been shown to significantly increase the density, strength and stiffness of wood. However, dimensional stability is still a concern. Active and passive chemical modifications have been developed which impart dimensional stability by chemically altering the wood substrate or physically blocking the vital pathways of water through the wood microstructure. The efforts of this research have been to develop an approach which combines the VTC process with a chemical modification process resulting in a novel wood-based product that exhibits improved structural properties, as well as a high degree of dimensional stability. Low-grade, plantation-grown hybrid poplar (*Populus* spp.) was impregnated with low molecular weight phenol-formaldehyde resin, acetic anhydride or tung oil and then densified in the VTC process. Water soak and boil tests

were performed to investigate the influence of each treatment on thickness swell, anti-swelling efficiency (ASE), irreversible swelling, and thickness recovery. Modulus of elasticity (MOE) was also examined for each treatment. Fluorescence microscopy was applied to determine the physical location and distribution of the impregnating reagents to better understand their role in imparting dimensional stability.

PF and acetylation treatments were shown to increase the stability of VTC treated samples. ASE values for both PF and acetylation treatments were high, with a maximum value of 86% for the PF treatment and 56% for the acetylation treatment. Two different low molecular weight PF resins were tested and it was found that the higher MW resin was retained within the cellular structure to a greater degree and imparted greater dimensional stability. MOE was positively correlated to density but negatively correlated to weight percent gain for PF treated samples. All chemically modified samples had lower increases in MOE than unmodified control specimens compressed to the same final thickness. A sub-sample of higher density PF treated specimens had significantly higher MOE values and similar stability values compared to lower density samples.

Tung oil treated samples showed no ability to swell the wood cell wall and remained in the cell lumens. Although dimensional stability may have increased on a very short-term basis due to physical obstruction of moisture, long-term stability was not improved with tung oil treatments.

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Chemical Modification of Wood: Dimensional Stabilization of Viscoelastic Thermal  
Compressed Wood

by  
Christopher P. Gabrielli

A THESIS

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Presented on March 17, 2008

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Christopher P. Gabrielli, Author

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# CHEMICAL MODIFICATION OF WOOD: DIMENSIONAL STABILIZATION OF VISCOELASTIC THERMAL COMPRESSED WOOD

## **Chapter 1: Introduction**

### ***1.1 Background***

Worldwide per capita wood consumption has remained constant for many decades; however, exponential population growth has resulted in a sharp increase in demand on the world's forest resources (Sutton, 1993). In lieu of this increased pressure, attempts have been made from both ends of the forest products industry to understand and prepare for future supply obstacles. From the forestry and silvicultural standpoint, better land management and sustainable harvesting have been the focus. From the processing end, wood scientists have been working to better utilize raw material, reduce production inefficiencies and develop more sustainable industrial practices. The development of Viscoelastic Thermal Compression (VTC) is an example of a step in this direction. The VTC process uses a dynamic heat, steam, and mechanical compression treatment to densify wood. This process takes advantage of the mechano-sorptive effect, compressing the wood without fracturing the cell wall, thus maintaining the structural integrity of the wood. Large increases in density, strength and stiffness are realized (Kamke, 2005). The VTC process utilizes plantation grown, short-rotation, low-density species whose initial mechanical properties are often inadequate for structural purposes. The increase in mechanical properties obtained through the viscoelastic thermal compression process can open the door for

further utilization of these species to a much broader range of applications. VTC wood is not intended to be used independently, but rather as a laminate component in reinforced wood composites. These composites can be engineered with tailored mechanical properties for specific applications. Although the use of heat and steam increases the dimensional stability of VTC wood, there is still room for improvement. This remains a key obstacle is perfecting viscoelastic thermal compression.

The relationship between wood and moisture is one of the most significant factors governing the use of wood as a material. The inherent dimensional instability of wood limits its applications and confines its use to a narrowed range of environments compared to that of many other materials. Chemical modifications have been developed to alleviate this detrimental quality and thus, allow for the use of wood in applications where it would otherwise be inadequate.

The main focus of this research is to integrate a chemical modification process with the VTC process to produce a dimensionally stable wood-based composite with superior mechanical properties. Three different chemical treatments are being studied: Acetylation with acetic anhydride, low molecular weight phenol formaldehyde (PF) impregnation, and tung oil impregnation. The acetylation process chemically replaces free hydroxyl groups in the wood cell wall with hydrophobic acetyl groups. Lowering the hygroscopicity and bulking of the wood structure decreases moisture absorption and increases dimensional stability. PF resin imparts dimensional stability by swelling the cellular structure of the wood and then polymerizing in-situ. This bulking effect leaves the wood in a permanently swollen

state and reduces or eliminates any further swelling by moisture. Physical bonding between cell walls may also contribute to dimensional stability. Tung oil has some ability to swell wood; however, its large molecular size causes most of it to remain in the cell lumen. Tung oil's ability to dimensionally stabilize wood is realized through bulking the void spaces of the macrostructure and partial bulking of the cellular structure. Eliminating the key pathways for water movement through wood slows moisture absorption and increases dimensional stability.

### ***1.2 Technical Objectives***

- Demonstrate the technical feasibility of adapting current chemical modification techniques with the Viscoelastic Thermal Compression (VTC) process.
- Quantify the dimensional stability of untreated VTC processed wood compared to chemically modified VTC wood.

### ***1.3 Justification***

The relationship between humans, forests and the materials harvested from them has been integral to the development of our society. As world populations increase, so does the strain we put on our finite resources. The supply of raw materials necessary for day to day life is increasing and equilibrium must be found. Wood scientists are faced with the continued challenge of developing new methods and new materials which better utilize our resources. Moving away from traditional harvesting of naturally forested regions and focusing towards the development of plantation style forests is one approach to help preserve our wilderness areas. The trend towards

plantation forests has created challenges in the forest products industry due to the shifting properties of raw the material. The forest products industry has responded by developing new products which accommodate the new properties. Viscoelastic thermal compression is one such process that allows for better utilization of these raw materials. Further refinement of the VTC process is necessary to tackle concerns of dimensional stability and ultimately widen the range of application for VTC wood. The research conducted for this thesis is intended to develop an approach which combines chemical modification techniques to dimensionally stabilize VTC wood, while also retaining the desired increase in structural properties.

## **Chapter 2: Literature Review**

### ***2.1 Introduction***

Wood is often regarded as a natural composite. It is the combination of materials that when joined, form a unique parent material which exhibits superior qualities from its standalone constituents. Wood is comprised of 3 main components; cellulose, hemicellulose and lignin, which make up approximately 40, 30, and 25% of the total dry wood mass, respectively (Bowyer et al. 2003). Cellulose, which is semi-crystalline in nature, gives wood its structural integrity, while lignin provides stiffness and acts as an encrusting matrix. Hemicellulose operates as a coupling agent between the highly polar surface of cellulose and the less polar surface of lignin (Hill 2006). The macro, micro and molecular structure of wood have been studied extensively and will not be covered to great depths in this review; the reader should refer to the following texts for additional information: Forest Products Laboratory (1999), Rowell 2005, Bowyer et al. (2003), Panshin and deZeeuw (1980), Hon (1996b), Stamm (1964).

Wood-based composites have been slowly replacing the use of solid wood in many applications. The declining timber size and quality of America's wood basket has facilitated this growth and ensures continued growth in the future. This has sparked a great interest within the forest-products industry to produce new wood-based composites which exhibit properties that meet or exceed those of solid wood.

Recently, a novel approach has been developed which utilizes a dynamic heat, steam, and pressure environment to densify and strengthen low grade, low density wood. This process, known as Viscoelastic Thermal Compression (VTC), softens the wood by exploiting a phenomenon known as the mechano-sorptive effect. Through precise timing and control of temperature and steam, the VTC process is able to render the wood into a highly softened state. In this state, mechanical compression is applied which collapses the wood cell walls, but does so without fracturing them. This critical attribute of the VTC processes results in a final product whose structural components are still intact but have been densified to fill a volume 2 to 3 times smaller than its original form. Large increases in MOE are realized and have been shown to be roughly proportional to the increase in density (O’Conner 2007). Other properties including MOR and hardness are also increased. Although the cell wall substance is less hygroscopic as a result of the VTC process, the increased density of the wood increases the swelling potential upon exposure to water. Consequently, dimensional stability is still of concern. The efforts of this research will be to develop an approach which combines viscoelastic thermal compression with a chemical modification process to produce a product with improved structural properties as well as a high degree of dimensional stability.

## ***2.2 Wood and Water Relations***

Dimensional instability of wood has been a blessing and curse to wood users for thousands of years. Egyptians were known to drive wooded wedges into granite slabs, swelling the wood with water and ultimately splitting the stone (Rowell, 2005).

Although this is an example of a beneficial aspect of swelling, this property is more commonly considered a hindrance than a help. Edge swell in composite panels, delamination of plywood, and cracking and checking of sawn timber are all negative aspects of the dimension instability of wood. For more than a century scientists have been studying the structure of wood to better understand its interactions with water. This knowledge has been used to develop various forms of wood modification, all of which attempt to instill some degree of stability into an otherwise unstable material. There have been numerous types of modifications with numerous approaches to the problem. Some have been as simple as coating wood with a waterproof layer, while others use complicated multi-step chemical processes that ultimately alter the composition of the wood itself.

Wood is a naturally hygroscopic material. Its hygroscopicity is a direct result of the large number of polar functional groups, specifically hydroxyl groups, found in its cellular structure. Imparting dimensional stability upon wood can be a complex process involving various degrees of chemical, heat and pressure treatments. Although processing may be complex, these methods are all based on the fundamental concept of either preventing water from accessing the wood, or in turn, reducing wood's attraction to water (i.e. lowering its hygroscopicity).

Wood retains water in three different forms: as water vapor, as free water and as bound water. Water vapor and free water occur in the cell lumens and do not directly impact the properties of wood. Bound water, which is held in the cell wall structure through adsorption forces, has a direct effect on the stability and properties

of wood. A change in moisture content (MC) below the fiber saturation point (FSP) will result in dimensional changes in the wood, as well as changes in its mechanical properties. The majority of manufactured wood products are dried to a moisture content below their FSP, thus any significant change in MC will lead to unfavorable changes in dimensions and may render the product unusable. The ability to limit dimensional change in wood is extremely advantageous and allows wood to be used in a wider range of applications.

Wood shrinks and swells in an anisotropic fashion, (i.e. different amounts in different orientations). Although shrinkage and swelling values vary between and within species, there are some general values which are accepted throughout the industry. On average, from green to oven-dry MC, total tangential shrinkage will be around 7-10%, while radial shrinkage will be roughly 3-5%. Dimensional change in the longitudinal direction is comparatively small and therefore, often ignored. Charts of shrinkage values have been developed for many common North American and exotic species to allow for easy shrinkage and swelling calculations below FSP (Simpson, 1991).

There are many factors influencing the degree to which wood shrinks or swells. The two most important are density and extractive content.

Density has the largest influence on shrinking and swelling, both between and within species. The amount of shrinkage is generally proportional to the amount of water removed from the cell wall (Bowyer et al. 2003). Because of this, species with

higher densities have more wood substrate per unit volume, and therefore more bound water per unit volume to lose, which results in a larger percent shrinkage.

Extractives have a smaller effect on the shrinking and swelling of wood, however, their influence is still significant. It is not uncommon for the heartwood of a species to be more dimensionally stable and have a lower FSP due to the bulking effect that extractives can have on the cell wall (Bowyer et al. 2003). Extractives block or take up bonding sites that would otherwise be occupied by water and ultimately reduce the hygroscopicity of wood and increase its stability.

Wood-based composites are known for having a much higher swelling potential than that of solid wood. This is a result of two factors: the higher density of wood composites means there is physically more wood per unit volume to swell, and the tendency of composites to undergo two forms of swelling, reversible and irreversible. Reversible swelling is the natural swelling that occurs when any wood, composite or not, changes its bound water content. A sample exposed to moisture will swell but will also return to its original size upon drying. Irreversible swelling occurs from the release of built up stresses that develop during the manufacturing process. This is also known as springback. Increased moisture content causes the release of these stresses which breaks the bonds between the adhesive in the composite and the wood substrate. The swelling caused by the release of these stresses is permanent and even if moisture is removed the composite will remain in a permanently swollen and often unusable state (Hsu et al. 1988). To alleviate this problem, attempts have been made to reduce the build up of internal stresses during the formation of the composite.

Pre-treatments with steam have shown to be extremely successful and are the most commonly implemented process to eliminate irreversible swelling (Hsu et al. 1988). More information on steam treatments will be provided later in this chapter.

### ***2.3 Wood Modification***

Wood has been used for thousands of years as a building material, as fuel, and for decorative purposes without the need for extensive modification. Over the last century, better technology coupled with the pursuit to use wood in increasingly specialized applications has driven researchers to modify wood by enhancing certain characteristics, eliminating others, and even creating new ones. The goal of these wood modifications has typically been to improve mechanical properties, dimensional stability, or biological resistance. Modifications either introduce new chemicals into the wood or change the chemical structure of the wood itself. Homan et al. 2004 summarizes wood modification into three main categories; lumen filling, bulking and chemical modification. These three categories are distinguished by the form of action taken by the chemical being used.

Lumen filling is a technique which introduces a chemical into the cell lumens that blocks the vital pathways of moisture movement through wood. Although short-term water adsorption is prevented by physical obstruction, there tends to be no long term effect on the water sorption behavior of wood treated in this manner. Bulking refers to chemicals which are able to penetrate and swell the cellular structure of wood, but don't chemically react with it. When the reagent is cured, the wood remains in a swollen state and contact with moisture will not induce further swelling.

Chemical modification is distinguished by the formation of covalent bonds. Bonds form either between an introduced chemical and the wood substrate or between multiple reactive sites within the wood substrate. The end result leaves the wood in a chemically altered state. This type of modification can be subdivided into three categories: heat treatments and chemical treatments which will be discussed in further detail, and enzymatic treatments which is beyond the scope of this thesis (Rowell 1991).

Lumen filling and bulking are often referred to as passive modifications since little or no chemical reaction takes place between the reagent and the wood substrate. Chemical modification is subsequently viewed as an active modification due to the fact that the wood substrate undergoes some form of chemical reaction.

The viscoelastic thermal compression process is an active chemical modification in and of itself. The wood substrate undergoes a reorganization of its molecular structure due to the presence of a chemical, in this case water in the form of saturated steam. The VTC process also imparts a heat treatment on the wood, leading to partial thermal degradation – primarily of the hemicellulose component. The additional chemical modification which this thesis refers to involves the incorporation of chemical reagents aimed to impart further dimensional stability on VTC treated wood.

The research conducted for this thesis will examine the benefits of impregnating hybrid poplar (*Populus deltoides* x *Populus trichocarpa*) with one of three different chemical reagents prior to VTC processing. The three reagents chosen

include two low molecular weight PF resins, acetic anhydride and tung oil. These chemicals represent the three forms of chemical modification described earlier. PF resin is able to swell the cellular structure of wood and when cured forms an insoluble cross-linked network. The cured resin does not react chemically with the wood substrate and is therefore categorized as a passive bulking modification. Acetic anhydride chemically alters the wood substrate through a reaction known as acetylation. This process replaces free hydroxyl groups with acetyl groups and is considered an active chemical modification. Tung oil polymerizes within the lumens of the wood and it is not believed to react with cell wall components categorizing it as a passive lumen filling modification.

Chemical modification and hydro-thermal-mechanical modification have both been studied to great lengths as separate entities. This research will focus on coupling the two forms of modification to create a novel wood-based composite with superior structural and stability qualities.

### ***2.3.1 Active Chemical Modification***

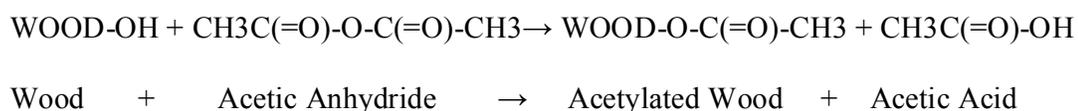
Active chemical modification of wood, as defined by Hill (2006), is "...the reaction of a chemical reagent with the wood polymeric constituents, resulting in the formation of a covalent bond between the reagent and the wood substrate." The properties of wood are determined by the chemical composition of the wood substrate. This is the basis from which active chemical modification applies itself; by chemically altering the cell wall components one can modify the basic properties of wood (Rowell, 2005). Increased dimensional stability can be achieved through various

means of active chemical modification. Bulking the cell wall with a bonded chemical leaves the wood in a swollen state and prevents further swelling. Cell wall polymer components can be crosslinked which ultimately restrains swelling forces through covalent bonding. Finally, functional groups can be bonded to reduce hydrogen bonding and increase hydrophobicity (Rowell, 2005).

Over the years, a wide range of chemicals and chemical systems have been researched and implemented. Rowell, 2005 provides an excellent and updated review of many of these chemicals, which include, but are not limited to: anhydrides, acid chlorides, ketene carboxylic acids, various types of isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, dimethyl sulfate, and epoxides such as ethylene, propylene, and butylene oxide. There are also other comprehensive reviews published in the literature and the reader is referred to these reviews for further information (Rowell 1975, 1983, 1991, 1999, Kumar 1994, Hon 1996ab).

### *Acetylation*

Acetylation has been the most widely studied active chemical modification for wood. It is the only active chemical modification to be expanded into a commercial process. Acetylation involves the reaction of acetic anhydride with the accessible hydroxyl groups found on wood's polymeric components. This reaction forms ester bonds replacing active hydroxyl groups with stable acetate groups and forming acetic acid as a byproduct (Rowell, 1982). The removal of potential bonding sites for water reduces the hygroscopic nature of wood and increases its stability. The chemical reaction of acetylation is displayed below.



**Figure 2.1.** Reaction of acetic anhydride and wood substrate.

Unreacted acetic anhydride and the acetic acid byproduct must be removed in a chemical recovery phase after acetylation is complete. This is necessary because in large enough quantities the acetic acid byproduct has detrimental effects on the structural integrity of wood (Rowell, 1982). The acetic anhydride does not polymerize inside the wood, but rather undergoes single site addition reactions with hydroxyl groups. This implies that the number of hydroxyl groups blocked can be easily calculated using the weight gain of acetyl (Rowell, 2006). When hydroxyl groups are replaced with an ester (i.e. blocked) the hydrophilic nature of the wood is reduced, which in turn decreases its tendency to swell in the presence of water. This chemical modification also bulks the wood, leaving the acetylated wood in a permanently swollen state, minimizing further swelling if high humidity or direct water contact occur. Acetylation was first attempted in 1928 by the German scientist Walter Fuchs while trying to isolate lignin in pine wood (Fuchs, 1928). In 1946, Tarkow was the first to publish results on the use of acetylation for the dimensional stabilization of wood (Rowell, 2006). Since then, the acetylation process has been applied extensively in the forest products industry to a large number of species, numerous wood-based composites, as well as many non-woody plant fibers (Narayanamurti and Handa 1953, Rowell 1983, Rowell et al. 1986, Rowell and Norimoto 1987, Anderson and Tillman

1989, Imamura et al. 1989, Plackett et al. 1990, Chow et al. 1996, Gomez-Bueso et al. 1999).

The methods by which wood is acetylated have been studied nearly as much as the properties of the acetylated wood itself. Factors such as moisture content, temperature, pressure, and the presence of catalysts have all been examined to streamline the process in order to produce an economically feasible product.

Although higher moisture contents allow for easier penetration of acetic anhydride, excess moisture also reacts with the reagent creating acetic acid. The acetic acid not only dilutes the reagent, but also degrades the wood substrate at high concentrations. Rowell et al. (1990) noted no difference in the rate of acetylation between samples of 0, 5, and 7% moisture content. Beckers and Militz (1994) studied the degree of acetylation while varying moisture contents between 0 and 26%. It was found that WPGs generally decreased with increasing MCs. Moisture contents between 2% and 5% produce optimum reaction conditions and are most often used in laboratory scale acetylation processes (Ramsden et al. 1997).

Many different catalysts and organic co-solvents have been used over the years to assist in the acetylation of wood (Rowell, 2006). Both catalysts and co-solvents add complicated steps to chemical recovery and can often be extremely caustic to humans and the environment. Catalysts often include strong mineral acids or acid salts which hydrolyze various carbohydrates in wood and can lead to strength loss (Li et al. 2000). Co-solvents aid in the penetration of the anhydride reagent, but simultaneously reduce the reaction rates through dilution. Rowell et al. (1986) developed a simplified method

for the acetylation of hardwood and softwood flakes in which catalysts and co-solvents were removed from the process. Dimensional stabilization results were identical to or better than that obtained with boards acetylated using catalysts or co-solvents. The new procedure expedited the process and rendered acetylation commercially feasible. This method has also been adapted for solid wood.

Temperature and time are significant factors in the acetylation process. Li et al. (2000) studied the effect of temperature and time on weight percent gains (WPG), reactions rates and Anti-Swelling Efficiency (ASE). It was shown that as temperature rises from 90 °C to 125 °C, reactions rates increase, which induces higher WPGs and consequently increase ASE values. Temperature was shown to have more influence over final ASE and WPG values than reaction time, with 120 °C being the optimal reaction temperature.

Over the year's cyclical water soak and relative humidity tests have repeatedly shown acetylation to be an extremely effective dimensionally stabilizing process. At near 20% WPG Obotaya et al. (2002) reported ASE values between 60 and 70 percent for various hardwood and softwood species. Rowell et al. (1986) showed a marked reduction in oven-dry thickness after repeated water soak tests of acetylated aspen flakeboard compared to that of non-acetylated control boards. Further, Rowell et al. (1992) investigated the long term stability of acetyl groups by cycling acetylated pine and aspen flakes between 90 and 30 percent RH. After 41 cycles (3 month cycle time), no significant loss of acetyl occurred. Equilibrium moisture contents of the same

species dropped significantly as WPGs increased from zero to near 20% (Rowell et al. 1991).

### ***2.3.2 Passive Chemical Modification***

Passive chemical modification involves impregnating a chemical or combination of chemicals into the lumen of the wood cell, or wood cell wall (Hill, 2006). The reagent then reacts to form a solid which is physically locked in place, but with no chemical connection to the wood substrate itself.

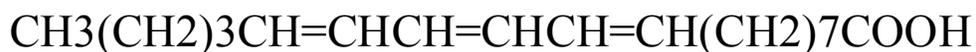
#### *Lumen Filling*

The process of filling cell lumens with a chemical agent to achieve greater dimensional stability is uncommon. Dimensional stability is only achieved on a short term basis due to the physical blocking of water through the porous structure of wood. In the presence of high humidity or liquid water, long term swelling is unchanged. Due to the large amounts of chemicals required to fill the lumens this method is not cost effective for the limited benefits obtained.

Methyl methacrylate has been studied as a reagent for lumen filling modification. Results showed limited gains in dimensional stability. Weight percent gain of 100 percent (Meyer 1977, 1984) and anti-swelling efficiencies of only 10 to 20 percent (Rosen 1976, Siau and Meyer 1966) have made this form of passive modification mostly obsolete due to high chemical costs and few positive effects.

### *Tung Oil*

Tung oil, also known as China wood oil, has been used as a finishing oil for wood for more than a thousand years. Within the last century, it has also found use as a component in paints, chalks, inks and mortar. Categorized as a drying oil, it cures through 2 methods; autoxidation in which it absorbs free oxygen from the environment and chain polymerization. The end result is a flexible water-insoluble crosslinked network (Russel, 2006; Rhodes and Ling 1928). Metal salts are often added to tung oil to accelerate the oxidation process to facilitate faster drying (Rhodes and Ling, 1928). The chemical makeup of pure tung oil is shown below.



**Figure 2.2.** Chemical formula for pure tung oil.

Tung oil has been used in the forest products industry as a surface treatment for tempered hardboard. There is minimal literature on the use of tung oil as a surface treatment (Wexler, 1964; Yoshimura, 1984; Schumann, 1916; Feist et al., 1985), however, it is generally recognized to reduce water absorption and thickness swell (Carll 1997). There exists no literature for the use of tung oil as an impregnating agent, however, it is believed that the chemical make up of tung oil promotes its absorption into the wood microstructure. In theory, when cured, tung oil produces a cross-linked polymerized network that is not directly bonded to the wood substrate but is able to impart some degree of dimensional stability to the wood. Since tung oil is naturally

occurring, it maintains an advantage over non-sustainable synthetically produced polymers.

### *Cell Wall Swelling*

Impregnating wood with cell wall penetrating chemicals has been practiced for more than 70 years. Although these chemicals reside in the wood cell wall, they are not chemically bonded to the wood substrate. The impregnant is fixed in the cell wall by either of two mechanisms: the polymerization of a monomer or oligomer, or the curing of a soluble chemical which diffuses into the wood cell wall (Hill, 2006).

Alfred Stamm and colleagues did much of the early work on resin impregnation in the late 1930's and early 1940's. Two veneer-based products, Impreg and Compreg, were produced from their research. These phenol-formaldehyde impregnated composites show tremendous dimensional stability with ASE values of 75% and 95% at WPGs of 35% and 30% for Impreg and Compreg respectively (Stamm, 1959).

### *Phenol Formaldehyde Resin Impregnation*

To date, highly water soluble, low molecular weight phenol-formaldehyde resin systems have been the most studied and most successful non-bonding impregnating processes (Rowell 1999, Wallstrom et al 1999, Ohmae 2002). PF resin acts as a bulking agent and a mechanical interlocking agent. It contributes to dimensional stability by penetrating and swelling the cell wall (Farmer, 1967, Stamm and Seborg 1936, Stamm and Elwin 1953) reducing hygroscopicity (Hill, 2006) and forming a rigid cross-linked network upon curing (Stamm, 1959).

Galperin et al. (1995) has reviewed 25 years of thermochemical wood modification carried out at the Byelorussian Institute of Technology. PF, UF and polyester resins were widely used at the laboratory with good results in dimensional stability through conventional heat curing as well as microwave curing of the resins.

ASE values of 70% were observed by Stamm and Bachler (1960) when Sitka spruce (*Picea sitchensis*) was vacuum impregnated and subsequently heat cured with low molecular weight PF resin. Deka and Saikia (2000), reported a 33.7% WPG and an associated 70.6% ASE value when they pressure impregnated a fast grown softwood, *Anthocephalus cadamba*, with phenolic resin at 30% concentration.

Although PF resin is known to penetrate the wood cell well, there has been little research conducted to garner evidence of its exact location within the wood substrate. Smith and Cote (1971) used Scanning Electron Microscopy (SEM) and an energy dispersive X-ray analyzer to examine the penetration of brominated phenolic resins in wood cell walls. He and Riedel (2004) used Differential Scanning Calorimetry (DSC) to study the curing kinetics of phenol formaldehyde resin in the presence of wood substrate. It was found that, although secondary interactions of hydroxyl groups occur, almost no covalent bonding occurs between the wood substrate and the PF resin.

Furuno et al. (2004) used light microscopy, SEM and Electron Probe X-ray Microanalysis (EPMA) to investigate the penetration of phenolic resins into cell walls on a submicroscopic and ultramicroscopic level. A bromine indicator was used to detect the presence of phenolic resin. Low and medium molecular weight ( $M_n = 290$

and 480, respectively) PF resins proved to reside primarily in the cell walls and contributed largely to the dimensional stability and decay resistance of the wood. The high molecular weight ( $M_n = 820$ ) PF resin was not able to penetrate the wood cell wall, remaining mostly in the cell lumens and imparting little if any dimensional stability. Furuno et al. (2004) also showed a direct relationship between anti-swelling efficiency and resin loading, with maximum ASE values of 60% at nearly 50% resin loading levels.

Due to the high cost of resin, most processes which obtain resin loading levels of 30% or more have been deemed uneconomical if scaled up to large production levels. In light of this, Wan and Kim (2006) examined the effectiveness of impregnating southern pine at low resin solids loading levels of 1% and 5%. Samples were vacuum/pressure impregnated with 3 different molecular weight PF resins ( $M_n = 310, 370, 451$ ). Samples were then thermally compressed to 80% of their original radial thickness and three consecutive water soak treatments were conducted. ASE values were recorded between each treatment. Results showed significant improvements in dimensional stability at 5% resin solids levels, while 1.0% solids imparted little dimensional stability.

When PF resin is impregnated into the cellular structure of wood it has a softening effect which, like steam or heat, plasticizes the wood cell wall. In this softened state, compression applied in the presence of heat allows not only for the deformation of the cell walls without fracturing, but also the curing of the resin while the wood is in its compressed and densified form (Yano et al. 1997). Yano et al.

(2000) compressed Japanese birch (*Betula meximowicziana*) at 150 °C between 30 and 100 MPa. Resin impregnated compressed samples showed equilibrium moisture contents that were one tenth and one fourth that of uncompressed impregnated samples, respectively.

Research has also been conducted on wood products of smaller element size. Kajita and Imamura (1991) observed large reductions in swelling when three different methods were used to impregnate particleboard at low phenolic resin loading levels. Haygreen and Gertjansen (1971) used particleboard to investigate the difference in stabilizing properties of bonding versus impregnating phenolic resins. Bonding resins are generally of high molecular weight and cannot penetrate the wood cell wall as easily, while the lower molecular weight of the impregnating resins weight allows for bulking of the cell wall. Boards were formed either with a mix of bonding and impregnating phenolic resins, or with just bonding resin. The total resin content in all boards remained constant. A considerable increase in dimensional stability was observed for panels which contained any amount of impregnating resin, implying that the effectiveness of PF resin as a stabilizing agent stems from its ability to bulk the cellular structure of wood.

#### ***2.4 Hydro-Thermo Mechanical Wood Modification***

It is well known that mechanical and physical properties of wood can be modified through various hydro, thermal and mechanical processes. Stamm and Seborg (1951) introduced one of the first commercially available modified compressed wood products, Compreg. Veneers impregnated with low molecular

weight PF resin are stacked, densified and subsequently heat cured. The resulting product displays increased specific gravity, hardness and strength, as well as high dimensional stability.

There has been a great deal of research on wood modification without the use of added chemicals. Combinations of heat, steam and pressure have been shown to permanently modify the chemical structure of wood. These products often exhibit properties which are completely different to those of their parent material.

Heat and steam have been shown to plasticize the cellular structure of wood (Stamm, 1964). Pretreatments using this process enable wood to be densified without fracturing of the cell wall, thus maintaining wood's mechanical integrity. A common drawback to mechanically modified wood is the lack of compression set. Untreated compressed wood exposed to moisture will incur springback, losing most if not all of its compressed form (Kamke, 2004). Post treatments have been developed using heat, steam, and the combination of the two, to fix wood in its compressed state. This process works by relieving internal stresses built up during compression. The combination of pre and post heat and steam treatments applied collectively with mechanical densification has been coined Thermo-Hydro-Mechanical (THM) modification. Tomme et al. (1998) and Navi and Girardet (2000) investigated THM treatments for the purpose of producing dimensionally stable densified wood. Kamke (2004) has produced a similar treatment procedure known as Viscoelastic Thermal Compression (VTC), which can be applied to veneer, sawn wood, or strand composites. The VTC process takes advantage of the mechano-sorptive phenomenon

to compress wood using relatively low compressive force. Although a small degree of dimensional stability is imparted during this process, there is much room for improvement. By impregnating the wood with reactive chemicals prior to the VTC treatment, it is believed that greater dimensional stability can be realized.

To date, heat, steam, chemical, and mechanical treatments have all been used individually, or in combinations of two or three to modify the original properties of wood. This thesis attempts to combine all four treatments into one unifying procedure to produce a novel wood-based product with overall superior qualities.

## **Chapter 3: Chemical Modification and Viscoelastic Thermal Compression**

### ***3.1 Introduction***

The addition of a chemical modification step prior to viscoelastic thermal compression has never been researched before. The basic process includes 1) vacuum/pressure liquid impregnation of wood, 2) mechanical compression with the VTC apparatus, and 3) evaluation of swelling and mechanical properties of the treated sample. Three chemical treatments were studied. Approximately six months were spent developing the techniques to first introduce the desired chemicals into the wood and then process the modified samples in the VTC apparatus. This proved to be exceptionally challenging due to the conditions of the modified samples being drastically different from optimal sample conditions needed for viscoelastic thermal compression. New schedules were developed to adjust for the changes in sample conditions and the three different chemical treatments were able to be incorporated into the VTC process.

### ***3.2 Background***

The apparatus used for the chemical modification stage of this research was a small-scale pressure-treating cylinder located at Oregon State University. The interior dimensions of the cylinder were 12 inches in diameter by 96 inches in length. A specimen container, with a liquid volume capacity of 2 liters, was used to hold the specimens inside the cylinder with the purpose of reducing the amount of chemical

required for the treatment. VTC processing was performed using a device that was developed for previous research (Lenth 2001a, Lenth 2001b, Kamke et al. 2000, Kamke 2005, Reynolds 2005, O’Conner 2007).

### ***3.3 Experimental***

#### ***3.3.1 Materials***

The VTC device is a 50-litre stainless steel reaction chamber. Electrical heating blankets surround the exterior of the cylindrical chamber and heat the reactor to its operating temperature. Housed in the lid of the chamber, a hydraulic ram is connected to aluminum platens which are heated using internal electrical heating cartridges. The platen temperature is controlled independently of the reactor temperature. The hydraulic ram is controlled using an Enerpac remote hydraulic pump which can apply up to 1200 psi of pressure to the platens. A stainless-steel bellows isolate the platens from the outside environment while allowing the hydraulic ram to freely move the platens vertically inside the treating cylinder. The aluminum platens have been machined with mechanical stops to allow for specific thickness control of the wood specimens. A final thickness of 2.5 mm was used for all samples in this study except for highly densified samples which were pressed to a final thickness of 1.5 mm. The platens are guided by two tension pins to maintain alignment. Release springs are used to separate the platens when not under pressure. The lid/platen system attaches to the chamber with six ¾-inch diameter bolts evenly spaced around the lid. A ceramic gasket ensures a tight seal while under steam pressure. A boiler supplies the reactor with up to 150 psi saturated steam pressure.

Hybrid poplar (*Populus* spp.), a cross between Eastern and Black Cottonwood (*Populus deltoides* and *trichocarpa* respectively) was chosen for this research. This species is used mainly for pulpwood but is gaining share as a raw material for the wood composites industry. Hybrid poplar is most often grown as a highly managed rotation crop and is the fastest growing hardwood in the temperate regions of North America. In comparison with Douglas-fir (*Pseudotsuga menziesii*) which produces 4 dry tons of biomass per acre per year and has a 50 year rotation, the typical hybrid poplar species can produce up to 10 dry tons per acre per year with a rotation of only 6 to 8 years (Johnson, 2007). This tremendous growth rate coupled with its ease of propagation makes this diffuse porous hardwood a good source of raw material for many wood-based products.

The wood used for this research was harvested in March 2007 from Columbia County in northwest Oregon. The trees were approximately 16 years old. Logs of 10 to 12 foot length were delivered to Oregon State University where a portable bandsaw was used to reduce them to 1-inch thick rough sawn boards. At this point, the boards were placed in a conditioning room at 20 °C and 65% RH for 1 month. The final samples were then machined from this stock material to an approximate size of 170 x 30 x 6 mm (longitudinal x tangential x radial). Samples were machined so that densification occurred in the radial direction. Initial wood density ranged from 0.34 to 0.40 g/cm<sup>3</sup> at 12% MC. A final target thickness of 2.5 mm resulted in a final density after compression near 0.80 g/cm<sup>3</sup>. A small side sample of highly densified PF impregnated samples were made in which samples were compressed to a final

thickness of 1.5 mm which produced a final density of roughly  $1.10 \text{ g/cm}^3$ . Actual final densities varied depending on chemical treatment and initial starting density. Once machined, samples were stored in a conditioning room at  $20 \text{ }^\circ\text{C}$  and 65% RH.

The reagents used for chemical modification include two phenolic based resins, pure tung oil and acetic anhydride. The phenolic resins were commercial products that were developed for paper impregnation and insulation products (to be referred to as PF1 and PF2). PF1 had a resin solids content of 39% and a weight average MW of approximately 780. PF2 had a resin solids content of 57% and a weight average MW of approximately 172. The resins were stored at  $-10 \text{ }^\circ\text{C}$  and then only a portion was thawed at room temperature when needed.

Woodcraft® 100% pure tung oil was purchased from an online merchant. It was stored at room temperature in an airtight container. The 98% pure acetic anhydride was purchased through an online chemical supplier and also stored at room temperature, CAS # 108-24-7 .

### **3.4 Methods**

#### *3.4.1 Chemical Modification*

Phenol formaldehyde resin was diluted to the desired resin concentration by mixing with deionized water in a household blender. Samples were impregnated with 5, 10, or 20% resin solids content by mass. Samples were placed between thick mesh screening in a Pyrex dish to ensure maximum contact with the resin solution. Metal weights were placed over the samples to keep them submerged and the phenolic resin was poured into the dish. Ten samples were treated at a time. The samples were

immediately placed in the treating cylinder and a vacuum of 14 psig was pulled for 15 minutes. The vacuum was released over a period of 5 minutes and then positive pressure of 90 psig was applied for an additional 30 minutes. The pressure was then released and the samples were removed from the treating solution and placed in a plastic bag. They were not blotted dry. The treated samples were then either set in a room temperature fume hood for 24 hours (referred to as “conditioned”) or processed immediately with the VTC apparatus (referred to as “not conditioned”).

Treatment of the tung oil impregnated samples was identical to that of the PF impregnated samples. It should be noted that the tung oil was diluted to the desired concentration of 25% by volume by using mineral spirits as a thinning agent. At the end of the treatment samples were again, either placed in a room temperature fume hood for 24 hours to condition, or immediately processed in the VTC device (not conditioned).

Acetylation with acetic anhydride is a more complex multi-step treating procedure. Samples were submerged in acetic anhydride and underwent the same vacuum pressure treatment as the tung oil and PF samples. However, once this step was completed, the samples were placed in a preheated, sealed glass container, which was located in an oven set at 120 °C. The samples were left for 2 hours during which the acetylation reaction took place. After this treatment, a vacuum was pulled for an additional 2 hours at 120 °C to remove excess unreacted acetic anhydride as well as the reaction byproduct acetic acid. The oven temperature was then lowered to 103 °C and the samples were left for an additional 12 hours. Due to time constraints the

samples were not pressed immediately, but rather sealed in plastic and processed the following day.

#### *3.4.2 VTC Processing*

The VTC process works by softening the polymeric constituents of the wood cell wall through the mechano-sorptive effect. Once in the softened state, mechanical compression is applied to collapse the cell walls. The softened state of the specimen enables the wood cell walls to collapse without fracturing, thus maintaining their structural integrity. After compression, samples are cooled below 100 °C before mechanical pressure is released. This final step sets the sample in its newly densified form. Figure 3.1 shows a schematic of a typical VTC schedule

Although specific pressing schedules had already been developed, they were designed for samples with an initial moisture content of 12%. The chemical modification process leaves the PF and tung oil treated samples in a fully saturated state and therefore, it was necessary to develop new pressing methods to accommodate this change in conditions (tables 3.2 through 3.4). A drying step was added by using the preheated platens to flash dry the samples before compression occurred. The addition of this step raised many new questions regarding other possible pressing and drying techniques and which combinations of these would produce the greatest dimensional stability and increase in mechanical properties. During preliminary work, it was noted that much of the resin migrated to the surface during the drying step. It was believed that the resin was being forced out by the quickly evaporating moisture and by the low level of compression. A 24 hour conditioning step, which consisted of

air-drying samples in a room temperature fume hood after chemical modification, was added for some samples. These conditioned samples could be processed in the VTC device without the need to dry them with the hot platens first. It was of interest to determine if conditioned samples were more dimensionally stable due to the likelihood of having a more uniform resin distribution.

A further observation led to the removal of the steam treatment during the VTC processing for some samples. It was noted that the additional drying stage was mimicking a steam treatment. The moisture in the samples evaporated so quickly that it produced a localized low-steam pressure environment surrounding the sample and most likely also within the samples microstructure. In essence they were being self-steamed and the samples appeared to already be in a highly softened state prior to VTC processing. Eliminating the steam step in the VTC process could have huge implications on the scale-up of this technology. One of the most technically challenging aspects about the VTC process is the demanding environment at which it occurs. Platens must be able to apply pressure in a sealed high temperature and high pressure environment. The removal of the steam step allows samples to be processed in an open environment - significantly simplifying the procedure. A set of samples was, therefore, tested without the use of steam to determine if their mechanical and dimensional properties were adversely affected by the change in processing procedures. These samples are referred to as “no steam”, since they lack the normal steaming step inherent to the VTC process.

Table 3.1 displays the test matrix used for this research. Three separate chemical treatments were studied with variations in treatment conditions and processing schedules. Phenol formaldehyde impregnation was the main interest for this research and as such, received the most testing. Two PF resins of varying molecular weight were examined at concentrations of 5, 10 and 20% resin solids content by weight. At 10% resin solids content additional batches were also tested with the inclusion of a conditioning step as well as the removal of the steaming step from the VTC process. Tung oil samples were treated at a 25% by volume concentration level with and without a conditioning step. It was determined through pilot testing that this concentration of tung oil produced the desired target WPG of 10%. Acetylation was only tested at one concentration level, which was chosen after a review of the literature. All samples were compressed to a final thickness of 2.5 mm and labeled as standard density. Two additional sets of PF impregnated samples were created to test the effect of higher densities. These samples were impregnated with either PF1 or PF2 at a resin solids concentration of 5% and then densified to a final thickness of 1.5 mm following the steam inclusive pressing schedule.

#### *3.4.3 Controls*

Various sets of control samples were also created for comparison. Samples which were not chemically modified were processed in the VTC device using the standard pressing schedule. These control samples were used for comparison in swelling and mechanical tests between chemically modified VTC processed samples. Further, controls which were not chemically modified or processed with the VTC

device were created to determine inherent levels of shrinkage and swelling through various water tests. PF impregnated control samples were also created which were cured in an oven at 105 °C for 24 hours but not processed with the VTC device. These samples were used to understand the stabilizing characteristics of the PF resin in undensified samples.

**Table 3.1.** Test matrix displaying the combination of treatments that were tested for this research.

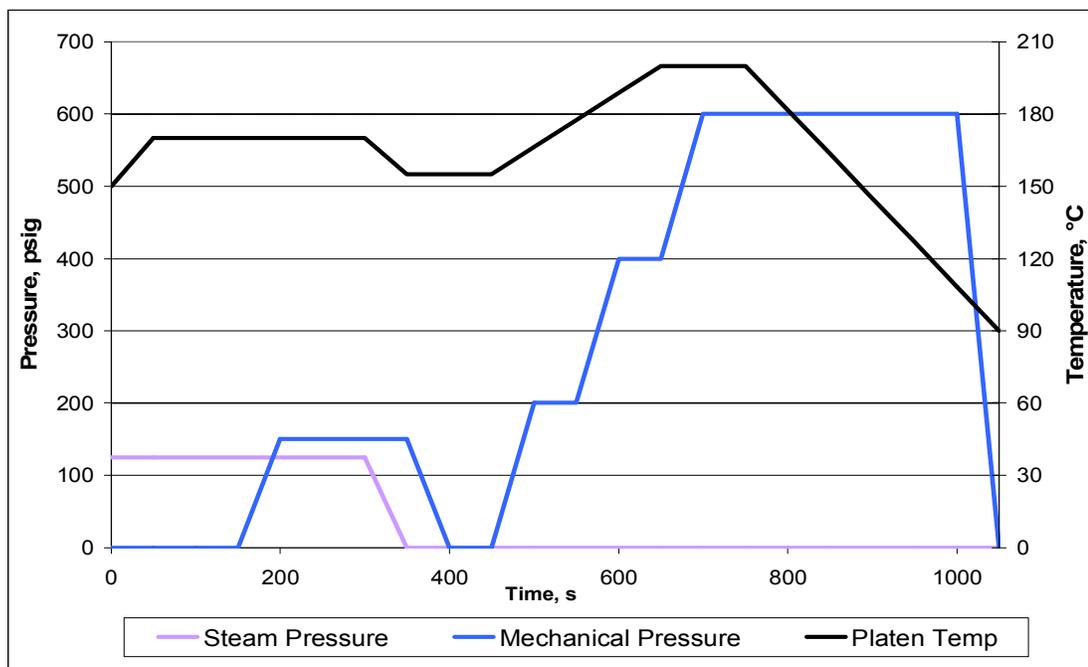
Chemical Treatment	Density	Concentration	Steam			
			Yes		No	
			24hr Conditioning		24hr Conditioning	
			Yes	No	Yes	No
PF1	High	5		X		
	Standard	5		X		
		10	X	X		X
		20		X		
PF2	High	5		X		
	Standard	5		X		
		10	X	X		X
		20		X		
Tung Oil	Standard	10	X	X		
Acetic Anhydride	Standard	20		X		
Control	Standard	-		X		
*Note: Each X represents 1 batch with 10 replicates						

Please refer to the example labeling code below for identification of individual batches and their processing parameters.

**PF<sup>1</sup> 1<sup>2</sup> 10<sup>3</sup> S<sup>4</sup> C<sup>5</sup>**

1. Chemical treatment: PF - Phenol Formaldehyde, TO - Tung Oil, AA - Acetic Anhydride
2. Resin Identifier (only applicable for PF treated samples): 1 - high MW PF, 2 - low MW PF.
3. Target WPG for each treatment, for PF treated samples this value also represents the concentration of the treating solution: 5, 10 or 20%.

4. Use of steam (S) or No Steam (NS) during VTC processing. No Steam is also referred to as “Self-steamed”.
5. Conditioning (C) or No Conditioning (NC) before VTC processing.



**Figure 3.1.** Graphical representation of VTC processing schedule for control samples, as well as conditioned PF and tung oil treated samples using steam.

**Table 3.2.** VTC schedule for unconditioned PF and tung oil impregnated samples using steam.

Cumulative Time (s)	Step Time (s)	Specimen Pressure (psi)	Platen Temp Set Point (C)	Steam Pressure (psi)	Vent Valve	Platen Power	Notes
0	100	15	150	0	Open	On	Turn platens on, load sample and close platens. Secure VTC lid.
100	100	50	175	0	Open	On	Increase platen pressure
200	180	0	175	125	Closed	Off	Turn platens off, purge vessel with steam, open platens once purged
380	120	150	175	125	Closed	Off	1st stage compression
500	70	25	175	0	Open	Off	Dump Steam Pressure
570	100	0	175	0	Open	Off	Open platens
670	100	150	175	0	Open	On	2nd stage compression
770	200	Max (900)	175	0	Open	On	3rd stage compression
970	0	0	175	0	Open	Off	Open lid and cool platens below 100C

**Table 3.3.** VTC schedule for acetic anhydride, control, and conditioned tung oil and PF samples using steam.

Cumulative Time (s)	Step Time (s)	Specimen Pressure (psi)	Platen Temp Set Point (C)	Steam Pressure (psi)	Vent Valve	Platen Power	Notes
0	0	15	175	0	Open	Off	Sample loaded and lid secured
0	180	0	175	125	Closed	Off	Purge vessel with steam, open platens once purged
180	120	150	175	125	Closed	Off	1st stage compression
300	50	150	175	0	Open	Off	Dump Steam Pressure
350	100	0	175	0	Open	Off	Open platens
450	300	Max(900)	175	0	Open	On	2nd stage compression
750	0	0	175	0	Open	Off	Open lid and cool platens below 100C

**Table 3.4.** VTC schedule for unconditioned PF and tung g oil impregnated samples without steam.

Cumulative Time (s)	Step Time (s)	Specimen Pressure (psi)	Platen Temp Set Point (C)	Steam Pressure (psi)	Vent Valve	Platen Power	Notes
0	100	30	150	0	Open	On	Turn platens on, load sample and close platens.
100	20	0	190	0	Open	On	Vent Sample
120	100	60	190	0	Open	On	Compress sample
220	20	0	190	0	Open	On	Vent Sample
240	100	90	190	0	Open	On	Compress sample
340	60	0	190	0	Open	On	Vent Sample
400	100	100	190	0	Open	On	Compress sample
500	100	160	190	0	Open	On	Increase compression pressure
600	100	Max (900)	190	0	Open	On	Increase compression pressure
700	0	0	190	0	Open	On	Open lid and cool platens below 100C

## **Chapter 4: Evaluation of Physical Properties of Chemically Modified Samples**

### ***4.1 Introduction***

The goal of this study was to impart dimensional stability to VTC treated wood through various chemical modifications. Although this was the main goal, identifying changes in mechanical properties was also of interest. In order to determine the effects of the chemical modification and variations in VTC processing, various tests were performed to evaluate the swelling characteristics and mechanical properties of the modified specimens. Modulus of elasticity, water soak, and water boil tests were run on all samples to this end. Large changes in properties were expected due both to the densification process, as well as the chemical modification. Although the effects of both chemical modification and the VTC processing are understood in their own right, it was unclear as to how the combination of the two would affect final properties. For example, it was hypothesized that modulus of elasticity would be much greater for PF treated samples versus control samples due to the reinforcing nature of the rigid crosslinked network formed by cured PF resin.

### ***4.2 Background***

Dimensional stability, according to Inoue et al. (1993), is most influenced by the hemicellulose component of the wood cell wall due to its highly hygroscopic nature. Altering the hemicellulose therefore can change the swelling characteristic of wood, and if done properly, can lead to increased stability. Thermal degradation of hemicellulose occurs within the operating temperature of the VTC process and is

considered one of the main components for imparting dimensional stability and compression set.

Steam treatments have been used widely as a means of stabilizing densified wood, not only from moisture fluctuations, but also as a means of relieving undesired stresses which form during processing. Again, this aspect of the VTC processing is also believed to impart some degree of dimensional stability to VTC treated samples. The inclusion of a chemical treatment step to the VTC process is simply another modification of the wood substrate aimed at creating improved material characteristics. This section will discuss the methods employed to monitor and identify changes in the wood substrate brought on by the hydrothermal chemical modification.

### ***4.3 Experimental: 24 Hour Soak, 2 Hour Boil and 3-Point Bending***

#### ***4.3.1 Materials***

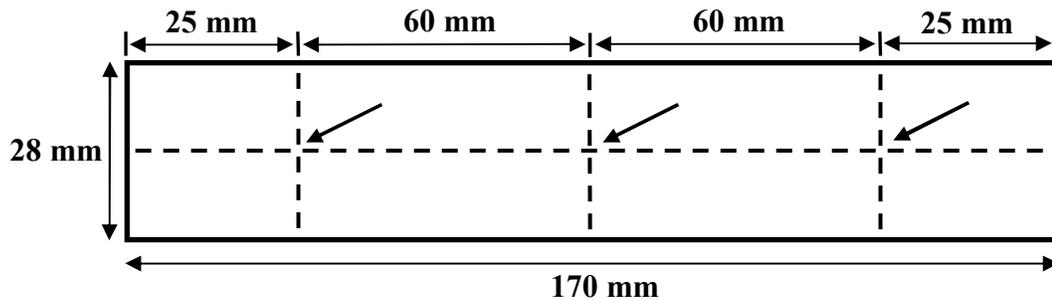
Prior to and after chemical modification and VTC processing, all specimens including controls, were subjected to 3-point bending to determine initial and final modulus of elasticity (MOE) values. Water soak and boil tests were performed on all samples after VTC processing to evaluate dimensional stability.

#### ***4.3.2 Specimen Preparation***

Samples were initially conditioned in an environmental room at 65% RH and 20 °C. Under these conditions a 3-point bending test was performed to evaluate unmodified MOE values. After chemical modification and VTC processing, samples

were oven dried at 103 °C for 24 hours whereupon they were subjected to a second 3-point bending test to determine their modified MOE value. From this oven dried state, samples were put through a 24 hour water soak, oven dried again, a 2 hour boil, and then a final oven drying step.

Measurements were taken at each step in the testing process, which included mass, length, width at three locations and thickness at three locations. The diagram below displays the measuring pattern laid out for each sample.



**Figure 4.1.** Specimen measurement grid. Thickness measurements were taken where arrows indicate and length and width measurements were taken along dotted lines.

#### 4.3.3 Three-Point Bending

Modulus of elasticity of each sample was tested using a non-destructive static three-point bending test prior to, and after, VTC processing. A Sintech 1/G universal testing machine, with a crosshead speed of 0.1 in/min and load cell capacity of 300lb, was used. Shear effects were neglected by using a span to depth ratio of greater than 24, span was 150 mm. Comparisons were made between control samples and modified samples to determine the effect of chemical modification and processing conditions on modulus.

#### *4.3.4 Stability Tests*

Dimensional stability values can be difficult to comprehend due to the vast number of ways to calculate stability and various ways in which to test it. In addition, with regards to composites, measurements can be further complicated due to the tendency of composites to have spring-back, reversible and irreversible swelling, and large edge effects. This often complicates the decision of when and where to take measurements and what comparisons, if any, are appropriate. In an attempt to reconcile some of this ambiguity, this research has aimed to measure dimensional stability in a number of different manners and attempts to clarify exactly how measurements were taken and what they represent. Although there is some redundancy in these measurements, each separate measure of dimensional stability offers valuable information that the other measurements do not.

Testing procedures for this research do not follow a particular ASTM standard; however, they were selected for their ability to aptly evaluate the effects of each chemical treatment and different processing parameters on dimensional stability and to tease out as much information as possible from each sample.

Samples were removed from the VTC process and volume and mass measurements were immediately taken. A 24-hour oven-dry at 103 °C followed to insure all samples began water testing at the same base moisture content. From there, mass and volume measurements were recorded again and samples began a 24-hour water soak. The water soak consisted of placing samples horizontally in a stainless-steel container and submerging in deionized water. A metal screen was placed over the

samples to hold them approximately 2.5 cm below the surface but not impart load on them. After 24 hours had passed, samples were removed and excess water was blotted from their surface. Mass and volume measurements were recorded and samples were placed back in the oven for 24 hours at 103 °C. The samples were then removed from the oven, weighed and measured again, and directly transferred to a 2 hour boil test. The setup was identical to that of the 24-hour water soak. Samples remained in boiling water for 2 hours. Upon completion, they were removed and excess surface water was blotted dry. Mass and volume measurements were taken and the samples were placed in an oven where they underwent a final 24-hour drying cycle at 103 °C. The final oven-dry mass and volume were recorded and samples were then placed in an environmental conditioning room for further testing.

Some concern may exist over the influence of the water soak test on the boil test. Some degree of irreversible swelling occurs in the soak test which in turn gets carried through to the boil test. It is important to note that, because all specimens were soaked for 24 hours, the boil test is treated as a combined soak and boil treatment. Measurements and references to the boil test are therefore meant to reflect the combination of the 24-hour soak and 2-hour boil, rather than just the boil.

#### *4.3.4 Values and measurements collected*

This section explains what measurements were taken for this research and provides an explanation of what values were reported and by what means they were calculated.

### ***Increase in Density (D)***

Increase in density is reported as a percent increase from initial density. Initial density values were taken with conditioned samples at 12% MC before chemical modification had occurred. Final densities were taken at oven-dry MC after VTC processing. Since moisture contents vary between the two measurements, the increase in density reported is slightly higher than the true increase, however, with such large overall increases in density the difference in moisture contents does not significantly change the final result. A subsample of 10 specimens showed that the average difference in MOE from conditioned MC to oven-dry was approximately 4.7%. In addition, since consistency was maintained throughout all batches, trends and comparisons are not influenced.

$$D = \frac{(Final\_Density - Initial\_Density)}{Initial\_Density} \times 100\%$$

### ***Weight Percent Gain (WPG)***

Weight percent gain is the mass of chemical reagent retained in a sample as a percent of the original theoretical oven-dry mass of the sample. An initial moisture content of 12% was assumed for all samples and was determined using a subset of 20 samples that were oven-dried after reaching equilibrium at 20°C and 65% relative humidity..

$$WPG = \frac{\frac{Processed\_Mass - \frac{Initial\_Mass}{1.12}}{Initial\_Mass}}{1.12} \times 100$$

Weight percent gain is an important value to better understand each treatment and how each chemical reagent interacts with the wood substrate. Other measurements can be normalized by WPG to produce a value per unit of resin retained by that sample. This allows for easy comparison between treatments and provides insight on the effectiveness of the chemical reagents used.

### ***Weight Percent Gain Potential (WPGP)***

WPGP is the amount of chemical reagent which is absorbed into the specimen prior to VTC processing as a percent of the theoretical oven-dry mass of the unmodified specimen. It represents the maximum WPG a sample could achieve if no chemical reagent were lost during VTC processing. WPG-P provides insight to the penetrability of the individual chemical reagents.

$$WPG\_P = \frac{(\text{impregnated\_Mass} - \text{Initial\_Mass}) \times \text{Chemical\_Concentration}}{\text{Initial\_Mass}} \times 100$$

1.12

### ***Percent Chemical Retention (CR)***

Percent chemical retention is a simple ratio of the WPG of a sample to the WPG-P of that sample. This value provides insight into how much chemical reagent is being lost during VTC processing and can provide useful comparisons between the different treating reagents.

$$CR = \frac{WPG}{WPG - P} \times 100$$

### ***Increase in Modulus of Elasticity (MOE)***

Increase in MOE is calculated as percent increase from initial MOE. Initial MOE values were taken at 12% MC, while final MOE values were measured in the oven-dry state. It could be argued that this discrepancy in moisture contents hinders direct comparisons to values found in literature; however, a sub-sample of 10 unmodified uncompressed specimens was tested for change in MOE from 12% MC to oven-dry. It was found that samples increased in MOE an average of only 2.5% between moisture contents. This small percentage increase is almost negligible when considering increases in MOE of more than 150% are common with VTC treated samples.

$$MOE = \frac{Final\_MOE - Initial\_MOE}{Initial\_MOE} \times 100$$

### ***Anti-Swelling Efficiency, Soak (ASE-S) and Soak and Boil (ASE-SB)***

ASE is the standard dimensional stability value reported for most chemical modification treatments. It is the comparison between the volumetric swelling of modified samples to that of unmodified samples. There can be some ambiguity to this value since the calculation used to derive ASE inherently incorporates the comparison between modified samples and controls, thus ASE values must be understood either by observing trends from treatment condition to treatment condition or by comparing actual values previously reported and accepted in the literature.

ASE values are often reported without reporting the swelling characteristics of the control from which the calculations are made from. The downfall of this with

regards to composites is the tendency of wood-based composites to have extremely high swelling potentials. With this in mind, the more a control sample swells the higher the ASE values will become for a modified sample regardless of its true (nominal) performance. The ambiguity comes when high ASE values are reported, which infer good dimensional stability, when in fact the high ASE value only infers good dimensional stability compared to the control treatment. The dimensional stability of the modifying treatment may still be poor.

A modified sample may swell to an unacceptable level, but may still be associated with a high ASE value, if the control sample swelled to a much greater extent. Although this point could be argued, it is believed that nominal thickness swell values should always be reported in addition to ASE values to give the reader a much more robust understanding of the swelling characteristics of the specimens. To further clarify this point and to relate it to the research conducted for this thesis, it was observed that ASE values actually increased from the 24-hour water soak to the combined soak and boil test, giving the reader the impression that the samples were actually more dimensionally stable in boiling water than in room temperature water. This however, is not the case; in fact what was really observed is that the modified samples performed almost identically in both the water soak and the boil tests, but the unmodified control samples fared much more poorly in the boil than in the soak. The additional swelling of the controls induced by the boiling test caused the ASE value to jump up even though the modified samples had not actually changed their swelling

characteristics. In light of this, additional stability values are reported to provide a more robust description of the efficacy of each chemical modification.

ASE values were calculated as follows:

$$S = \frac{V_1 - V_0}{V_0} \times 100$$

Where:

S = Volumetric swelling coefficient.

V<sub>1</sub> = Volume after water test.

V<sub>0</sub> = Oven-dry volume after VTC processing.

$$ASE = \frac{S_0 - S_1}{S_0} \times 100$$

Where:

ASE = Anti-swelling efficiency.

S<sub>1</sub> = Volumetric swelling coefficient of chemically treated sample.

S<sub>0</sub> = Volumetric swelling coefficient of control sample.

A positive ASE value implies that the modifying treatment was able to impart some degree of dimensional stability to the sample when compared to the control.

Holding the swelling of the control constant, the higher the ASE value the better the dimensional stability. An ASE of 0 implies that the modified sample performed identical to the control in swelling tests and that no additional dimensional stability was imparted through the modification treatment. A negative ASE value implies that

the modifying treatment had deleterious effects on stability and caused the modified sample to swell more than the unmodified sample.

***Anti-Swelling Efficiency Normalized, Soak (ASE<sub>SN</sub>) and Soak and Boil (ASE<sub>SBN</sub>)***

Anti-swelling efficiency per unit of resin retained.

$$ASE_{SN} = \frac{ASE}{WPG} \times 100$$

***Thickness Swell, Soak (TS-S), and Soak and Boil (TS-SB)***

Thickness swell was determined as the percent increase in thickness based on oven-dry thickness after VTC processing. This value allows easy comparisons to be made between treated samples and controls since all batches (except high density batches) were processed to the same final thickness.

$$TS = \frac{T_1 - T_0}{T_0} \times 100$$

Where:

T<sub>0</sub> = Initial oven-dry thickness after VTC processing.

T<sub>1</sub> = Oven-dry thickness after water test.

***Thickness Swell Normalized, Soak (TS-S-N), and Boil (TS-B-N)***

Thickness swell values can not be normalized directly, but rather have to first be compared to the thickness swell of the control samples and then divided by WPG. This value then represents the reduction in thickness swell caused by the modifying treatment per unit of resin retained by the specimen.

$$TS - N = \frac{TS_0 - TS_1}{WPG} \times 100$$

Where:

$T_0$  = Average thickness swell of unmodified control samples.

$T_1$  = Thickness swell of modified sample.

WPG = Weight Percent Gain of modified sample.

***Thickness Recovery, Soak (TR-S), and Soak and Boil (TR-SB)***

Thickness recovery is different from thickness swell and ASE values in that it is a comparison of swelling based on the initial unmodified thickness of the sample rather than on its densified thickness and thus, takes into account the level of densification applied to a sample. A value of 100% would imply that a sample regained all of its initial thickness, while a value of 0% implies the sample has complete compression set and that the OD thickness after a water test is the same as its OD thickness before the test. To do this calculation, initial uncompressed oven-dry thickness is required. However, since the initial oven-dry thickness ( $T_0$ ) was not measured for each sample, a shrinkage coefficient was established using a sub-sample of 20 specimens from the population. The sub-sample was oven-dried, and the oven-dry thickness was compared to the initial thickness of the sub-sample when equilibrated at 20°C and 65% relative humidity. The empirically calculated coefficient was consistent with Table 3-5 in the USDA Wood Handbook.

$$TR - S = \frac{T_R - T_1}{T_0 - T_1} \times 100$$

Where:

$T_R$  = Oven-dried thickness after water test.

$T_1$  = Oven-dried thickness after VTC processing.

$T_0$  = Estimated oven-dry thickness before processing.

***Irreversible Swelling Soak (IS-S), and Soak and Boil (IS-SB)***

Irreversible swelling is an important value to report with regards to composites or densified wood in general. Due to the release of stresses built-up during processing, densified wood may regain much of its initial volume if exposed to moisture. This swelling is often irreversible and much greater than the naturally occurring swelling that takes place when wood increases its moisture content below the fiber saturation point. To this effect, one of the most difficult challenges to the wood composites industry is producing products which have little or no irreversible swelling.

Irreversible swelling is similar to thickness recovery except that the amount of swelling that occurs is taken as a percentage of the total swelling rather than the initial undensified thickness. This provides a value which can give insight to the amount of residual stress left in a sample after processing. Higher IS values can indicate the release of larger amounts of stress.

$$IS = \left( \frac{V_{OD1} - V_{OD0}}{V_S - V_{OD0}} \right) \times 100$$

Where:

$V_S$  = Wet volume after water test.

$V_{OD0}$  = Ovendry volume after VTC processing.

$V_{OD1}$  = Ovendry volume after water test.

#### ***4.3.3 Statistical Analysis***

Statistical analysis for this thesis was conducted using the software package S-Plus Version 7.0 (Insightful Corp., Seattle, WA). The data collected for this thesis was evaluated using two-sample t-tests assuming unequal variance and multiple linear regression. Comparisons were made between different chemical treatments, within specific chemical treatments and between samples processed with various pressing schedules and processing parameters. The goal of this analysis was not only to determine which treatment produced the highest overall dimensional stability, but also to identify the influences and effects of various treatments and conditions on swelling properties of VTC treated wood.

## Chapter 5: Results and Discussion

Due to the large array of measurements and values obtained from the samples and the large number of comparisons which can be made, this results section is separated into two main segments based on the chemical modification applied. The first segment reviews the phenol formaldehyde treatment and is where the majority of focus is spent for this research. The PF section is broken down further with regards to the influence of molecular weight, concentration, steam treatment, conditioning treatment, final density, and the effect of each of these on modulus. Comparisons are made between different treatments as well as between treatments and unmodified controls. The second section discusses tung oil and acetic anhydride treatments and makes comparisons to PF treatments as well as controls.

To determine the effect of different chemical modifications, variations in processing schedules (i.e. steam vs. no steam, conditioning vs. no conditioning) and different compression ratios, comparisons are made between the following values:

Increase in Density, percent increase in MOE, weight percent gain, potential weight percent gain, chemical retention, ASE, normalized ASE, percent thickness swell, percent irreversible swelling, percent thickness recovery.

**Table 5.1.** Final values and measurements for all treatments tested. Values in parentheses indicate one standard deviation.

*Treatment	Increase in MOE, %	Increase in MOE/WPG	ASE Soak, %	Thickness Swell Soak, mm	Thickness Swell Soak, %	ASE Boil, %	Thickness Swell Boil, mm	Thickness Swell Boil, %
PF1 5 S NC	159 (24)	45.8 (10.6)	61.4 (11.7)	0.33 (0.11)	14.1 (4.5)	70.6 (5.4)	0.52 (0.11)	21.8 (4.3)
PF1 10 S C	182 (32)	18.0 (5.5)	73.0 (10.4)	0.24 (0.10)	10.0 (4.2)	72.7 (11.0)	0.49 (0.23)	20.4 (9.5)
PF1 10 S NC	150 (17)	13.7 (2.9)	69.0 (8.12)	0.28 (0.08)	11.4 (3.3)	74.7 (5.0)	0.47 (0.10)	19.0 (4.1)
PF1 10 NS NC	118 (19)	11.2 (2.7)	82.5 (5.1)	0.17 (0.05)	6.8 (2.1)	59.8 (18.0)	0.79 (0.38)	31.9 (14.7)
PF1 20 S NC	-	-	84.3 (10.9)	0.13 (0.10)	5.32 (4.2)	86.1 (6.5)	0.23 (0.12)	9.2 (4.8)
PF1 5 S NC HD	348 (116)	35.1 (14.0)	-	0.19 (0.05)	12.6 (3.7)	-	0.40 (0.07)	26.7 (5.0)
PF1 10 Uncompressed	15 (5)	57.0 (19.3)	-	0.08 (0.03)	1.3 (0.5)	-	0.09 (0.03)	1.4 (0.6)
PF2 5 S NC	131 (31)	35.9 (15.9)	41.3 (11.1)	0.58 (0.12)	23.1 (4.4)	50.3 (6.6)	1.01 (0.15)	39.7 (5.6)
PF2 10 S C	147 (17)	17.7 (3.9)	42.9 (16.4)	0.53 (0.17)	21.7 (6.7)	53.7 (12.8)	0.87 (0.27)	35.8 (10.6)
PF2 10 S NC	154 (23)	27.7 (7.5)	47.7 (7.9)	0.49 (0.05)	20.0 (2.1)	56.8 (5.4)	0.80 (0.12)	33.1 (5.0)
PF2 10 NS NC	104 (27)	15.0 (4.4)	39.0 (19.3)	0.61 (0.21)	24.8 (8.2)	46.5 (18.9)	1.07 (0.40)	43.5 (15.7)
PF2 20 S NC	138 (21)	8.5 (1.6)	60.5 (3.6)	0.35 (0.04)	14.7 (1.4)	66.5 (4.3)	0.62 (0.09)	25.8 (3.5)
PF2 5 S NC HD	335 (69)	68.4 (20.7)	-	0.26 (0.05)	17.0 (2.8)	-	0.56 (0.14)	36.7 (8.3)
PF2 10 Uncompressed	12 (3)	57.5 (15.2)	-	0.10 (0.02)	1.7 (0.4)	-	0.11 (0.03)	1.8 (0.5)
TO 10 S C	119 (41)	10.5 (3.0)	24.3 (16.0)	0.75 (0.16)	30.5 (6.4)	22.4 (13.4)	1.64 (0.28)	66.5 (11.4)
TO 10 S NC	140 (11)	14.9 (6.0)	-8.4 (27.6)	1.16 (0.30)	43.0 (10.8)	-2.9 (17.9)	2.30 (0.42)	85.7 (15.2)
AA 20 S NC	140 (14)	7.0 (0.7)	50.5 (12.2)	0.49 (0.12)	19.3 (4.8)	-33.0 (9.5)	2.79 (0.19)	110.7 (7.5)
Control	208 (19)	-	-	0.90 (0.24)	36.6 (10.8)	-	1.86 (0.29)	76.2 (0.1)
Control Uncompressed	-	-	-	0.20 (0.04)	3.4 (0.6)	-	0.22 (0.03)	3.7 (0.6)

\*Phenol Formaldehyde (PF), Tung Oil (TO), Acetic Anhydride (AA), Steam (S), No Steam (NS), Conditioning (C), No Conditioning (NC), High Density (HD).  
 \*\* Values represent averages of 10 replicates, with exception of PF1 5 S NC HD and PF2 5 S NC HD which had 5 and 6 replicates, respectively. Values in parentheses represent 1 standard deviation.

**Table 5.2.** Final values and measurements for all treatments tested. Values in parentheses indicate one standard deviation.

*Treatment	WPG Potential, %	WPG, %	ASE_Soak/ WPG	ASE_Boil/ WPG	Chem Retention, %	Irreversible Swelling Soak, %	Irreversible Swelling Boil, %	Thickness Recovery Soak, %	Thickness Recovery Boil, %
PF1 5 S NC	9.1 (0.9)	3.6 (0.7)	17.8 (5.0)	20.3 (3.6)	39.2 (5.2)	2.2 (4.5)	2.1 (4.4)	0.4 (0.8)	0.8 (1.3)
PF1 10 S C	15.3 (1.0)	10.6 (2.0)	7.2 (1.8)	7.2 (2.0)	69.2 (10.9)	6.8 (15.2)	4.4 (11.6)	6.4 (3.6)	13.4 (6.7)
PF1 10 S NC	17.2 (2.8)	11.3 (2.2)	6.3 (1.3)	6.8 (1.2)	65.3 (4.9)	5.3 (8.9)	1.5 (3.0)	0.3 (0.6)	0.6 (0.8)
PF1 10 NS NC	15.8 (1.9)	10.7 (1.2)	7.8 (1.3)	5.7 (1.9)	68.1 (4.0)	40.8 (21.7)	30.0 (13.0)	2.4 (1.7)	9.2 (6.8)
PF1 20 S NC	32.6 (4.6)	23.0 (2.6)	3.7 (0.7)	3.8 (0.6)	70.8 (5.5)	0.5 (1.4)	2.4 (7.7)	0.0 (0.0)	0.3 (0.8)
PF1 5 S NC HD	12.1 (1.8)	9.1 (3.4)	-	-	77.3 (36.0)	29.0 (10.7)	15.0 (13.2)	1.6 (0.6)	2.0 (1.5)
PF1 10 Uncompressed	23.9 (4.3)	26.2 (4.2)	-	-	110.0 (3.4)	2.3 (7.3)	0.8 (1.7)	-	-
PF2 5 S NC	17.1 (2.8)	4.1 (1.4)	11.8 (8.0)	13.8 (6.0)	23.4 (5.2)	26.0 (10.2)	20.6 (8.8)	6.6 (3.3)	8.7 (3.8)
PF2 10 S C	16.6 (1.8)	8.6 (1.4)	5.3 (2.4)	6.6 (2.4)	51.5 (5.0)	10.6 (12.9)	9.5 (11.9)	0.5 (0.5)	0.6 (0.7)
PF2 10 S NC	16.2 (1.8)	5.8 (1.2)	8.4 (1.9)	10.1 (2.0)	35.5 (3.9)	7.9 (5.3)	9.3 (6.0)	1.8 (0.9)	3.4 (1.9)
PF2 10 NS NC	16.4 (2.0)	7.1 (1.3)	5.6 (2.6)	6.6 (2.5)	43.2 (4.1)	49.0 (15.3)	38.3 (13.2)	10.7 (5.8)	14.7 (7.9)
PF2 20 S NC	32.9 (2.8)	16.5 (2.1)	3.7 (0.5)	4.1 (0.5)	50.1 (4.0)	6.6 (6.8)	7.5 (6.7)	1.2 (1.0)	2.5 (1.5)
PF2 5 S NC HD	10.9 (1.9)	5.0 (0.8)	-	-	46.9 (6.5)	1.9 (3.0)	7.1 (8.0)	0.4 (0.4)	2.1 (1.8)
PF2 10 Uncompressed	23.9 (3.8)	21.7 (2.9)	-	-	91.1 (2.6)	1.9 (4.2)	0.4 (1.2)	-	-
TO 10 S C	11.8 (1.8)	11.2 (1.8)	2.3 (1.5)	2.1 (1.4)	97.2 (22.6)	82.5 (22.2)	24.2 (17.9)	22.3 (8.6)	15.4 (10.7)
TO 10 S NC	12.0 (3.3)	11.0 (4.6)	-0.3 (2.7)	0.1 (1.8)	93.4 (32.5)	88.2 (14.7)	45.1 (16.0)	38.8 (14.9)	39.2 (17.8)
AA 20 S NC	-	20.1 (0.6)	2.5 (0.6)	-1.6 (0.5)	-	100.0 (0.0)	82.1 (12.3)	37.1 (11.9)	69.8 (9.7)
Control	-	-3.4 (0.4)	-	-	-	38.5 (0.2)	20.3 (0.1)	12.8 (7.3)	14.5 (8.0)
Control Uncompressed	-	-	-	-	-	-	-	-	-

\*Phenol Formaldehyde (PF), Tung Oil (TO), Acetic Anhydride (AA), Steam (S), No Steam (NS), Conditioning (C), No Conditioning (NC), High Density (HD).  
\*\* Values represent averages of 10 replicates, with exception of PF1 5 S NC HD and PF2 5 S NC HD which had 5 and 6 replicates, respectively. Values in parentheses represent 1 standard deviation.

## ***5.1 Phenol Formaldehyde Treated Samples***

### *5.1.1 Overall Effect of Phenol Formaldehyde Resin on Dimensional Stability*

Two phenol formaldehyde resins of different molecular weights were used as impregnating agents to bulk VTC treated hybrid poplar. The process took advantage of the energy input during viscoelastic thermal compression to cure the resin.

Concentrations of resin solids varied from 5, 10 to 20% by weight and various processing parameters and treatment conditions were used to provide a more robust understanding of the multitude of interactions influencing each sample during chemical modification and VTC processing. Although it was observed that some amount of resin was lost during processing, the remaining resin showed marked effects in stabilizing the treated samples when subjected to various water tests. This results section will begin by first giving a broad overview of general trends and values observed across all PF treatment conditions and processing parameters and will then go more in depth to review specific conditions.

Four values, thickness swell (TS), anti-swelling efficiency (ASE), irreversible swelling (IS), and thickness recovery (TR), were calculated for both water soak and combined soak and boil tests to evaluate the dimensional stability of each sample. These four values can be further separated into 2 categories; TS and ASE values which are based on differences in measurements of samples from an oven-dry state to a saturated state and represent overall swelling characteristics, and IS and TR values which are based on differences in measurements from oven-dry to oven-dry state after a sample has undergone a particular water test and was then re-dried. These values

allow the total swelling to be broken down into its components of reversible and irreversible swelling. Figures 5.1 through 5.4 display TS, ASE, IS and TR values for both the water soak and the boil tests.

All samples, regardless of resin molecular weight, concentration, processing parameters or treatment conditions showed increased dimensional stability compared to control specimens treated without PF resin. Thickness swell for the 24-hour water soak was near 37% for control samples, while the highest value obtained by any PF treated sample was 24% (PF2 10 NS NC) and proved to be significantly lower than the control ( $p = 0.011$ ). Samples treated with high molecular weight resin had a thickness swell distribution between 5% and 14% and low molecular weight treated samples had a thickness swell distribution between 15% and 24%.

ASE values proved to be well within the range of values reported in previous literature for all conditions tested (see literature review for discussion of previous studies). Values ranged from as high as 84% to as low as 39% with an overall average of 60% for both PF resins combined across the range of testing parameters.

Values for thickness recovery varied considerably between processing parameters and treatment conditions. No overall trend was observed, although more intricate trends did appear which will be discussed in more detail later. Thickness recovery values (TR-S) for the 24-hour soak ranged from 0% for PF1 20 S NC to almost 11% for PF2 10 NS NC and almost 13% for the control. Although values shifted slightly higher after the boil test (TR-SB) was included, the range was similar

with a low of 0% for PF1 20 S NC and a high of near 15% for PF2 10 NS NC. The control value was near 15% after the combined soak and boil test.

Results for irreversible swelling were much the same as thickness recovery and no overall trend was observed. Samples treated without conditioning or steam (PF1 NS NC and PF2 NS NC) proved to have the largest degree of irreversible swelling and exceeded the IS value for the control in both the soak and the boil tests. IS values for all other specimens, except PF2 5 S NC in the soak and the boil test, were significantly lower than the control.

Modulus of elasticity was also evaluated for each sample and Figure 5.5 shows an overall negative trend from the PF treatment. Except for the highly densified specimens, all PF treated samples had a smaller increase in MOE than the unmodified control. The overall average increase in MOE for PF treated samples, excluding highly densified samples, was 152% while the control samples increased an average of 208% from their original uncompressed state.

### *5.1.2 Influence of Molecular Weight*

Previous literature has shown low molecular weight PF resins to be superior to higher MW resins for instilling dimensional stability in almost all wood based products from composites to solid wood to densified solid wood (Stamm et al. 1960, Deka et al. 2000, Wan et al. 2006, Shams et al. 2004a, Ryu et al. 1993). It is believed that lower molecular weight resins more easily penetrate the cellular structure of the wood cell wall and ultimately bulk the wood material to a greater extent (Rowell

1999). Following this vein of thought, this research tested one resin with an extremely low MW and one with a much higher MW (780 weight average for PF1 and 172 weight average for PF2). The influence of molecular weight can be determined by comparing weight percent gain (WPG) values, chemical retention (CR) values, and stability values for similarly treated samples between the two resin types. Similarly treated samples refers to batches which varied in resin type, but whose resin concentration and processing parameters were identical. WPG values provide insight into which resin is better absorbed in the wood cell wall, and although multiple factors can influence this, molecular weight is considered a significant factor. The higher the WPG for a sample, the more that PF resin was able to bulk the cell wall. Since WPG is generally positively correlated to dimensional stability and the interest of this research is dimensional stability, ASE and TS values can also be used in an indirect manner to understand the influence of molecular weight.

It was believed that results similar to those found in previous studies would be observed in this research with regards to the absorption of the different molecular weight resins; however, the opposite effect was actually seen. WPG values, regardless of processing parameters, were significantly greater for the higher molecular weight resin, PF1, than the lower molecular weight resin, PF2, except at the 5% resin solids concentration which showed no significant difference between PF1 and PF2 (Figure 5.6). Further review shows that with the exception of the 5% concentration treatments, all other treatments had statistically similar WPG-P values (Figure 5.7). WPG-P is the theoretical maximum WPG a sample can achieve if it were to lose no resin during

processing. This value is based off of the resin concentration of the treating solution and the amount of solution absorbed during impregnation. Since all similarly treated batches with statistically similar WPG-P values had final WPG values in which PF1 was significantly greater, it can be assumed that some aspect of PF1 allows it to be more readily absorbed or retained in the cellular structure of the wood. Although the exact reason can not be determined through this study, it is theorized that the higher molecular weight resin may contain a certain molecular weight fraction that is able to swell the cell wall much more effectively than the lower molecular weight resin and thus cause a higher WPG. A further explanation may lie in the mobility of the two resins once absorbed into the wood. During VTC processing, mechanical compression, along with the development of steam pressure inside the specimen, forces out excess treating solution. The higher molecular weight resin may be less mobile, due to longer chain length, and thus may cure in the high heat environment before it is forced out of the sample.

Finally, chemical retention (CR) values, which give insight into how well a treating reagent remains in a sample during VTC processing, were significantly higher for PF1 than PF2 in all treatments tested, including high density samples (Figure 5.11). This may indicate that the lower molecular weight PF2 resin has a greater vapor pressure and simply volatilizes more in the high temperature environment of the VTC apparatus. Differential scanning calorimetry (DSC) revealed PF2 was a faster curing resin than PF1 (Figure 5.12).

To take the analysis one step further, stability measurements were compared. ASE and thickness swell values were normalized by each sample's WPG (Figures 5.8 and 5.9). This normalized value represents the amount of dimensional stability achieved per unit of resin retained. This value is essential in determining if a resin is more effective at providing dimensional stability because of some inherent quality within it, or if it is simply because there is physically more of that resin present in a sample. Many normalized ASE values were statistically similar when comparing different resin types of similarly treated batches for both the soak and the boil test. This provides some evidence that although the higher molecular weight resin is more readily absorbed, the capacity of each resin to impart stability is the same. This makes directly connecting molecular weight and dimensional stability difficult because on one hand, normalized ASE values imply that the resins have the same effectiveness for imparting stability on a per unit of resin basis and therefore molecular weight does not have an influence, however, on the other hand, the resin can only impart dimensional stability if it is able to penetrate and remain in the cell wall, and this is highly dependent on the molecular weight.

Results from this study can only show that molecular weight has an indirect effect on dimensional stability by influencing the physical amount of each resin type retained in the cellular structure of hybrid poplar. Some other test method would need to be conducted in order to gain a more robust understanding of the influence of molecular weight on resin absorption and ultimately dimensional stability.

### *5.1.3 Influence of Concentration*

It has been shown that greater resin loading leads to greater dimensional stability (Kajita and Imamura 1991, Wan and Kim. 2006). To achieve higher load levels, higher resin solids concentrations are used. A threshold exists in this relationship, however, and it is most often defined by two parameters: cost and effectiveness. Chemicals are often the most expensive portion of any wood based product and achieving maximum efficiency from a minimum amount of reagent is almost always of interest. In light of this, Wan and Kim (2006) did research to establish lower resin loading limits where benefits to strength and dimensional stability still existed, but where resin use was minimized. One percent and five percent resin solids concentrations were studied. It was found that 1% had no distinguishable effect from untreated controls, while 5% showed significant increases in dimensional stability.

In many research environments cost is not initially a concern, especially during the development of new technologies or processing techniques. If cost does not limit the amount or type of reagent used in a process, then the effectiveness of that reagent becomes the limiting factor. In the case of increasing resin concentrations, the effective limit is often determined by diminishing returns on the improvement of material properties with each incremental increase in chemical reagent used.

This research aimed to explore the threshold of PF resin loading on stability by studying three resin concentrations at increasing intervals of 5%, 10%, 20% resin solids content. All samples were processed with steam and without conditioning (i.e.

batches 5 S NC, 10 S NC and 20 S NC for both PF1 and PF2). All other treatment conditions and processing parameters were held constant for these batches.

Comparisons between stability values were made to determine the influence of treatment concentration and to determine the effectiveness of each concentration on a per-unit-of-resin used basis.

PF1 and PF2 both showed increasing dimensional stability with increasing resin concentration. ASE values increased from 61% to 84% after the soak test and from 71% to 86% after the boil test for PF1 as resin concentration increased from 5% to 20% (Figure 5.2). Further, with increasing resin concentration thickness swell decreased from 14% to 5% and from 21% to 9% after the soak test and the boil test, respectively. Control specimens had an average thickness swell of 37% after the soak test and 76% after the boil test (Figure 5.1). All PF modified samples, regardless of concentration or resin type had significantly less thickness swell than the controls. PF2 displayed similar trends as PF1 with ASE values increasing and thickness swell decreasing as resin concentration increased (i.e. an increase in overall stability). Although still significantly better than controls, PF2's stability values were lower than that of PF1 in all cases. As resin concentration increased from 5% to 10% the associated increase in ASE and decrease in thickness swell was not significantly different for either PF1 or PF2 resins, with the exception of PF2 in the boil test. A significant difference did exist, however, for ASE and thickness swell values when concentrations of both resins were increased from 10% to 20% (p-values can be found in the appendix).

Weight percent gain for PF1 at 5% concentration was only 3.5% (Figure 5.7). The associated ASE value (61%) is extremely high for such a minimal amount of resin and it is believed that a non-linear relationship exists where the addition of small amounts of resin produces large increases in stability initially, but as resin concentrations increase the increase in stability decreases. It is believed that this threshold exists somewhere around 5% resin solids concentration for PF1. Further research should be conducted to determine the exact relationship between resin concentration and dimensional stability for low resin solids levels.

ASE and thickness swell were normalized by WPG to better understand the relationship between dimensional stability and resin concentration. It was found that each successive increase in resin concentration produced diminishing returns for stability values (Figures 5.8 and 5.9). Generally, 5% resin concentration offered the most dimensional stability per unit of resin for both PF1 and PF2 in both water tests; however, due to large amounts of variability there was no statistical difference for normalized ASE or thickness swell values for PF2 between batches treated at 5% and 10% resin concentration. Normalized values provide insight into the effectiveness of each treatment at different concentration levels. In a commercial setting, this information would allow benchmark stability values to be set prior to production and then specific resin concentrations could be used to achieve desired product characteristics, thus eliminating possible waste in processing. Further testing of different resin concentrations, especially at lower concentrations, would provide an

even more robust understanding of the relationship between concentration and stability and would allow for more efficient use of resins.

The effects of resin concentration on irreversible swelling (IS) and thickness recovery (TR) were also reviewed for both PF resins (Figures 5.3 and 5.4). IS and TR both measure the degree to which a sample recovers from its compression set, while in contrast, TS and ASE provide insight to the degree of overall swelling from a dry state to a wet state. In essence, these measurements take into account two different swelling mechanisms, reversible and irreversible. IS and TR values afford information on the release of residual stresses built up during the pressing of samples. Greater stresses cause more spring-back during water testing which results in higher IS and TR values.

Shams and Yano (2004) studied the effect of PF resin impregnation on Japanese cedar. They showed that PF resin acts to plasticize the wood cell wall and as resin concentrations increase, so to does the extent of cell wall softening. Softening of the cell wall is a critical component of the VTC process and allows cell walls to collapse without fracturing or the build up of residual stress. As IS and TR can be used as an indicator for the existence of internal stresses, it was believed that as resin concentrations increased, samples would yield lower IS and TR values due to the resins plasticizing effect. IS and TR were also expected to decrease with increasing resin concentrations due to the resin physically restricting the cell walls from swelling.

Control samples had an average IS value of 38.5% in the soak and 20% in the boil. All samples treated with PF performed significantly better than the controls except for the treatment with PF2 at 5% concentration. Samples treated with PF1 at

20% resin concentration had a nearly 80 fold decrease in irreversible swelling compared to controls. On a per-unit-of-resin basis, samples treated at 5 resin concentration with PF1 provided the largest decrease in irreversible swelling compared to controls.

PF1 showed no distinguishable influence on IS values with increases in resin concentration. Ten percent concentration produced the highest mean IS value of 5%, while 20% resin concentration produced the lowest mean IS value of 0.5%. However, it was found that no statistically significant difference existed between any of the levels of resin concentration used.

The lower molecular weight resin, PF2, did however, show an inverse relationship with IS values in both the soak and the boil tests as resin concentration increased. IS values for the 24-hour soak decreased from 26% to 6.5% and then from 21% to 7.5% for the boil test. Increase in resin concentration produced significantly lower IS values for all conditions except between 10% and 20% concentration in the soak test.

Thickness recovery is a value not often reported in literature, however, it can provide useful insight to dimensional stability in regards to treatments involving densified wood. As mentioned before, thickness recovery is the amount of irreversible thickness swell as a percent of densification imposed on a sample. It is simply another way to represent irreversible swelling and provides additional information on the release of residual stresses built up from processing.

Control samples for this research had thickness recovery values of 13% and 14.5% for the soak and boil tests, respectively. PF1 recorded extremely low thickness recovery values with the highest single value being 0.77% for PF1 5 S NC after the boil test. All thickness recovery values for soak and boil tests were less than 1 percent for samples treated with PF1. Although thickness recovery increased with increasing resin concentration for PF1, there was no significant difference between any of the values. Thickness recovery results were so small for PF1 treated samples that an overall trend could not be established.

Samples treated with PF2 ranged in thickness recovery from a high of 9% for PF2 5 S NC after the boil test to a low of 1% for PF2 20 S NC after the soak test. Thickness recovery values dropped significantly with an increase in resin concentration from 5% to 10%, however, a further increase in resin concentration to 20% did not produce significantly different results. Thickness recovery values were much higher for PF2 than for PF1.

Significant differences in thickness recovery values between resin concentrations only existed with PF2 treated samples, while all PF1 treated samples were statistically similar. The cause for this is not completely understood, however, it is possible that a threshold exists where, once passed, the plasticizing effect of PF on the wood cell wall is no longer increased with increasing resin concentration. This theory is illustrated well with the two PF resins used in this study; PF1 is able to penetrate and soften the wood cell wall more effectively than PF2, and its concentration threshold may exist at concentrations lower than those tested for this

research. PF2 on the other hand, requires a higher resin concentration to produce the similar effects as PF1, and the significant decrease in TR as resin concentration increased from 5% to 10% may indicate the plasticizing threshold exists somewhere between these two concentrations. To reinforce this, the further increase in concentration to 20% showed no significant change in TR values.

IS values also strengthen this theory; PF1 treated samples showed no significant difference with increasing resin concentrations, however, PF2 treated samples showed significant decreases in IS values as concentration increased. This supports the idea that the wood cell wall can only be softened so much, and this threshold is reached at lower concentrations than those tested in this research for PF1, but within the concentrations tested for PF2. Although IS and TR are not direct measurements of the softening ability of each resin, it is an accepted value for measuring residual stress in densified wood, which is directly correlated to the softening of the wood cell wall during processing.

Overall, dimensional stability proved to be positively correlated to resin concentration for both PF1 and PF2. This finding is not one of surprise, as it is commonly observed that stability values increase with increasing resin loading. Normalizing stability values, however, has provided additional insight into the effectiveness of each resin at various concentrations and TR and IS values have shown that PF resin restricts a significant amount of irreversible swelling and may also aid in reducing internal stresses through plasticization of the wood cell wall.

#### *5.1.4 Influence of Steam*

There has been a multitude of studies conducted examining the effects of pre-steaming and post-steaming treatments of compressed wood aimed to increase dimensional stability and reduce the build up of internal stresses (Heger et al. 2004, Sekino et al. 1999, Yilgor et al. 2001, Inoue et al. 1993, Rowell et al. 2002). Thermal degradation of hemicellulose depends highly on environmental conditions, with degradation beginning as low as 100 °C and increasing with higher temperatures and higher moisture contents (Rowell et al. 2002). It has been found that steam pretreatments cause partial hydrolysis of hemicellulose which increases compressibility, reduces build up of internal stresses, and increases dimensional stability (Rowell et al. 2002, Shams et al. 2006).

During the development of processing methods for this research, it was noted that the PF treated samples were producing large amounts of steam when dried between the hot platens of the VTC device just prior to VTC processing. It was of interest to determine if this apparent self-steaming had the same effect as the steam treatment intrinsic to the VTC process. Similar results would enable the VTC process to be considerably simplified which would aid in its scale-up to an industrial setting. Samples treated with the same resin concentration were either processed with the normal VTC schedule or with an altered self-steaming schedule (i.e. PF1 or PF2 either 10 S NC or 10 NS NC).

Results for the comparison between steaming and self-steaming did not produce clear-cut trends with regards to ASE and thickness swell values (Figures 5.1

and 5.2). PF1 steamed samples performed better than PF1 self-steamed samples in ASE value for the boil test but not for the soak. PF2 steamed samples revealed a higher mean ASE in both the soak and the boil tests, although, statistically there was no difference. No obvious trend exists with ASE values. For thickness swell, steamed samples treated with PF1 performed better in the soak than self-steamed samples, but not in the boil; opposite to ASE results. PF2 treated self-steamed samples performed better in the soak but were statistically similar to steamed samples in the boil test. Again, no discernable trend was observed for differences between steamed and self-steamed samples based on ASE and thickness swell values. In comparison to control samples, however, both the steamed and the self-steamed treatments, regardless of resin type, were significantly more dimensionally stable.

A review of thickness recovery and irreversible swelling values for steamed versus self-steamed samples, however, does reveal a strong influence from the steam treatment (Figure 5.3 and 5.4). The steam treatment is integral in softening the wood cell wall before collapse, reducing the build-up of internal stresses. TR and IS values represent the release of these stresses and provide information regarding the effectiveness of treatments on softening the wood cell wall.

Differences were found between steamed and self-steamed samples for both PF resins in irreversible swelling measurements. IS values for steamed PF1 samples were 8 times lower than self-steamed in the soak test, and 20 times lower in the boil test. Results were similar for samples treated with PF2, with steamed samples having an IS value 6 times lower than non-steamed in the soak test and 4 times lower in the

boil test. Self-steamed samples, although not significantly different, also had higher mean IS values for both soak and boil in comparison to control samples.

Thickness recovery results mirror those found in irreversible swelling. Samples treated with steam, regardless of resin type, performed significantly better than self-steamed samples in both the soak and boil tests. Steamed PF1 treated samples performed 9 times and 16 times better than self-steamed samples in the soak test and boil test, respectively. PF2 steamed samples recorded a thickness recovery value of only 1.8% in the soak test, while self-steamed samples had a thickness recovery of 10.7%. Values for self-steamed PF1 treated samples in the boil test and PF2 treated samples in both the soak and the boil test were statistically similar to unmodified control samples, while all samples treated with steam had statistically lower thickness recovery values than controls.

Since steamed and self-steamed samples showed no distinguishable difference in their TS and ASE values, but were significantly different in IS and TR values it can be hypothesized that the swelling mechanism is different for steamed versus self-steamed samples. The swelling which occurs in steamed samples is mostly a result of the natural swelling which occurs in wood and is completely reversible. The swelling which occurred in the self-steamed samples is indicative of the release of internal stresses built up during processing. Once a sample is saturated, these stresses release and cause the sample to swell and permanently regain some portion of its original volume. Fukuta et al. (2007) reviewed the effect of open versus closed heat and steam treatments on the compressive deformation of Japanese cedar. Results showed that at

180 °C, even after 480 minutes of open heating, percent thickness recovery values were still greater than when samples were heated in a closed environment for only 15 minutes. This difference between the open and closed environment tested by Fukuta et al. is essentially the same as the difference between the steam and the self-steaming treatment with regards to the VTC research. Results are congruent between both studies.

It can be concluded that the steaming step involved in the normal VTC process is beneficial to the dimensional stability of treated samples. Although swelling between steamed and self-steamed samples was similar when samples were in their saturated state, once dried, self-steamed samples maintained much of their swollen volume compared to steamed samples. It is believed that the steaming process is better able to soften the cellular structure of the samples, reducing the build up of internal stresses when samples are densified. Microscopy work also showed that self-steamed samples had more cell wall fracture, again indicating a lower level of softening before densification occurred.

#### *5.1.5 Influence of Conditioning*

Conditioning of the samples was initially addressed as a means to prevent the loss of treating solution during VTC processing. While samples were being dried using the heated platens of the VTC device, much of the treating solution was being forced out of the wood cells by evaporation/gas expansion and mechanical compression. It was believed that allowing samples to air-dry after chemical

modification, but prior to VTC processing, would increase chemical retention and provide more uniform penetration across the cellular structure. To test this theory, comparisons were made between samples treated with a 24 hour conditioning step and samples treated with no conditioning (i.e. dried using the hot platens of the VTC device). Both PF resins were tested and samples were treated at a resin concentration of 10%.

PF1 and PF2 treated samples showed no significant difference between conditioned and unconditioned samples in ASE, TS, or IS values in either the soak or the boil test (Figures 5.1, 5.2 and 5.3). In addition, no significant difference was found between thickness recovery values for PF1 treated conditioned and unconditioned samples in both the soak and the boil test (Figure 5.4). PF2 treated samples were the only treatments to have significantly different thickness recovery values between conditioned and unconditioned samples. Conditioned samples had a 0.45% and 0.6% thickness recovery for the soak and boil tests respectively, while unconditioned samples had thickness swells of 1.8% and 3.4% for the soak and boil tests respectively. Although statistics show these values to be significantly different, they are nonetheless extremely small in size and taking into account that all other measurements were statistically similar, the difference in thickness recovery values for PF2 treated samples may exist simply due to inaccuracies in measurements. The additional 24 hour conditioning step implemented to aid in sample drying and reagent penetration does not appear to influence the dimensional stability of VTC treated hybrid poplar. In light of this, either treatment is recommended and each have their

strong and weak points. Unconditioned samples can be produced continuously; however, more energy is needed to dry samples since this is accomplished with the heated platens of the VTC device. Conditioned samples take little to no energy to dry since they are air-dried at room temperature in only 24 hours, however, this step may interfere with the continuity of processing.

#### *5.1.6 High density PF impregnated samples*

High density samples were not part of the original design matrix for this research. They were created out of curiosity after all other samples had been processed and tested. As it turns out, high density samples embody the results we were hoping to procure from the lower density samples with regards to increases in both stability and mechanical properties.

High density samples started at the same original thickness as standard density samples, but were compressed to a final thickness of 1.5 mm. PF1 and PF2 treated samples had final average OD densities of 1.08 and 1.05 g/cm<sup>3</sup>, respectively, while lower density samples treated at the same resin concentration had final densities of 0.83 and 0.79 g/cm<sup>3</sup>.

High density PF1 and PF2 showed greater dimensional stability than controls, with significantly lower TS, IS, and TR values for both resins in both the soak test and the boil test (Figures 5.1, 5.3, and 5.4). IS values for PF1 treated samples in the soak and boil tests are the exception to this, as their values were not statistically different than that of the controls. In comparison to similarly treated lower density PF1

impregnated samples, higher density samples showed a lower degree of dimensional stability. It should be noted however, that values such as thickness swell are based on a percentage of the sample thickness. Absolute thickness swell for high density samples was half that of low density samples, however, percent thickness swell was higher for high density samples. PF2 treated high density samples had significantly higher dimensional stability values than similarly treated low density samples. With the exception of TS values in the boil test which were not significantly different, all other TS, IS and TR values in both the soak and boil test showed significantly more stability for the high density samples.

High density samples were the only samples tested in this study in which PF2 treated samples outperformed PF1 samples in stability values. One possible explanation for this may be that at higher densities more intimate contact occurs between collapsed cell walls. PF2 is less able to penetrate the cell wall and is more likely to reside in the lumens than PF1. With more resin in the lumens and more wall to wall contact, PF2 may impart greater dimensional stability by physically bonding cell walls together and preventing them from swelling when exposed to moisture. Further testing should be conducted at higher density levels and at various resin concentrations to determine the true influence of density on dimensional stability.

## ***5.2 Influence of phenol formaldehyde treatments and processing parameters on Modulus of elasticity***

Modulus of elasticity was calculated for each sample prior to chemical modification and again post VTC processing. Figure 5.5 displays MOE as a percent increase from initial unprocessed values. Final MOE values were not recorded for PF1 20 S NC treated samples because water tests were accidentally performed on samples before MOE testing had occurred.

It was hypothesized that MOE values would increase with the presence of PF resin and would also increase with an increase in concentration of PF resin. Upon curing, thermosetting phenol formaldehyde resin forms a rigid crosslinked network that we believed would increase the stiffness of samples. With the exception of high density samples, all specimens, regardless of resin concentration or processing parameters, had significantly lower increases in MOE than the unmodified control samples. Controls increased in MOE an average of 208% while the largest increase in PF1 and PF2 treated samples were 182% and 154%, respectively. It is believed that the target density for these samples was too low and that the PF resin was unable to completely bridge the gaps between cell walls and thus, the potential for its highly rigid structure to increase the overall MOE was not captured. This theory is fortified by the results for the high density specimens treated with only 5 percent resin concentration. Not only did these samples outperform all other PF treated samples in percent increase in MOE, they averaged 70% higher for PF1 and 60% higher for PF2 in increase in MOE over control samples. O'Conner (2006) processed unmodified

eastern cottonwood (*Populus deltoides*) samples in the VTC device to a densification level similar to that of high density samples in this research. O'Conner found that MOE values increased from roughly  $1.5 \times 10^6$  psi to approximately  $4 \times 10^6$  psi, an increase of 167%. High density specimens for this research reached a maximum average MOE of  $5.2 \times 10^6$  psi for samples impregnated with PF1 and  $5.9 \times 10^6$  psi for PF2. This represents an increase in MOE of 350% and 335% from the unmodified state to the chemically impregnated and VTC processed state for PF1 and PF2, respectively. It is believed that a threshold density exists where the wood cell wall is compressed to such an extent that the cell wall and cured PF resin form a pseudo-solid structure with minimal void space.

Resin concentration showed little to no effect on MOE values. As resin solids levels were increased from 5% to 10% and then from 10% to 20%, no significant difference was noted in MOE for either of the two resins. This was a surprise as Shams and Yano 2004 showed increasing PF resin concentration caused greater softening of cell wall constituents which we believed would reduce fracturing when cell wall collapse occurred, thus producing higher MOE values. This is opposite to what was hypothesized. It was also expected that increasing resin concentrations would increase the amount of highly rigid resin in the sample, which would result in greater increases in MOE. A further explanation for these results may be based on pre-cure of the PF resin before sample compression was complete. The DSC scan in Figure 5.12 shows that resin cure for both resins occurs between 120 °C and 140 °C which is below the operating temperature of the VTC device. Since it is impossible to

know the exact point during the VTC schedule at which the resin fully cures, the presence of moisture in the sample may have kept the samples internal temperature below the curing point before final densification was complete. However, the high heat environment of the VTC process may have also caused the resin to cure prior to final compression, in which case the subsequent compression step would have fractured the rigid crosslinked PF network and rendered it ineffective at increasing MOE. The inclusion of a thermocouple into the wood during processing would easily answer questions regarding the internal temperature of the sample at various stages in the VTC process. Additionally, if resin did pre-cure in the cell wall it would lead to fracturing rather than buckling when compression was applied. This would most likely lead to a reduction in MOE. Microscopy work, however, showed little evidence of excessive cell wall fracturing. Samples impregnated with resin and then cured without densification showed a 15% and 12% increase in MOE for PF1 and PF2 respectively, indicating that without densification the rigid crosslinked network of cured PF resin does increase MOE values and that pre-cure for densified samples is a plausible explanation for the reduction in MOE.

MOE values for both PF1 and PF2 were significantly higher for treatments with steam versus self-steamed. Microscopy work showed a much higher percentage of cell wall fractures in self-steamed samples and it is believed that the self-steaming process does not fully soften the cell walls before compression is applied. It can be concluded that fracturing of the cell wall during compression is one of the main causes for a reduction in MOE values between steamed and self-steamed samples.

The effect of conditioning on MOE varied with the resin type, as PF1 had significantly higher MOE values for conditioned samples, but PF2 showed no difference in values between conditioned and unconditioned samples. It is unclear as to what aspect of the conditioning step would cause differences in MOE values in comparison to unmodified samples. One could speculate that the longer exposure time of conditioned samples to the uncured PF may cause increased softening of the cell wall. As PF2 has been shown to penetrate or be retained by the cell wall less effectively, it could be expected that no difference would exist between conditioned and unconditioned PF2 treated samples. PF1, which is able to penetrate and soften the cell wall more effectively, would produce samples with higher increases in MOE due to less cell wall fracture as a result of greater softening, just as the results have shown. To test this theory further, stress-strain measurements could be taken while samples are densified. Comparisons of the stress or strain necessary to initiate collapse of the cell wall may provide additional information on the softening effects of various treatment conditions. This would further lead to a better understanding of the correlation between conditioning treatments and MOE.

Overall, for samples compressed to the standard 2.5 mm final thickness, the phenol formaldehyde treatment had detrimental effects on modulus of elasticity. Further studies should be conducted to determine the relationship between densification level and phenol formaldehyde treatments to enable higher increases in modulus. Although current treatments cause MOE to be lower compared to controls,

the treatment still significantly increases MOE values from their unmodified state and depending on the needs of a final product, may be within satisfactory limits.

### *5.2.1 Relationship of Density and Modulus*

In a multistage research project, Shams et al. (2006) studied the compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (average MW  $\approx$  300). Besides the effects of processing parameters, steam pretreatments, pressing pressure and pressure holding, Shams also reviewed the influence of species. It was found that compared to higher density species, lower density species exhibited greater compressibility at low pressing pressures and that higher final densifications could be achieved with species whose initial densities were lower. The cause for this was shown to be a combination of the plasticizing effect of PF on wood, as well as the lower collapse initiating pressure needed to densify low density species. When compressed at a constant pressure, low density species showed greater increases in mechanical properties than higher density species.

Hybrid poplar used for this research is considered a low density hardwood species and shows great potential for being a valuable raw material for the PF impregnated VTC process. High levels of densification can be easily achieved and mechanical properties can be tailored to fit specific needs based on initial and final densities, as shown by O'Conner (2007).

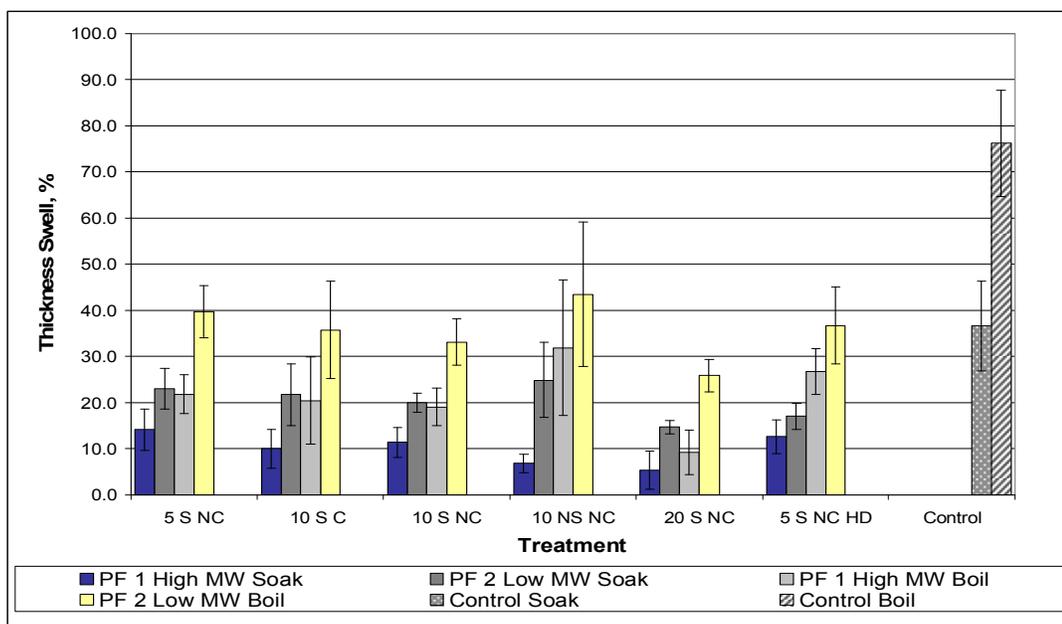
Multiple linear regression analysis was conducted to determine relationships between density, WPG and resin type on increases in MOE. Two multiple linear

regression models were formed. The first model used WPG as a numerical value, resin type as a categorical variable with 2 levels (PF1 and PF2), and densification as a categorical variable with 3 levels (high, standard, and no densification).

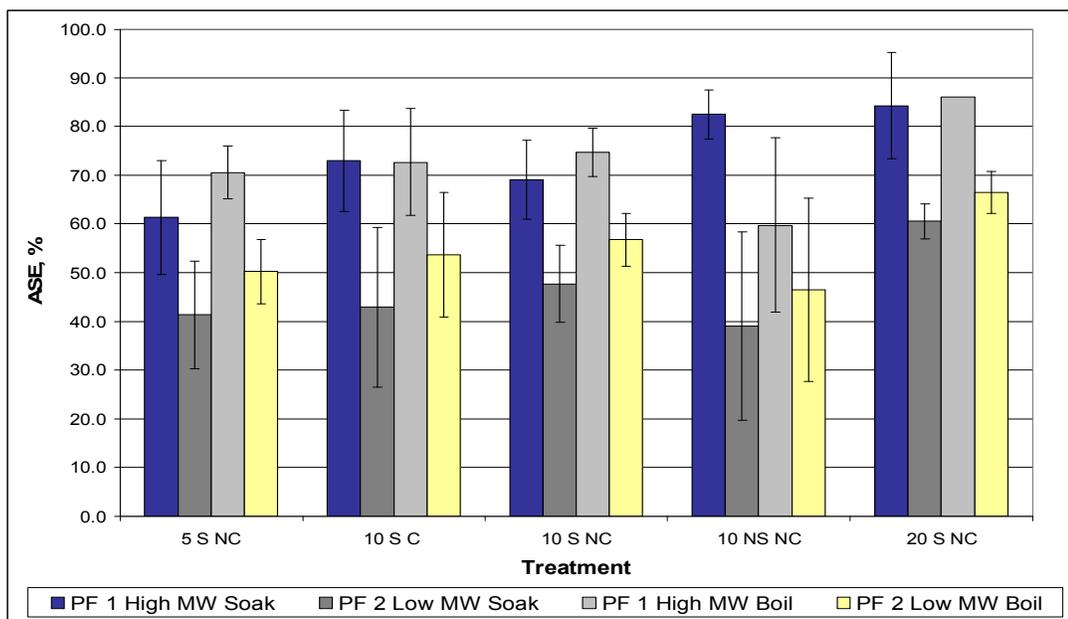
Since the multiple categorical variables exist, direct interpretation of regression coefficients is complicated, therefore, full and reduced models were constructed to allow F-tests to be performed to determine significance of each variable. It was found that only density was able to explain a significant proportion of the variability associated with MOE values when the other variables were accounted for (significance level of 0.05 p-value < 0.0001 ). Density is positively correlated to MOE when all density levels and WPG and resin type are account for. Resin type and WPG did not prove to be significant when other variables were accounted for (Resin type p-value = 0.217, WPG p-value = 0.963). See appendix for statistical output.

The second multiple linear regression model was constructed to look at the relationship of WPG, density and resin type on MOE for only the standard level of densification. This resulted in a model which had WPG and density as numerical variables and resin type as a 2 factor categorical variable (PF1 and PF2). Density and WPG were found to be significant (p-values = 0.003 and 0.008 for density and WPG, respectively) and a more simplistic interpretation can be applied to coefficient values. Regression analysis showed that once density and resin type were accounted for, WPG had a negative correlation on MOE. It is believed that at this densification level, the presence of PF resin in the molecular structure of wood acts much like that of bound

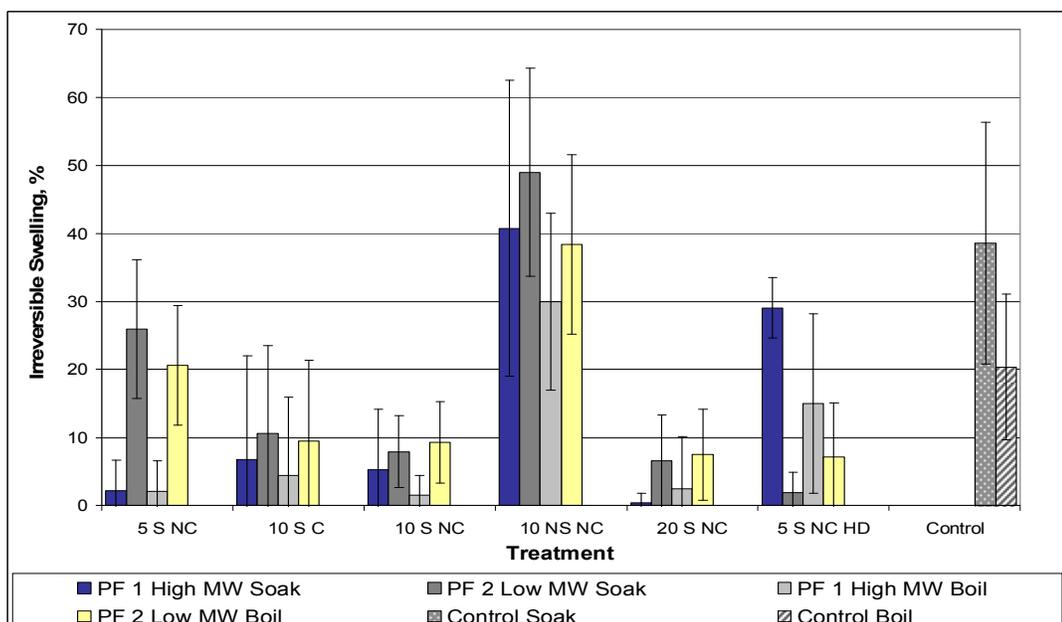
water and reduces the overall MOE by limiting stiffness inducing interactions between molecules in the wood substrate.



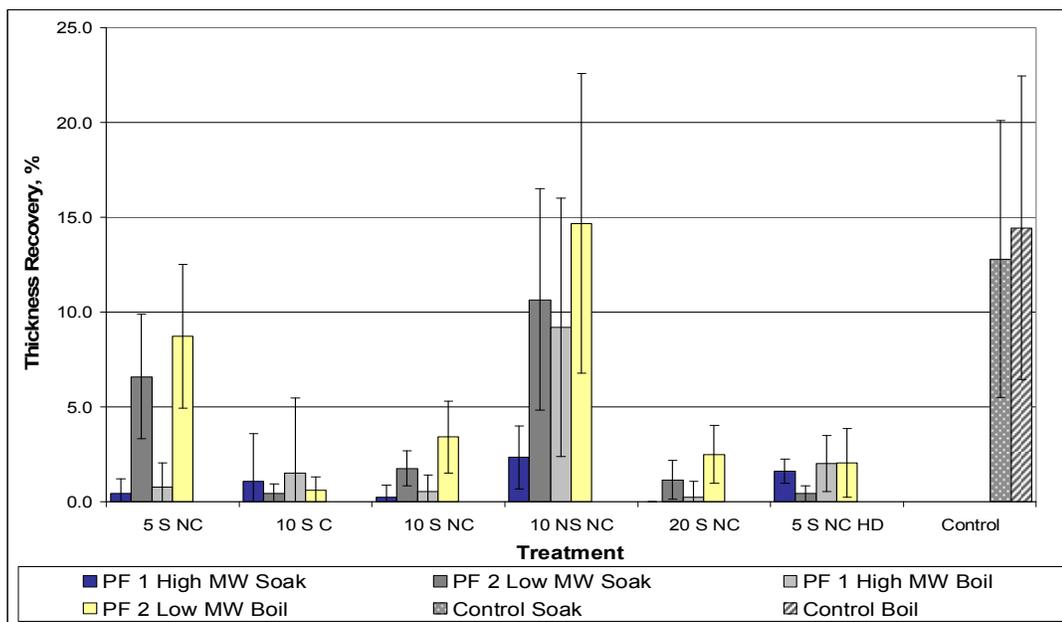
**Figure 5.1.** Percent thickness swell for high and low molecular weight PF impregnated samples and control samples after water soak test and boil test. Error bars represent +/- 1 standard deviation.



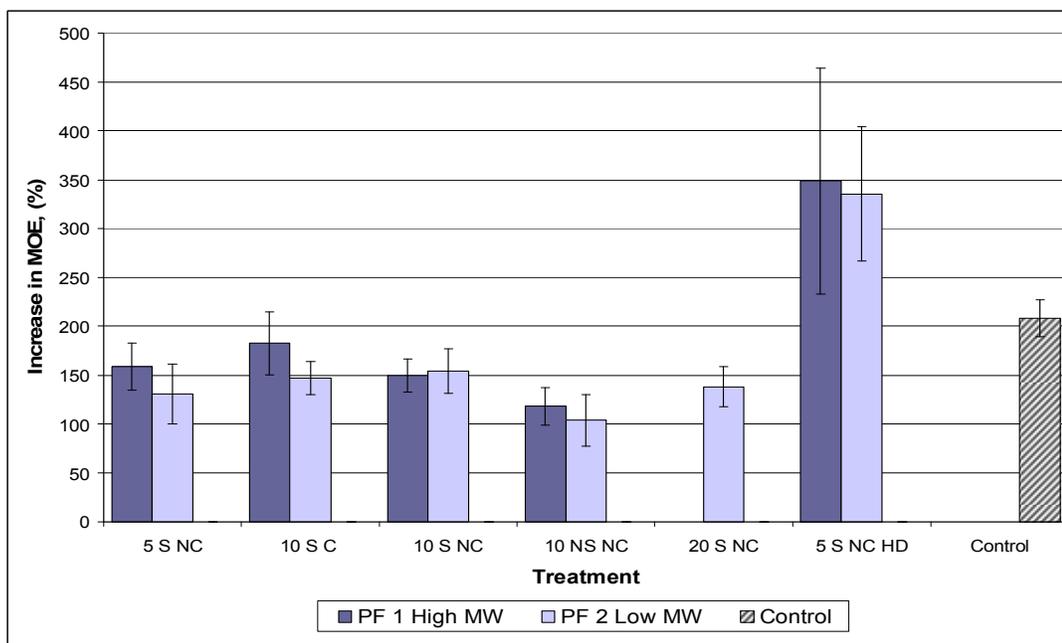
**Figure 5.2.** Anti-swelling efficiency for high and low molecular weight PF impregnated samples and control samples after water soak test and boil test. Error bars represent +/- 1 standard deviation.



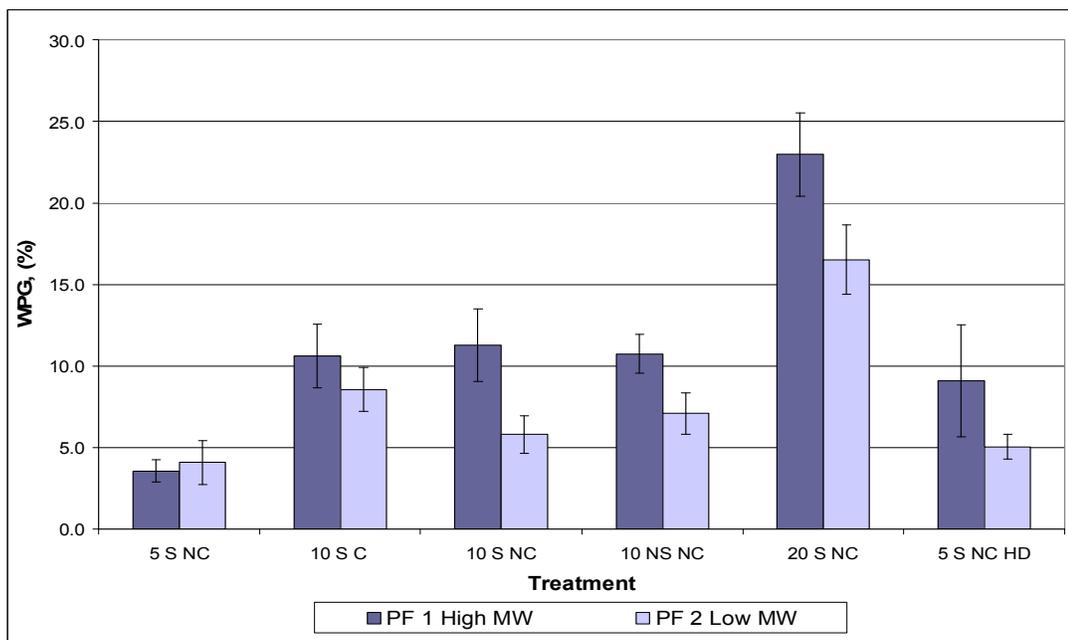
**Figure 5.3.** Irreversible swelling for high and low molecular weight PF impregnated samples and control samples after water soak test and boil test. Error bars represent +/- 1 standard deviation.



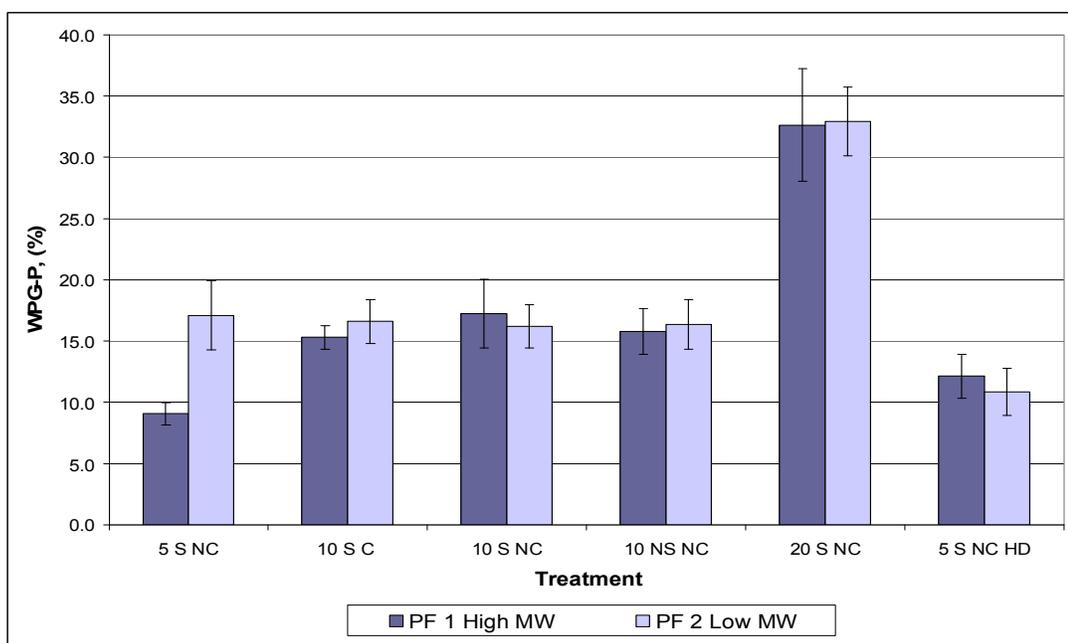
**Figure 5.4.** Thickness recovery for high and low molecular weight PF impregnated samples and control samples after water soak test and boil test. Error bars represent +/- 1 standard deviation.



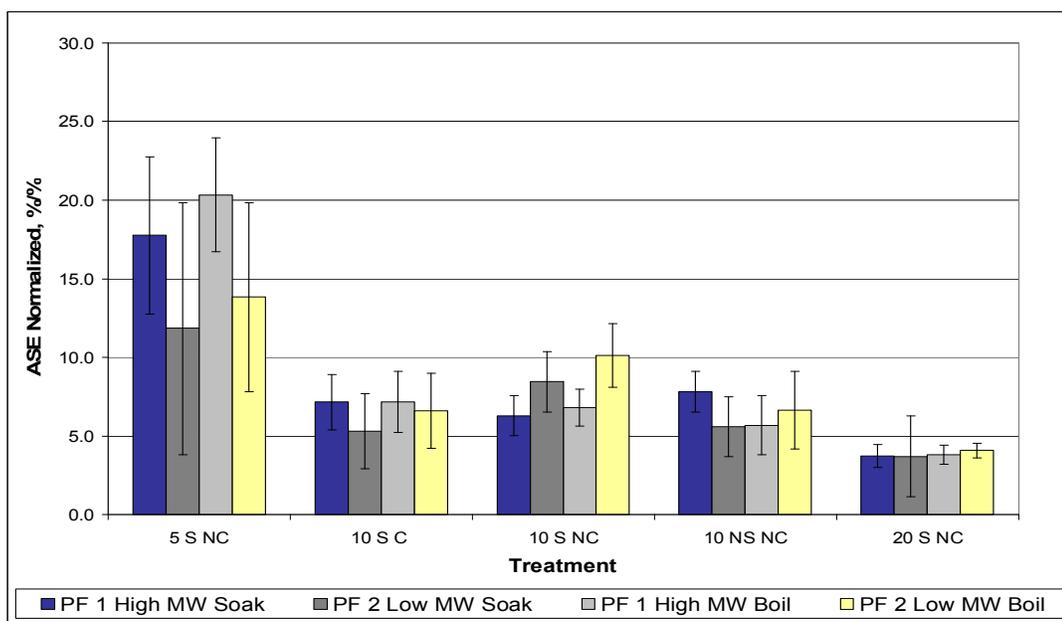
**Figure 5.5.** Increase in modulus of elasticity for high and low molecular weight PF impregnated samples and control. Error bars represent +/- 1 standard deviation.



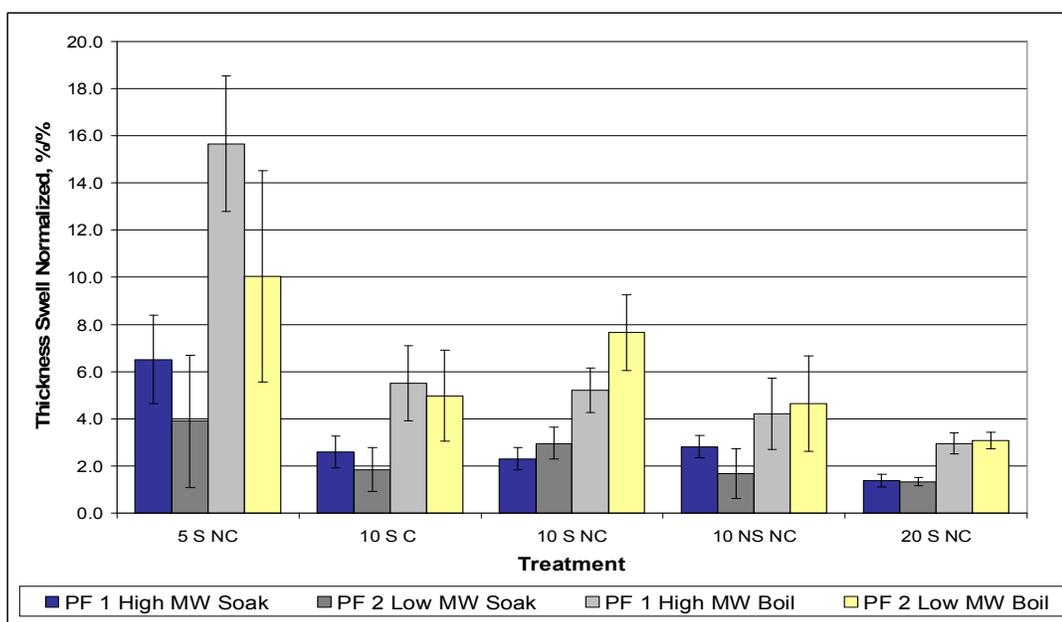
**Figure 5.6.** Weight percent gain for high and low molecular weight PF impregnated samples. Error bars represent +/- 1 standard deviation.



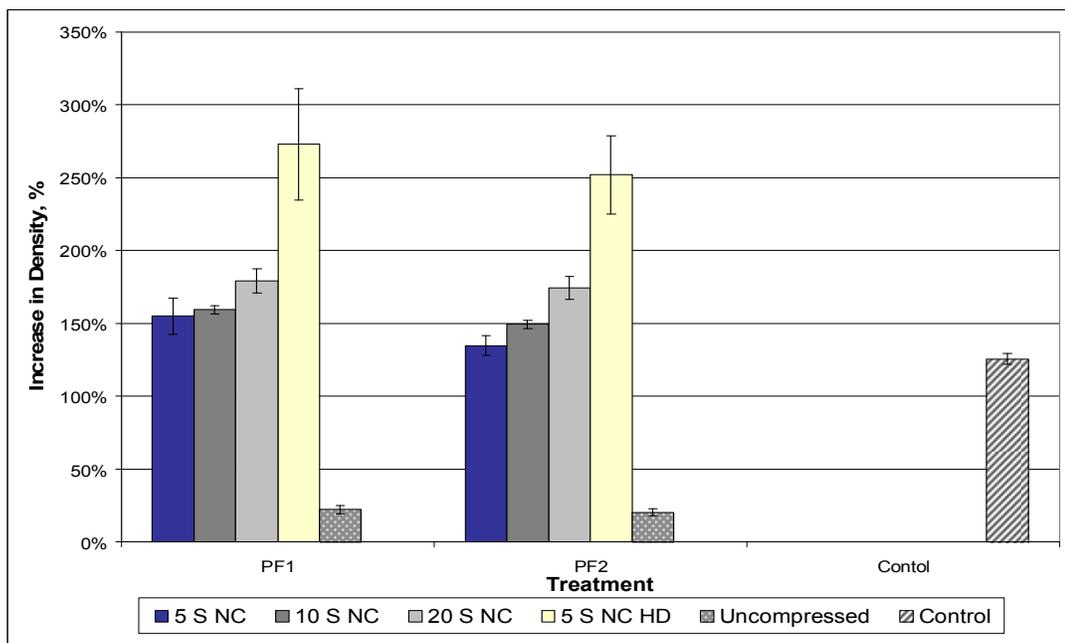
**Figure 5.7.** Weight percent gain potential for high and low molecular weight PF impregnated samples. Error bars represent +/- 1 standard deviation.



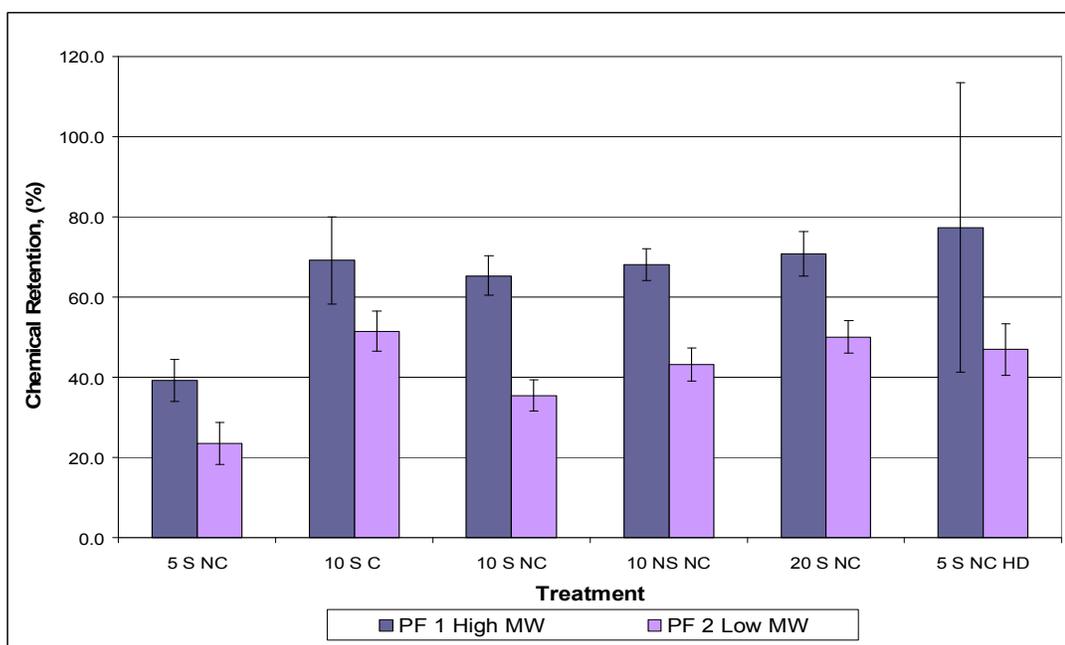
**Figure 5.8.** Normalized ASE values for high and low molecular weight PF impregnated samples after 24-hour room temperature water soak and 2-hour boil. Error bars represent +/- 1 standard deviation.



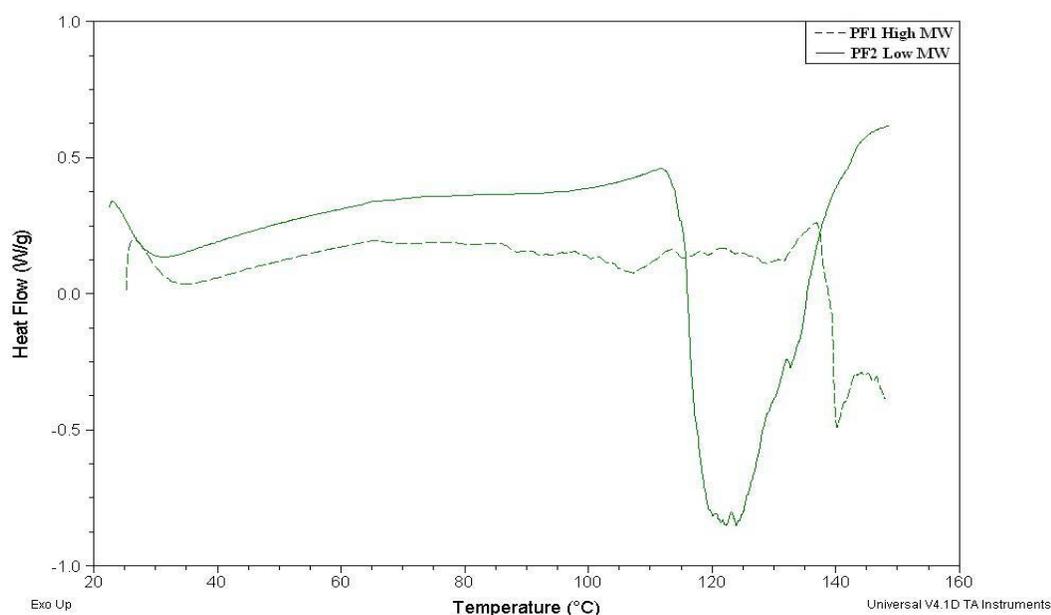
**Figure 5.9.** Normalized thickness swell values for high and low molecular weight PF impregnated samples after 24-hour room temperature water soak and 2-hour boil. Error bars represent +/- 1 standard deviation.



**Figure 5.10.** Increase in Density for high and low molecular weight PF impregnated samples.



**Figure 5.11.** Chemical retention for similarly treated PF impregnated samples. Error bars represent +/- 1 standard deviation.



**Figure 5.12.** Differential scanning calorimetry results for PF1 and PF2.

### ***5.3 Tung Oil and Acetic Anhydride Treated Samples***

#### ***5.3.1 Effect of Tung oil on Dimensional Stability and Modulus of Elasticity***

The use of tung oil to slow water adsorption and to provide some level of dimensional stability is common in the hardboard industry. Panels are often surface coated during final processing steps with a mixture of oils and waxes to produce a water resistant barrier. This knowledge provoked interest in using tung oil as an impregnating agent for VTC treated wood. Although its known use is as a surface treatment, it was hoped that tung oil would have some cell wall bulking properties and provide additional stability beyond that of a physical barrier as a lumen-filling modification.

It was unclear initially if tung oil would penetrate the cell wall or if it would remain mostly in the lumens. Pure tung oil proved too viscous to completely penetrate samples, therefore, mineral spirits was used as a thinning agent. Various degrees of thinning were tested to determine the optimal concentration level and it was found that a 3:1 ratio by weight of mineral spirits to tung oil produced full penetration of treating solution into samples, as well as the desired 10% loading level.

Tung oil treated samples were tested at 25% concentration. The pressure impregnation processes left tung oil treated samples saturated in treating solution. Similar to saturated PF samples, these tung oil samples appeared to lose much of their chemical treatment when dried using the hot platens of the VTC device. It was of interest to determine if the addition of the 24 hour conditioning step would provide better chemical retention and more uniform penetration. Comparisons of dimensional stability and increase in modulus were made between batches made with the conditioning step and without the conditioning step. The same VTC processing schedules used for conditioned and unconditioned PF treated samples were also used for tung oil treated samples.

In comparison to similarly processed phenol-formaldehyde treated samples, tung oil treated samples performed significantly worse in all dimensional stability tests. Figure 5.13 provides ASE values for all chemical modifications performed under all processing parameters. It clearly illustrates the minimal degree to which tung oil was able to stabilize VTC treated wood. Conditioned samples maintained a positive ASE value of 24% and 22% for the soak and boil tests respectively, while

unconditioned samples had values of -8% and -2% for the soak and boil tests respectively. The negative ASE value implies that the tung oil treatment destabilized the wood compared to unmodified controls and caused it to swell more than if the treatment hadn't been applied at all. Unconditioned tung oil treated samples had higher TR and IS values than control samples, however, TS values were not significantly different. Conditioned samples had statistically similar TS values than controls, and had significantly greater TR and IS values in the soak test and statistically similar, TR and IS values in the boil test.

Overall, compared to control samples and compared to similarly treated PF samples, tung oil showed little ability to impart dimensional stability into VTC treated hybrid poplar. Microscopy work showed that the majority of the tung oil polymerized in the lumens of the vessels. Safranin was used as a cell wall stain to determine if treating reagents were able to penetrate cellular structure of the samples. Cell wall material which could not be stained by the safranin was thought to have been bulked by the treating reagent. The cell walls of tung oil treated samples completely accepted the stain. Volumetric measurements taken before and after impregnation showed minimal swelling. Average volumetric swelling from tung oil impregnation was 0.54%, while average volumetric swelling of samples impregnated with deionized water was 6.6%. These observations lend credence to the theory that tung oil is unable to significantly penetrate the cell wall structure. Tung oil acts merely as a lumen filling agent, which is capable of slowing water sorption through physical obstruction, but has no long-term effect on stability.

Tung oil treated samples, both conditioned and unconditioned, had significantly lower increase in modulus than control samples. Values of 120%, 140% and 208% were recorded for conditioned, unconditioned and control samples, respectively (Figure 5.14). With the exception of conditioned samples treated with PF1 at 10%, tung oil treated samples had statistically similar increase in modulus as similarly treated PF samples.

At the density, concentration, and treatment conditions tested, tung oil showed little ability to impart satisfactory dimensional stability to VTC processed hybrid poplar. Compared to both control and PF treated samples, tung oil performed lower in nearly all stability categories. However, it had similar increase in modulus for some similarly treated PF samples. Further testing of more highly densified samples may reveal improvements of stability for tung oil impregnated samples, however, its apparent lack of cell wall penetration may limit its ability to impart stability at any density level.

### *5.3.2. The Effect of Acetic Anhydride on Dimensional Stability and Modulus of Elasticity*

Acetylation of wood with acetic anhydride is a well understood and highly researched area. Previous research has produced highly stable wood-based products, led to the development of an efficient treatment process, and proven commercial viability (Rowell et al. 1986). Although no plants currently exist in the United States,

commercial facilities are producing acetylated wood in Europe, where it is starting to replace many naturally durable tropical hardwood species.

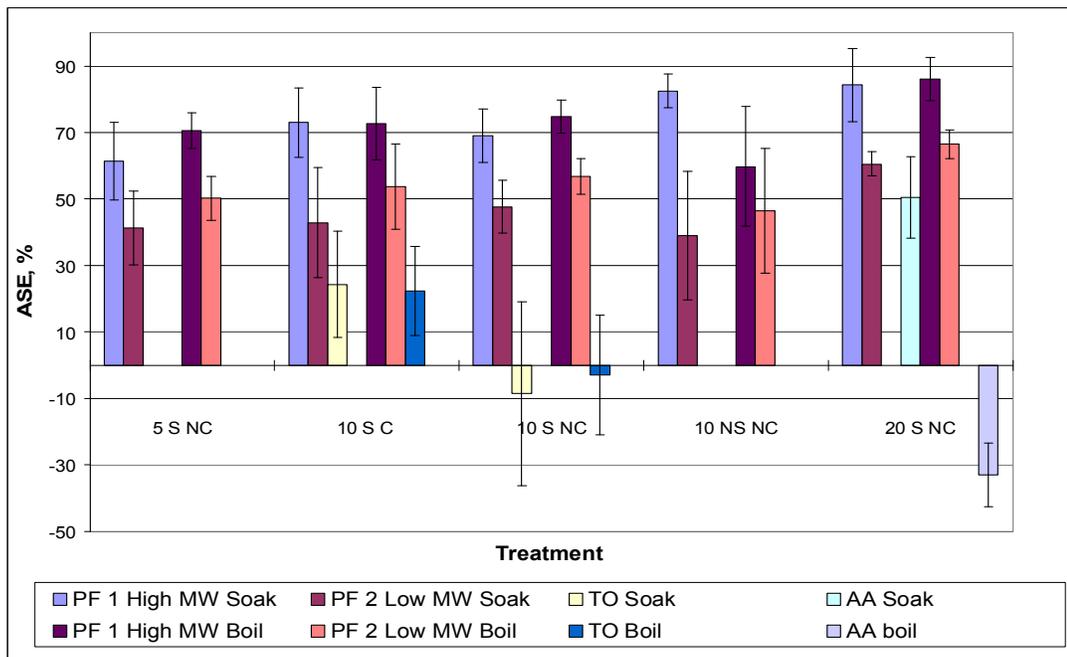
The research conducted for this study aimed to determine if the acetylation process could be easily adapted with the VTC process to produce dimensionally stable wood. Work done by Rowell et al. 1986 examined various temperature and concentration levels to determine what combination of processing parameters furnished optimal results. Knowledge gained from their work was extended to this research and it was decided that a single treatment would be tested with a target WPG of 20%. The more complex treatment procedures involved with acetylation leaves samples in an oven-dry state at the end of the chemical modification. Preliminary testing revealed the standard VTC schedule to be adequate for processing oven-dry acetylated samples. Comparisons of stability and modulus values were made between acetylated samples and control samples, as well as to PF treated samples of the same processing conditions (i.e. PF1 20 S NC and PF2 20 S NC).

Dimensional stability tests for acetylated VTC processed wood resulted in thickness swell values of 19% and 111% , and ASE values of 50% and -33% for the soak test and the boil test, respectively (Figure 5.13). Compared to the control sample, acetylated samples had significantly less thickness swell in the soak test. However, compared to both PF1 and PF2 treated samples, the soak value for acetylated samples was significantly higher. Although the 50% ASE value for the soak test was significantly lower than either of the two PF resins at the same treatment conditions, the value was similar to previous literature for the same WPG.

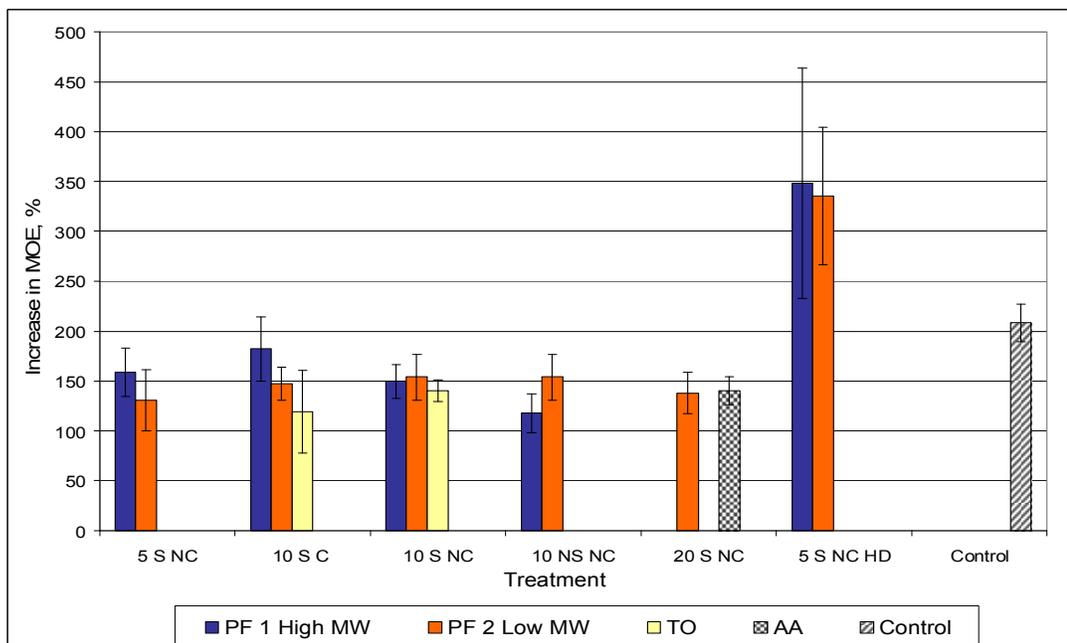
The mechanism by which acetylation provides stability (i.e. the increase in hydrophobicity through the esterification of hydroxyl groups with less hydrophilic acetyl groups) is susceptible to hydrolysis. On account of this, it was thought that acetylated samples would perform poorly in the boil test. As this was the case, it is of little value to make comparisons of these values to other modifications or to the control samples.

The satisfactory ASE soak value, along with a thickness swell equal to half that of the control samples, demonstrates the viability of acetylation as a means of dimensionally stabilizing VTC treated hybrid poplar. The increased processing steps, added chemical cost and caustic nature of acetic anhydride, however, may prevent it from being a feasible method for stabilizing VTC wood.

Figure 5.14 shows the increase in MOE for acetylated samples to be statistically similar to PF2 treated samples under the same treatment conditions, and significantly lower than the untreated control samples (comparisons cannot be made to PF1 treated samples since values were not recorded for treatment batch PF1 20 S NC). During VTC processing, the high heat and moisture environment causes a change in the molecular structure of the cell wall and may result in an increase in entanglements and crosslinking as the various constituents, specifically hemicellulose, degrade and rearrange their structure. The replacement of reactive hydroxyl sites during the acetylation process may result in less chain to chain hydrogen bonding for VTC processed acetylated wood and may explain the lower MOE values compared to controls.



**Figure 5.13.** ASE values for all chemical modifications tested for water soak test and boil test. Error bars represent +/- one standard deviation.



**Figure 5.14.** Increase in MOE for all chemical modifications tested and control. Error bars represent +/- one standard deviation.

## Chapter 6: Microscopic Evaluation

Microscopy work was conducted on samples after undergoing all moisture testing. Goals were to gain a better understanding of the relationship between wood and chemical reagent and to assess the penetration characteristics and final location of the various treating reagents used in this study. It was hoped that qualitative visual information gained from microscopy work would strengthen quantitative results with regards to dimensional stability and modulus.

One sample was randomly chosen from each treatment to be microtomed and viewed under magnification. Samples were cut in half with respect to the length, boiled in water for 5 minutes to soften, and then microtomed from the center of the specimen to produce a transverse surface for observation. This additional boiling was deemed short enough to have negligible effects on the characteristics we wished to view in the samples, since the samples had previously been boiled for two hours. Once microtomed, the 30 micron thick sections were placed in a 10% safranin solution for 5 minutes, followed by deionized water, 70% ethyl alcohol, and 90% ethyl alcohol each for an additional 5 minutes before being mounted on standard microscopy slides. A wetting solution of 50% glycerol and 50% deionized water was used to mount samples.

A Nikon Eclipse E400 microscope with an attached Photometrics Cool Snap digital camera and a Nikon 100 watt, high pressure mercury lamp was used. Samples were viewed using a 330-380nm excitation filter, 400nm dichromatic mirror, and a

420nm long-pass emission filter. Images were captured using Metaview Imaging Series 6.1 software (Universal Imaging Corp., Downingtown, PA). Fluorescence microscopy was deemed the most appropriate method for viewing samples since wood substrate, treating reagent, and the safranin stain all fluoresce at different wavelengths. This allows for easy visual identification of the different substances.

Safranin acts as a chemical reagent indicator by staining all cell wall material which is not bulked by a reagent. This produces a negative, and intuitively, regions that are not stained are those in which the cell wall material has been bulked by a treating reagent. Under fluorescent light, safranin stained wood appears reddish orange, while the remaining unstained bulked wood appears bluish-white. PF or tung oil that has polymerized in cell lumens appears green or orange and is easily identifiable.

Specific key features were noted in samples which include: the identification and degree of cell wall fractures to determine the success of the densification, the location of the treating reagent in the wood cell walls as well as the presence of cured reagent in lumens, depositional patterns of reagent across the samples cross-section and the location and degree of densification maintained after the water testing.

Figures 6.1 and 6.2 show control samples after the water soak and boil tests. These samples were stained with safranin as well, and act as a control for the color of chemically unmodified stained wood substrate and also as a benchmark in regards to the physical condition of the wood cell wall after successful VTC processing. Minimal

fracturing has occurred, and although almost all densification was lost during water tests, evidence of cell wall buckling still exists.

### ***6.1 Phenol Formaldehyde Treated Samples***

Figures 6.3 through 6.8 display PF1 and PF2 treated samples at 5, 10, and 20 percent resin concentration processed with steam and without conditioning. All samples treated under these parameters, regardless of resin type or concentration, showed good cell wall buckling, with minimal fracturing and a high degree of densification. Figures below are displayed for easy comparisons between the different PF resins at the same concentration, as well as between the same PF resin at increasing concentrations.

Batch PF1 5 S NC shown in Figure 6.3, illustrates a characteristic of resin distribution found in almost all samples treated with steam and without conditioning. An edge effect exists where it appears that a higher concentration of resin cured near the surface of the sample, as distinguished by the increase in blue color (unstained bulked cell wall) near the edge. It is believed that during the drying stage, resin migrates to the surface with evaporating water and then cures in this location. Figure 6.4 shows a PF2 treated sample at 5 percent concentration with the same characteristic edge effect, however, to a lesser degree than with the PF1 treated sample. At 5 percent concentration very little resin can be found in the cell lumens for either PF1 or PF2 and it is believed that the majority of the resin is able to penetrate and bulk the cell wall. Much of the compression set still exists for both samples after the water tests and

a visual comparison of PF1 to PF2 shows a slightly higher level of densification remaining in the PF1 sample, which corresponds well to the higher level of dimensional stability exhibited during water testing.

Figures 6.5 and 6.6 show the effect of increasing resin concentration to 10% for PF1 and PF2, respectively. A higher level of densification was maintained for both samples when compared to samples treated at 5% resin solids and is indicative of the increase in dimensional stability with the increase in resin. The image in Figure 6.5 was taken at the center of the sample (midpoint of length, width and thickness) and shows that even after processing, a considerable amount of resin remained in the deepest part of the sample. A very minimal amount of resin can be seen in the lumens and indicates that at this loading level the majority of the resin is still penetrating and bulking the cell wall for PF1 resin. The PF2 treated sample shown in Figure 6.6 has a greater amount of cured resin in the cell lumens compared both to the PF2 treated sample at 5% concentration and the PF1 treated sample at 10%, which strengthens the hypothesis that PF2 is able to penetrate the cell wall of the wood to a lesser degree. Although more resin exists in the lumens, samples treated at 10% concentration with PF2 still exhibit a high level of dimensional stability.

Samples treated at 5% and 10% concentration had only localized regions remain fully densified after water testing. However, at 20% concentration a broader degree of high densification was maintained (Figures 6.7 and 6.8). Cured resin in the lumens is more prominent for both PF1 and PF2 at this loading level, and more cell wall material remained unstained by the safranin indicating greater resin penetration

which is presumably the cause for greater dimensional stability. Excess resin that cures in the lumens may also add dimensional stability by physically bonding cell walls together; this is of debate because the exact moment at which the resin cures is unknown and if resin cure occurs prior to final compression then this mechanism would not be present. In addition, the level of densification may not be high enough to produce enough intimate contact for the PF resin to bond cell walls together. High density samples treated at 5% concentration show much greater dimensional stability and higher increase in modulus compared to lower density samples at both the same and at higher concentrations. It is believed that higher densifications provide the intimate contact between cell walls necessary for PF resin to act as a binder and form a solid material void of open lumens.

It should also be noted that for both PF1 and PF2, resin that remained in the lumens coalesced as small spheres rather than adhering to the lumen walls. Even in samples where entire vessel lumens were filled, they were filled by a conglomeration of resin balls and not a contiguous solid. The reason for this is not currently understood, but it is believed that pre-cure of the resin may be the cause.

Figures 6.9 and 6.10 show self-steamed, unconditioned samples treated at 10% resin concentration with PF1 and PF2, respectively. The replacement of the standard steaming step with a self-steaming step showed no effect on the swollen dimensions of samples after water testing when compared to samples that were steamed. However, once dried, self-steamed samples exhibited a high degree of irreversible swelling. This led to the conclusion that the steaming step was critical in providing complete fixation

of the compression set imparted during VTC processing. Self-steamed samples have a very different resin distribution pattern than steamed samples, display greater cell wall fracturing, and lower densification levels after water testing. As stated earlier, self-steaming most likely provides inadequate softening of the wood cell walls, which leads to fracturing when buckled. This is evident in Figure 6.10 and can also be inferred from smaller increases in MOE values compared to control samples and PF treated steamed samples.

Samples treated with the additional conditioning step are displayed in Figures 6.11 and 6.12 for PF1 and PF2, respectively. Samples conditioned for 24 hours at room temperature prior to VTC processing showed no significant difference in their stability characteristics compared to unconditioned samples. Microscopy work revealed a tendency for conditioned samples to have more resin cured in cell lumens. However, this seemed to have no adverse effects on swelling. Although resin distribution was expected to be more uniform for conditioned samples, this was not evident from microscopy work. Conditioned samples showed similar characteristics as unconditioned samples treated with the same resin concentration in regards to cell wall fracturing and the location of resin across the samples cross-section. Effects of conditioning on MOE were minimal and differences which did exist could not be identified visually through microscopy.

High density samples treated at 5% resin concentration for both PF1 and PF2 are shown in Figures 6.13 and 6.14. High density samples appear to have less open space in vessel lumens and much of the collapsed cell walls have remained in contact

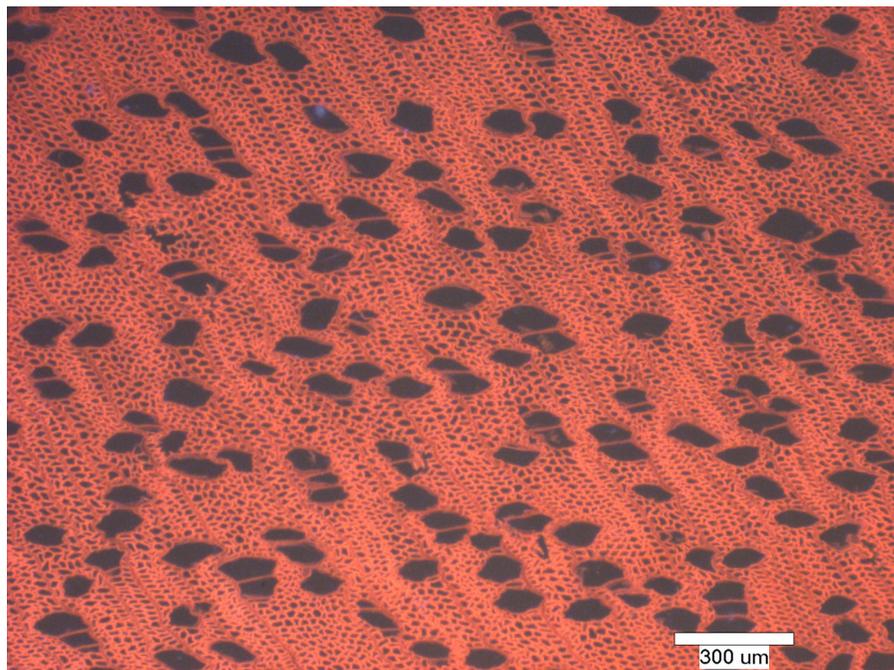
with each other even after water testing. Low levels of cell wall fracturing were observed and extremely high increases in MOE were realized.

Overall, the phenol formaldehyde treatment proved to be highly compatible with the VTC process. Alterations in the processing parameters (i.e. conditioning and self-steaming) did not prove to be beneficial to either the final product or the ease of production. Drying samples with the heated platens of the VTC device and applying the standard VTC processing schedule resulted in the highest quality modified samples based on ease of production and the greatest increases in stability and MOE.

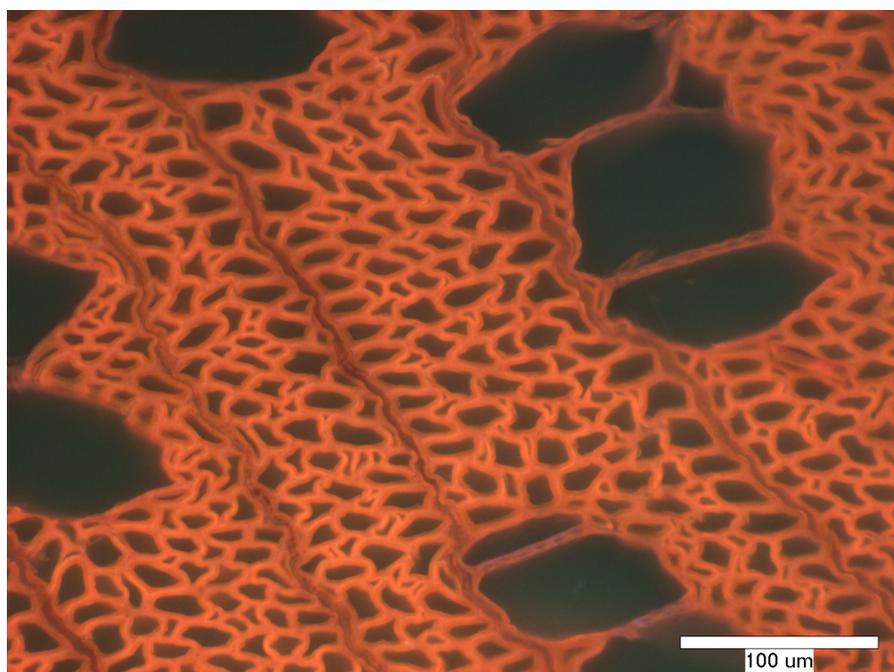
### ***6.2 Tung Oil and Acetic Anhydride Treated Samples***

Microscopy work done on tung oil treated samples for both conditioned and unconditioned batches showed no evidence of tung oil absorption into the cell wall. Lumens of both vessels and fibers were filled with polymerized tung oil and the safranin staining dye was able to penetrate nearly 100 percent of the cellular structure of the samples (Figures 6.15 and 6.16). Almost full recovery of compression set was achieved after boiling the samples, much higher than control VTC samples, indicating that tung oil interferes with the normal fixation process under standard conditions. Visual evidence, along with volumetric measurements that show no swelling of the wood structure after impregnation, confirms tung oil's inability to penetrate the wood cell wall. Tung oil is thus limited to physical obstruction of moisture on a macro level, and while it may impart some degree of short-term dimensional stability, long-term stability is not improved.

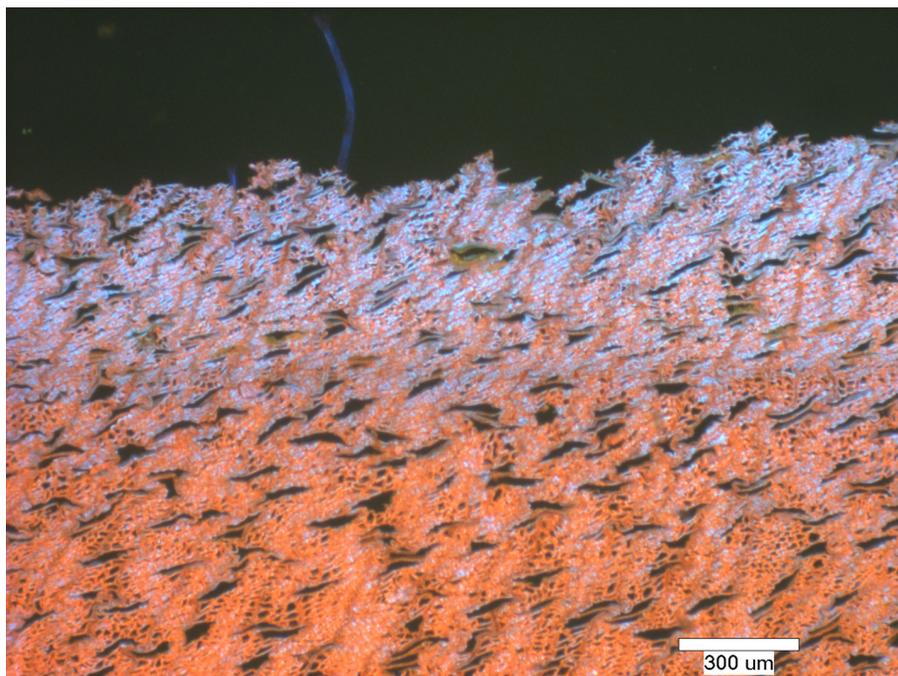
Microscopy work conducted on acetylated samples showed that minimal cell wall fracturing occurred during the VTC process. Increase in modulus was lower than control samples; however, similar to PF2 treated samples at 20% resin concentration. Although the boil test caused nearly complete recovery of compression set, (Figure 6.17) results were expected to be poor and emphasis should be put on the high stability values achieved in the water soak test. The acetylation process is able to penetrate the entire cross-section of the sample as seen by the uniform spectrum of blue where safranin was unable to penetrate the cell wall. Acetylation with acetic anhydride proved to be completely compatible with the VTC process.



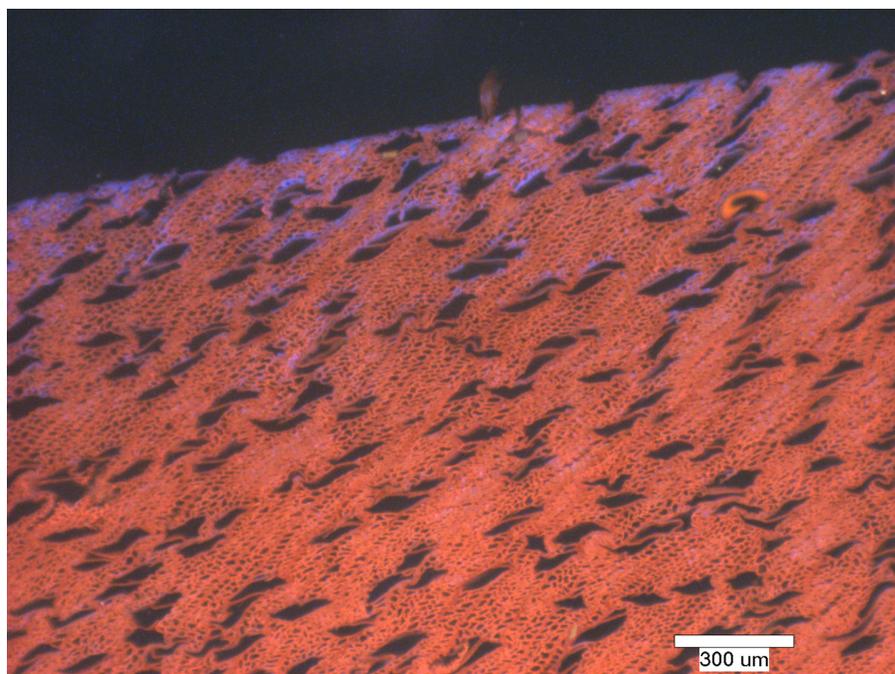
**Figure 6.1.** Control sample. VTC processed with no chemical modification.



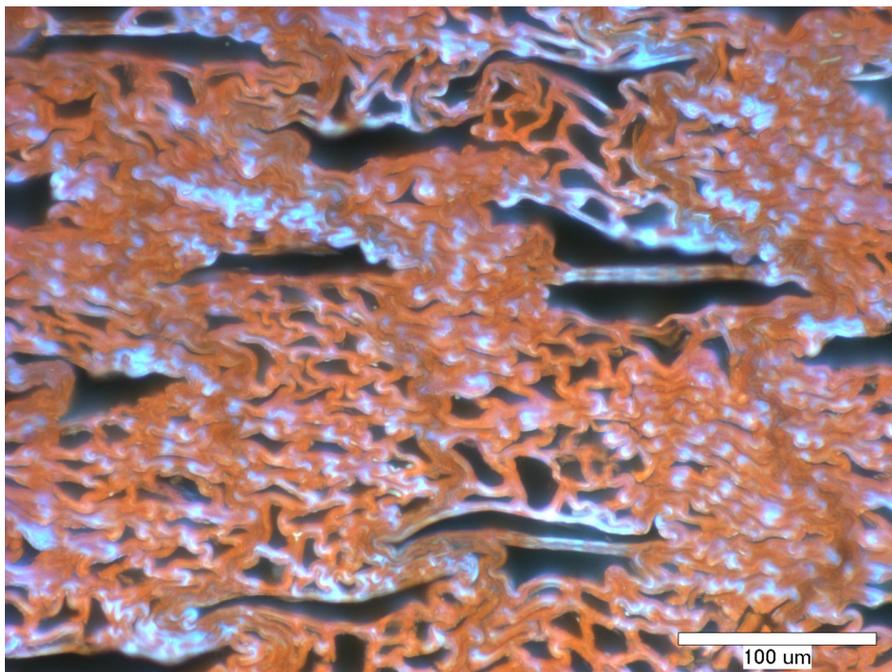
**Figure 6.2.** Control sample. VTC processed with no chemical modification.



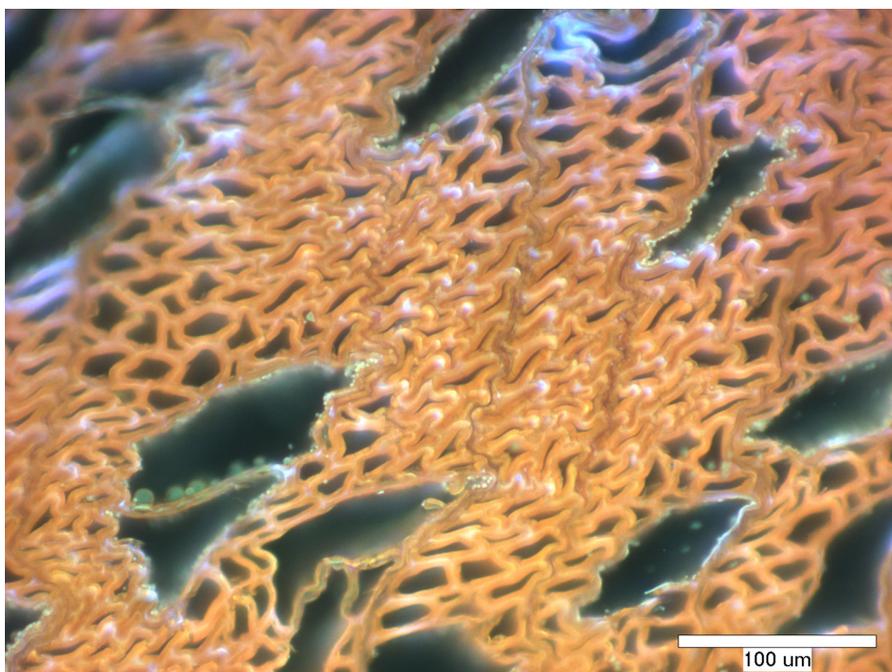
**Figure 6.3.** Sample PF1 5 S NC. Impregnated with PF1 resin at 5% concentration and processed with steam and without conditioning.



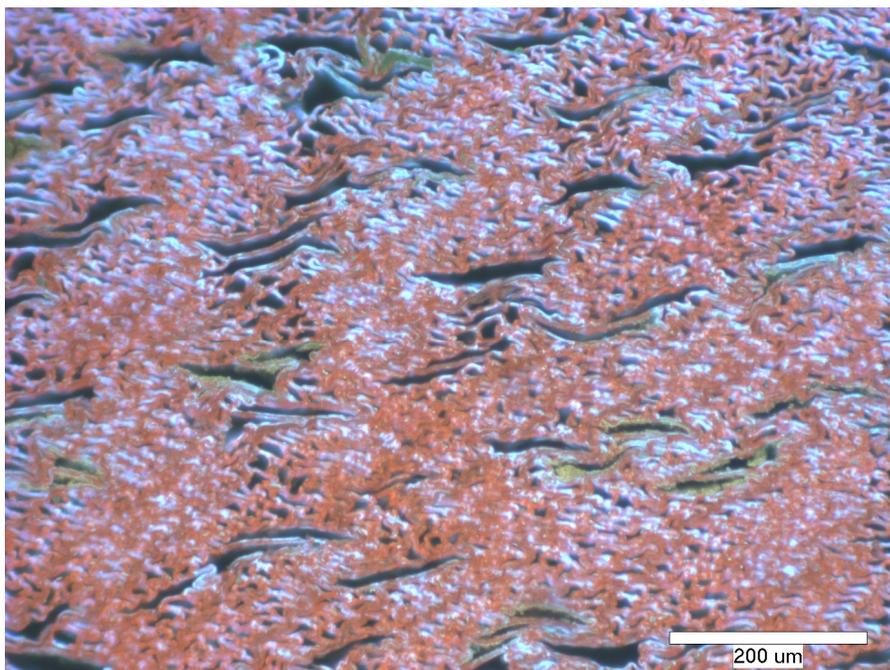
**Figure 6.4.** Sample PF2 5 S NC. Impregnated with PF2 resin at 5% concentration and processed with steam and without conditioning.



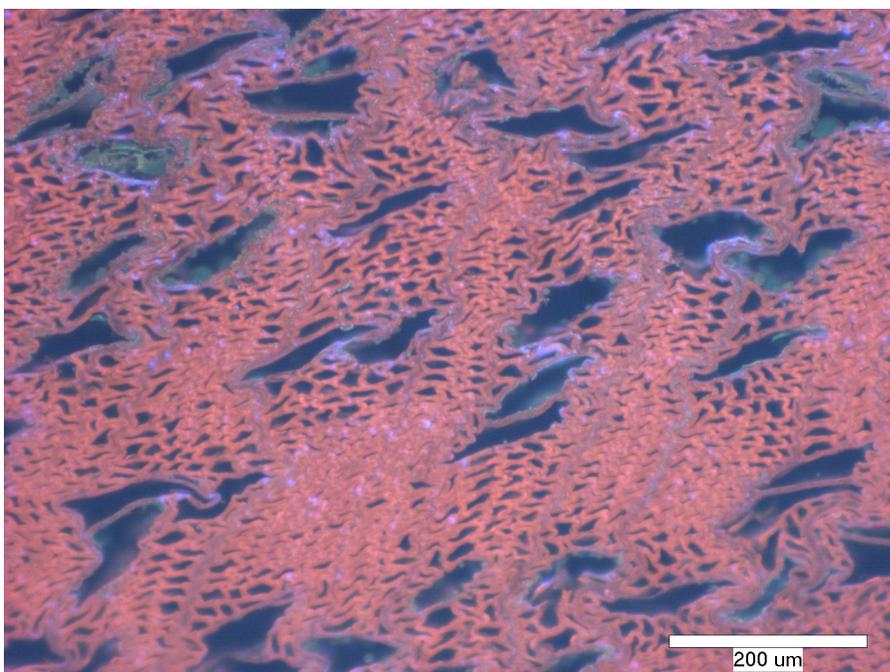
**Figure 6.5.** Sample PF1 10 S NC. Impregnated with PF1 resin at 10% concentration and processed with steam and without conditioning.



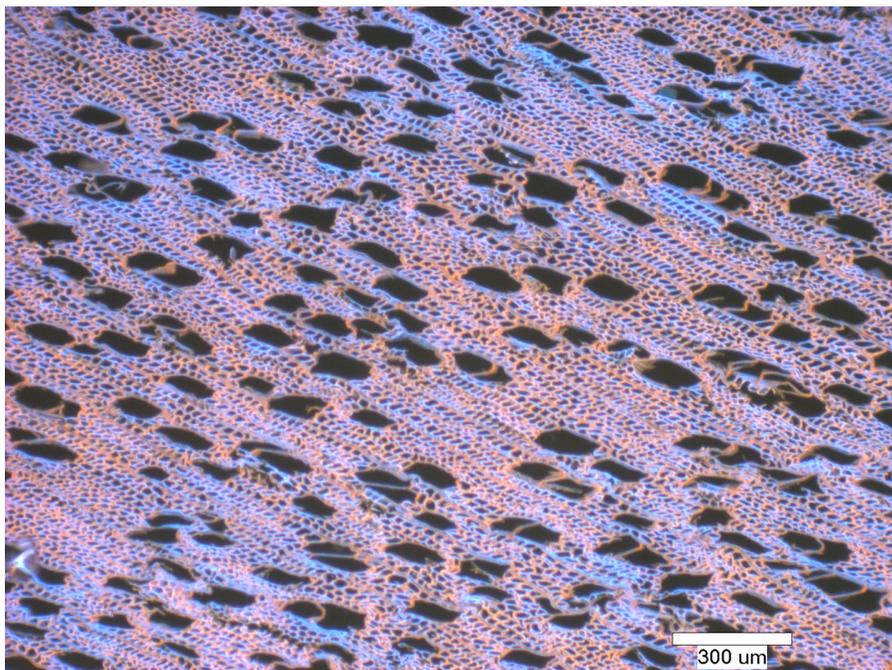
**Figure 6.6.** Sample PF2 10 S NC. Impregnated with PF2 resin at 10% concentration and processed with steam and without conditioning.



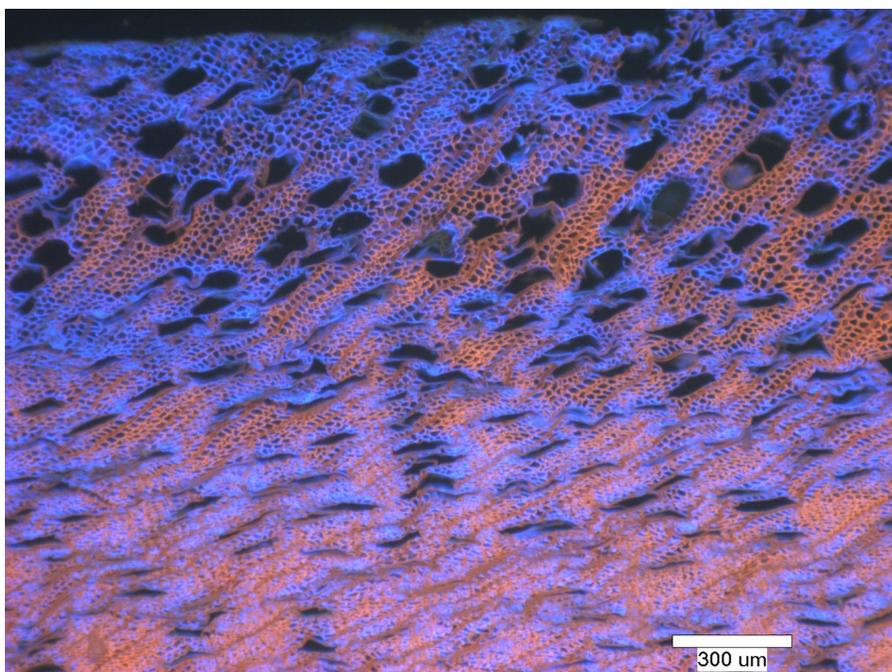
**Figure 6.7.** Sample PF1 20 S NC. Impregnated with PF1 resin at 20% concentration and processed with steam and without conditioning.



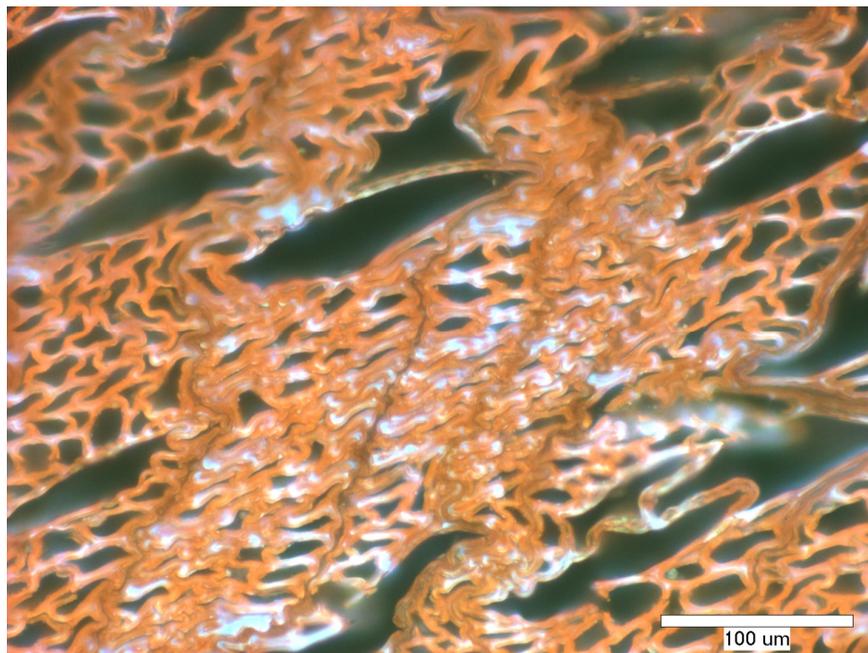
**Figure 6.8.** Sample PF2 20 S NC. Impregnated with PF2 resin at 20% concentration and processed with steam and without conditioning.



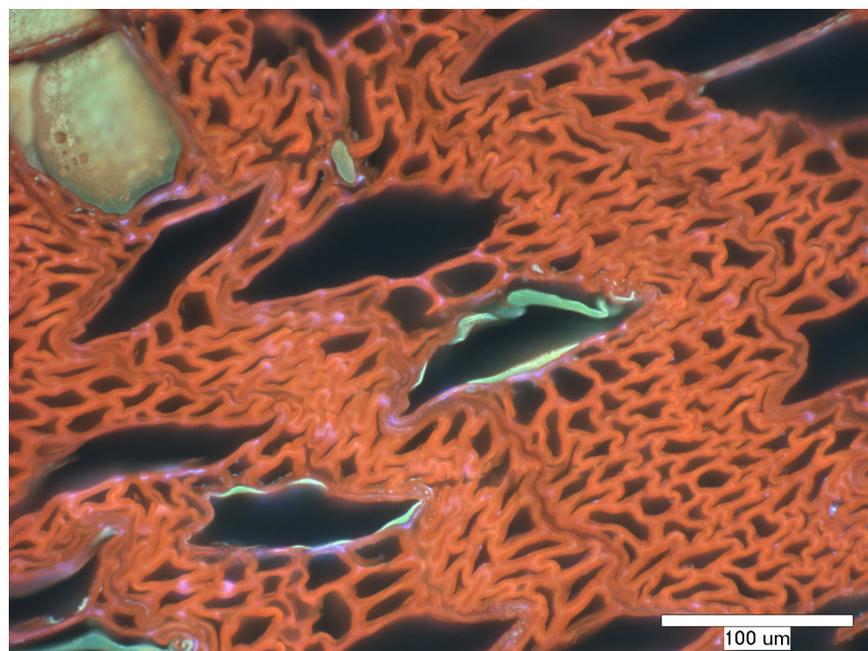
**Figure 6.9.** Sample PF1 10 NS NC. Impregnated with resin PF1 at 10% concentration and processed without steam or conditioning.



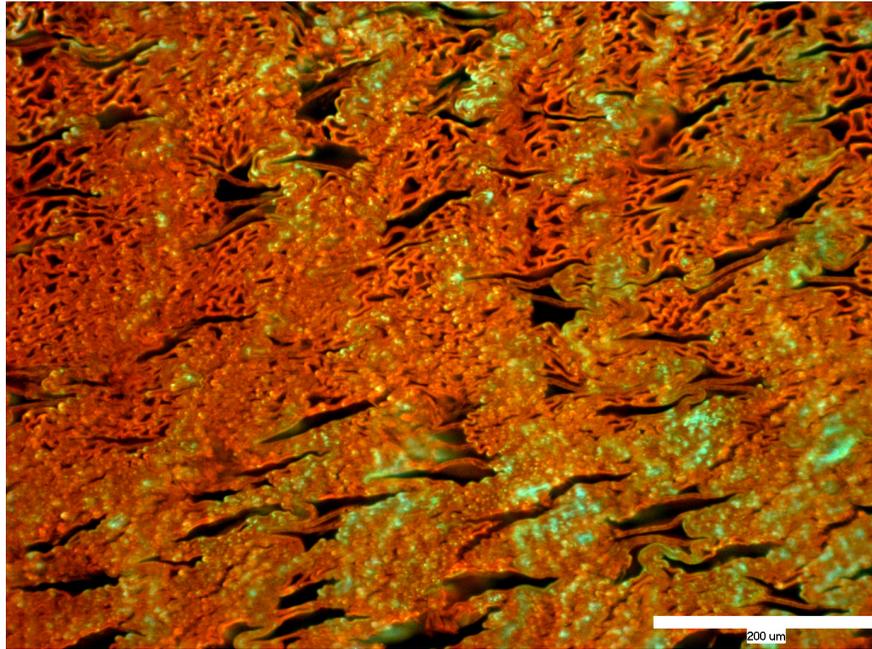
**Figure 6.10.** Sample PF2 10 NS NC. Impregnated with resin PF2 at 10% concentration and processed without steam or conditioning.



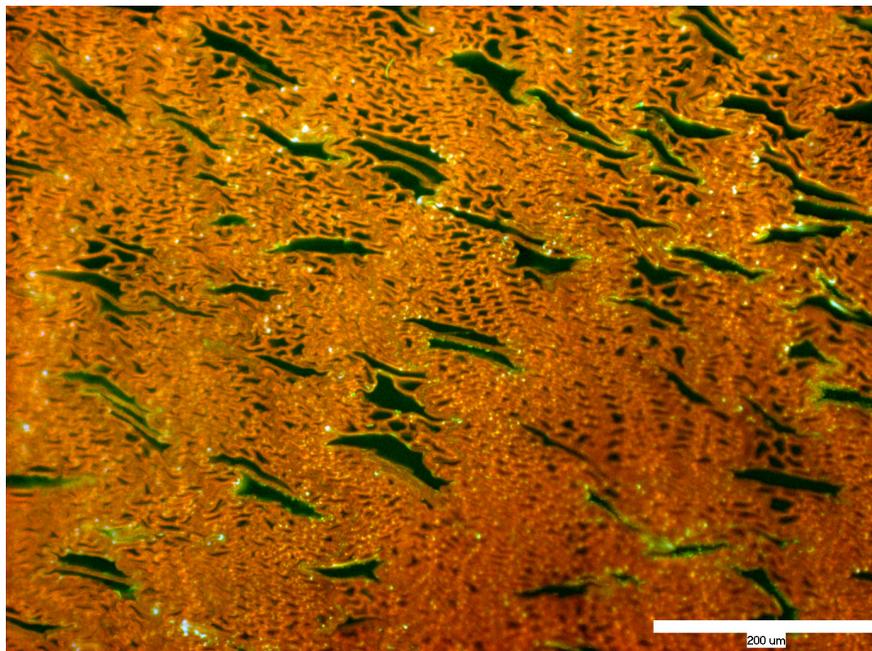
**Figure 6.11.** Sample PF1 10 S C. Impregnated with resin PF1 at 10% concentration and processed with steam and conditioning.



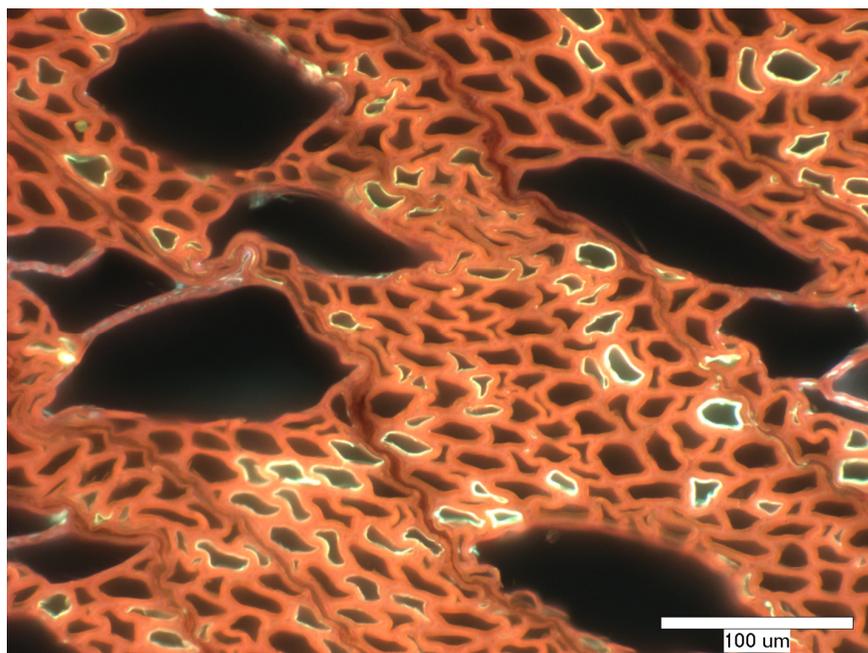
**Figure 6.12.** Sample PF2 10 S C. Impregnated with PF2 resin at 10% concentration and processed with steam and conditioning.



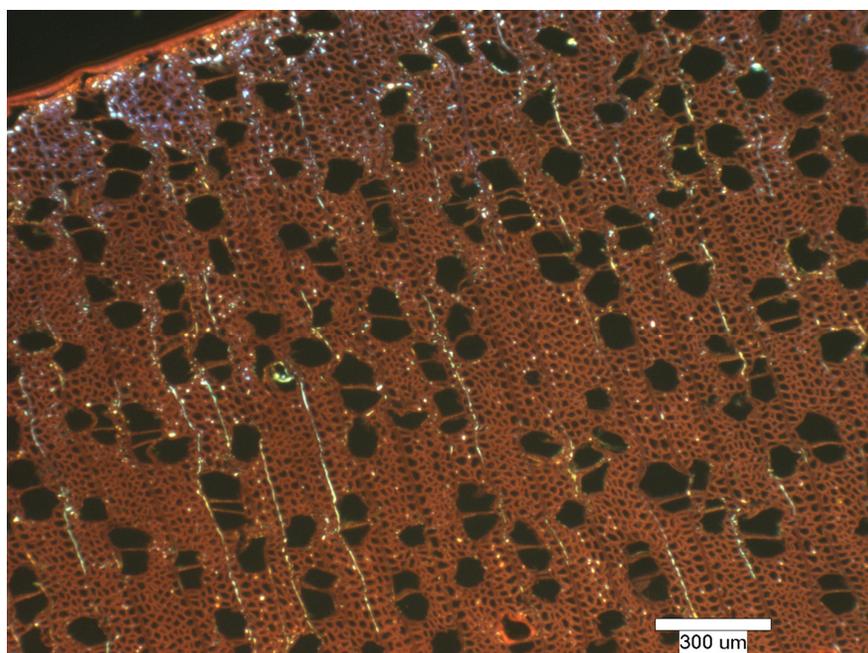
**Figure 6.13.** Sample PF1 5 S NC HD. Impregnated with resin PF1 at 5% concentration and processed with steam and without conditioning to high level densification.



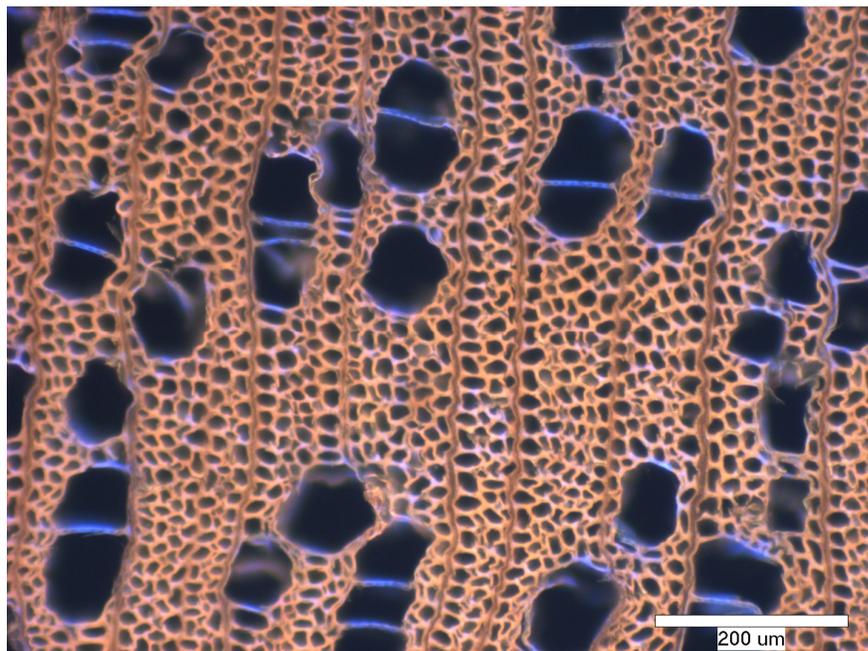
**Figure 6.14.** . Sample PF2 5 S NC HD. Impregnated with PF2 at 5% concentration and processed with steam and without conditioning to high level densification.



**Figure 6.15.** Sample TO 10 S C. Impregnated with tung oil at 10% concentration and processed with steam and conditioning.



**Figure 6.16.** Sample TO 10 S NC. Impregnated with tung oil at 10% concentration and processed with steam and without conditioning.



**Figure 6.17.** Sample AA 20 S NC. Impregnated with acetic anhydride to achieve a final WPG of approximately 20% and processed with steam and without conditioning.

## Chapter 7: Summary and Conclusions

The objectives for this study were to determine the feasibility of combining chemical modification techniques with the viscoelastic thermal compression process, and further to quantify the resulting effect of each modifying technique on dimensional stability and mechanical properties. This was achieved through the use of various thickness swell analyses, mechanical testing and microscopic evaluation. A variety of treatment and processing parameters were tested to explore relationships between dimensional stability and treatment conditions. The following conclusions were made from the results of this study:

1. Phenol formaldehyde and acetic anhydride were successfully coupled with the viscoelastic thermal compression process to produce a more dimensionally stable product compared to control samples, however, at the concentrations and density tested, tung oil did not prove to impart dimensional stability to VTC processed samples.
2. All chemically modified samples, regardless of chemical reagent or processing parameters, had smaller increases in MOE than control samples.
3. Dimensional stability increased with increasing resin concentration for both high and low molecular weight PF resins.
4. The high molecular weight resin, PF1, was able to stabilize VTC treated hybrid poplar more effectively than the low molecular weight PF resin.

5. A nonlinear trend exists between chemical retention and dimensional stability for PF treated samples, with lower WPG producing the highest stability per unit of resin retained.
6. PF treated samples processed with steam and without conditioning produced the best combination of increase in dimensional stability and MOE.
7. Replacing the standard steaming step in the VTC process with a self-steaming step had no beneficial result. Samples were more prone to irreversible swelling and had lower increases in MOE - most likely due to fractures in the cell wall.
8. Conditioning impregnated samples prior to VTC processing had little to no influence on overall stability or modulus values.
9. Nearly all irreversible swelling was eliminated for PF1 treated samples, and most of the irreversible swelling was eliminated for PF2 treated samples.
10. Overall, samples modified with PF1 at 20% resin solids concentration and VTC processed with steam and without conditioning had the highest absolute dimensional stability, however samples modified with PF1 at 5% resin solids concentration and VTC processed with steam and without conditioning had the highest stability per unit of resin retained.
11. Acetylation with acetic anhydride produced similar stability values as PF treated samples under water soak conditions, however, acetyl bonds were

most likely cleaved through hydrolysis when boiled and resulting stability values were extremely poor.

12. High density PF treated samples had relatively similar stability values compared to lower density samples processed under the same conditions. MOE values were significantly higher than both lower density PF treated samples and controls.
13. Higher density, resin-impregnated VTC wood is believed to impart greater increase in MOE due to more intimate contact between collapsed cell walls.

## Chapter 8: Future Research

The research conducted for this study has answered many questions which in turn have also revealed new ones. Future work focusing on low resin concentrations using various molecular weight resins would be highly beneficial for determining optimal chemical treatments. Stress-strain analysis of samples during the VTC process would provide a greater understanding of the collapse behavior of the specimens and the plasticizing effect of chemical treatments. Biological resistance has yet to be studied with VTC processed wood, however, it can be speculated that the low EMC's of both chemically modified and unmodified VTC wood would result in a biologically resistant material.

In the scope of scaling up the VTC process, during the time this study was conducted a larger scale VTC device was assembled enabling small composite panels to be processed. The ability to make larger scale test specimens opens the door for new research to be conducted using various types and sizes of parent material to produce a varying array of final products. As the wood-based composites field broadens with the applications of new technologies, the VTC process will grow hand in hand.

## Bibliography

- Anderson M, AM Tillman (1989) Acetylation of jute. Effects on strength, rot resistance and hydrophobicity. *Journal of Applied Polymer Science* 37:3437-3447.
- Beckers EPJ, H Militz (1994) Acetylation of solid wood. Initial trials on lab and semi industrial scale. Second Pacific Rim Bio-Based Composites Symposium, Vancouver, Canada, 6–9 November. Wood Science Department, Faculty of Forestry, University of British Columbia, Vancouver, pp 125–133.
- Bowyer J, R Shmulsky, JG Haygreen (2003) *Forest Products and Wood Science: An Introduction* (4th Ed.) Iowa State University Press, Des Moines.
- Carll CG (1997) Review of thickness swell in hardboard siding: Effect of processing variables. Gen. Tech. Rep. FPL-GTR-96. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 10 p.
- Chang HT, ST Chang (2002) Moisture excluding efficiency and dimensional stability of wood improved by acetylation. *Bioresource Technology* 85:201-204.
- Deka M, P Das, CN Saikia (2000) Chemical modification of wood with thermosetting resin: effect on dimensional stability and strength property. *Biosource Technology* 73:179-181.
- Farmer RH (1967) *Chemistry in the Utilization of Wood*. Pergamon Press, New York.
- Feist WC, JK Little, JM Wennesheimer (1985) The moisture excluding effectiveness of finishes on wood surfaces. Res. Pap. FPL USDA Forest Products Lab, Madison, WI.
- Furuno T, Y Imamura, H Kajita (2004) The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls. *Wood Sci. Tech.* 37(5):349-361.
- Simpson W, A TenWolde (1999) *Wood Handbook: Wood as an Engineering Material*. USDA General Technical Report FPL-GTR-113 USDA Madison, WI.
- Fuchs, Walter 1928. Genuine lignin. I. Acetylation of pine wood. *Chemische Berichte* 61b:948-951.

- Fukata S, Y Takasu, Y Sasaki, Y Hirashima (2007) Compressive deformation of Japanese cedar (*Cryptomeria japonica*). *Wood and Fiber Sci* 39(4):548-555.
- Fuller CS (1931) Oxidation of solid films of tung oil: Mechanism of the reaction at elevated temperature. *Industrial and Engineering Chemistry* 23(12):1458-1462.
- Galperin AS, GG Kuleshov, VI Tarashkevich, GM Shutov (1995) Manufacturing and properties of modified wood: a review of 25 years work. *Holzforschung* 49(1): 45-50.
- Haygreen JG, RO Gertjeansen (1971) Improving the properties of particleboard by treating the particles with phenolic impregnating resin. *Wood and Fiber* 3(2):95-104.
- He G, B Riedl (2004) Curing kinetics of phenol formaldehyde resin and wood-resin interactions in the presence of wood substrate. *Wood Sci Tech.* 38: 69-81.
- Heger F, M Groux, F Girardet, C Welzbacher, AO Rapp, P Navi (2004) Mechanical and durability performance of THM-densified wood. Pages 1-10 *in* COST Action E22 Environmental Optimisation of Wood Protection Final Workshop, March 23-24, 2004, Lisboa, Portugal.
- Hill C (2006) *Wood Modification: Chemical, Thermal and Other Processes*. John Wiley & Sons Ltd., England.
- Homan WJ, JM Jorissen (2004) Wood modification developments. *HERON* 49(4): 361-386.
- Hon DNS (1996a) *Chemical Modification of Lignocellulosic Materials*. Marcel Dekker, New York.
- Hon DNS (1996b) *Chemical Modification of Wood*. Marcel Dekker, New York.
- Hsu WE, W Schwald, J Schwald, JA Shields (1988) Chemical and physical change required for producing dimensionally stable wood-based composites. *Wood Sci. Tech.* 22: 281-289.
- Immaru Y, B Subiyanto, RM Rowell, T Nelsson (1989) Dimensional stability and biological resistance of particleboard made from acetylated albizzia wood particles. *Japan J. Wood Res.* 76:49-58.

- Inoue M, M Norimoto, M Tanahashi, RM Rowell (1993) Steam or heat fixation of compressed wood. *Wood and Fiber Sci* 25(3): 224-235.
- Johnson JD Hybrid Poplar: An Overview. Washington State University.  
[http://www.puyallup.wsu.edu/poplar/SAFPoplarOverview\\_files/v3\\_document.htm](http://www.puyallup.wsu.edu/poplar/SAFPoplarOverview_files/v3_document.htm) (17 November 2007).
- Kajita H, Y Imamura (1991) Improvement of physical and biological properties of particleboards by impregnations with phenolic resin. *Wood Sci Tech* 26(1):63-70.
- Kamke FA (2006) Densified radiata pine for structural composites. *MADERAS: Ciencia y Tecnología* journal 8(2):83-92.
- Kamke FA, EV Kultikova, CA Lenth (2000) Viscoelastic thermal compression of wood. In: Proc. 5<sup>th</sup> Pacific Rim Bio-Based Composites Symp., December 10-13, 2000, Canberra, Australia. Ed. P. Evans, Dept. Forestry, Australian National University, Canberra, Australia, pp. 292-302.
- Kumar S (1994) Chemical modification of wood. *Wood and Fiber Sci* 26(2): 270-280.
- Lenth CA, FA Kamke (2001a) Equilibrium moisture content of wood in high temperature pressurized environments. *Wood and Fiber Science*, 33(1):104-118.
- Lenth CA, FA Kamke (2001b) Moisture dependant softening behavior of wood. *Wood and Fiber Science*, 33(3):492-507.
- Li JZ, T Furuno, Katoh, T Uehara (2000) Chemical modification of wood by anhydrides without solvents or catalysts. *Journal of Wood Science* 46: 215-221.
- Meyer JA (1977) Wood-polymer composites and their industrial applications. *Wood Technology: Chemical aspects*. I. S. Goldstein, American Chemical Society Symposium Series. 43: 301-325.
- Meyer, J. A. (1984). *Wood-polymer Materials. The Chemistry of Solid Wood*. R. M. Rowell. American Chemical Society Washington, D.C.
- Narayanamurti, V.D. B.K. Handa.(1953). Acetylated wood. *Das Papier* 7:87-92.
- Navi P and F Girardet (2000) Effect of THM treatment on the structure and properties of wood. *Holzforschung* 54:287-293.

- Obataya E, M Sugiyama, B Tomita (2002) Dimensional stability of wood acetylated with acetic anhydride solution of glucose pentaacetate. *Journal of Wood Science* 48: 315-319.
- Ohmae K, K Minato, M Norimoto (2002) The analysis of dimensional changes due to chemical treatments and water soaking for Hinoki (*Chamaecyparis obtusa*) wood. *Holzforschung* 56(1):98-102
- Panshin AJ, DeZeeuw C (1980) *Textbook of Wood Technology* (4th ed.). McGraw-Hill, New York.
- Ramsden M, Blake FSR, Fey NJ (1997) The effect of acetylation on the mechanical properties, hydrophobicity, and dimensional stability of *Pinus sylvestris*. *Wood Science and technology* 31: 97-104.
- Rhodes FH, Ling TT (1925) The Oxidation of Chinese Wood Oil. *Industrial and Engineering Chemistry* 17(5): 508-512.
- Rosen HN (1976) Moisture adsorption and swelling in polyethylene glycol and polymethyl methacrylate treated wood a high relative humidity. *Forest Products Journal* 7(4): 249-255.
- Rowell RM (2006) Acetylation of wood, journey from analytical technique to commercial reality. *Forest Products Journal* 56(9): 4-12.
- Rowell RM (1982) Distribution of acetyl groups in southern pine reacted with acetic anhydride. *Wood Science* (15): 172-182
- Rowell RM (1975) Chemical modification of wood: advantages and disadvantages. *Proc. Am. Wood Preservers' Assoc* 71: 1-10. AWPA, Granbury, TX.
- Rowell RM (1983) Chemical modification of wood: A review. *Commonwealth Forestry Bureau, Oxford, England* 6(12): 363-382.
- Rowell RM (1996) Chemical modification of lignocellulosics. In: *Proceedings, International Workshop on Frontiers of Surface Modification and Characterization of Lignocellulosic Fibers*, Gatenholm P Chihani T, eds. Fiskebackskil, Sweden.
- Rowell RM (2005) Chemical modification of wood. *Handbook of wood chemistry and wood composites*. RM Rowell, ed. Chapter 14, 381-420, CRC Press, Boca Raton, FL.

- Rowell RM, ed. (1991) *Chemical Modification of Wood*. Handbook on Wood and Cellulosic Materials. New York, Marcel Dekker.
- Rowell RM, Norimoto M (1987) Acetylation of bamboo fiber. *J. Jap. Wood Res. Soc.* 33(11):907-910.
- Rowell RM, Tillman A, R Simonson (1986) A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. *Journal of Wood Chemistry and Technology* 6(3): 427-448.
- Rowell, RM, JA Youngquist, JS Rowell, JA Hyatt (1991). Dimensional stability of aspen fiberboards made from acetylated fiber. *Wood and Fiber Sci* 23(4):558-566.
- Rowell RM, Lange S, McSweeney J, Davis M (2002) Modification of wood fiber using steam. Pages 606-615 *in* Proceedings of the 6<sup>th</sup> Pacific Rim Bio-Based Composite Symposium, 27 Oct 2002, Portland, OR, Oregon State University, Corvallis, OR.
- Rowell RM, Lichtenberg RS, Larsson P (1992) Stability of acetylated wood to environmental changes. *Wood and Fiber Sci.* 25(4):359-364.
- Rowell RM, Simonson R, Tillman AM (1990) Acetyl balance for the acetylation of wood particles by a simplified procedure. *Holzforschung*, 44(4): 263-269.
- Rowell RM, Simonson R, Tillman AM (1986) A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. *Journal of Wood Chemistry Technology* 6(3):427-448.
- Rowell RM, Ellis WD (1978) Determination of dimensional stabilization of wood using the water-soak method. *Wood and Fiber* 10(2):104-111.
- Russell SD. Tung and Linseed Oils. Sydney Wood Turners Guild Inc.  
<http://www.sydneywoodturners.com.au/site/articles/finishing/oils.html>. (27 Dec 2006).
- Ryu JY, Imamura Y, Takahashi M, Kajita H (1993) Effects of molecular weight and some other properties of resin on biological resistance of phenolic resin treated wood. *Mokuzai Gakkaishi* 39(4):486-492.
- Shams MI, Kagemori N, Yano H (2004) Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin I: effects of pressing pressure and pressure holding. *J Wood Sci* 50:337-342.

- Shams MI, Kagemori N, Yano H (2004b) Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin II: effects of processing parameters. *J Wood Sci* 50:343-350.
- Shams MI, Kagemori N, Yano H (2006) Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin IV: species dependency. *J Wood Sci* 52:179-183.
- Shams MI, Kagemori N, Yano H (2006a) Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin V: effects of steam pretreatment. *J Wood Sci* 52:389-394.
- Sekino N, Inoue M, Irle M, Adcock T (1999) The mechanics behind the improved dimensional stability of particleboards made from steam-pretreated particles. *Holzforschung* 53(4):435-440.
- Shumann CL (1916) Polymerization of Chinese wood oil. *The Journal of Industrial and Engineering Chemistry* 8(1): 5-15.
- Siau JF, Meyer JA (1966) Comparison of the properties of heat and radiation cured wood-polymer combinations. *Forest Products Journal* 16(8): 47-56.
- Simpson WT, ed. (1991). *Dry Kiln Operator's Manual*. Agric. Handbook AH-188. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.
- Smith LA, Cote WA (1971) Studies of penetration of phenol-formaldehyde resin into wood cell walls with the SEM and energy-dispersive X-ray analyzer. *Wood and Fiber Science* 3(1): 56-57.
- Stamm AJ, Seborg RM (1936) Minimizing wood shrinkage and swelling - treating with synthetic resin-forming materials. *Ind. Eng. Chem.* 28(10): 1164-1169.
- Stamm AJ, Elwin EH (1953) *Chemical Processing of wood*. New York, Chemical Publishing Co. Inc.
- Stamm AJ (1956) Dimensional stabilization of wood with carbowaxes." *Forest Products Journal* 6(5): 201-204.
- Stamm AJ (1959) The dimensional stability of wood. *Forest Products Journal* 9(10): 375-381.

- Stamm AJ, Bachler RH (1960) Five modified Woods. *Forest Products Journal* 10(1): 22-26.
- Stamm AJ (1964) *Wood and Cellulose Science*. The Ronald Press Company, New York.
- Sutton WRJ (1993) The World's Need for Wood. Pages 21-28 *in* *The Globalization of Wood: Supply, Processes, Products, and Markets*. Forest Products Society, Portland, OR.
- Tomme F, Girardet F, Gfeller B, Navi P (1998) Densified wood: an innovative product with highly enhanced characters. *World Conference on Timber Engineering, Switzerland*. Vol. 2, Pp. 640-647.
- Yano H, Hirose A, Inaba S (1997) High-strength wood-based materials. *Journal of Materials Science*. 16:1906-1909.
- Yano H, Mori K, Collins PJ, Yazaki Y (2000) Effects of element size and orientation in production of high strength resin impregnated wood based materials. *Holzforschung*. 54:443-447.
- Yilgor N, Unsal O, Kartal SN (2001). Physical, mechanical and chemical properties of steamed Beech wood. *For Prod J*. 51(11/12):89-93.
- Yoshimura Y (1984) Polymerization of tung oil by reaction of phenols with tung oil. *Journal of Applied Polymer Science* 29(9):2735-2747.
- Wallstrom L, Lindberg KAH (1999) Measurement of cell wall penetration in wood of water-based chemicals using SEM/EDS and STEM/EDS technique. *Wood Science and Technology* 33:111-122.
- Wan H, Kim MG (2006) Impregnation of southern pine wood and strands with low molecular weight phenol-formaldehyde resins for stabilization of oriented strandboard. *Wood and Fiber Science* 38(2):314-324.
- Wan H, Kim MG (2006a) Distribution of phenol-formaldehyde resin in impregnated southern pine and the effects of wood stabilization. *Forest and Wildlife Research Center, Mississippi State University*. Unpublished Report.
- Wexler H (1964) Polymerization of drying oils. *Chemical Reviews* 64(6): 591-609

## Appendix A: Studentized T-Tests and Calculated Raw Values

**Table A.1.** Statistical P-values for all Studentized t-tests performed for comparisons made between values of different treatments. P-values smaller than 0.05 were considered statistically significant.

COMPARISONS		Increase in MOE	Increase MOE/WPG	ASE Soak	Thickness Swell Soak	Percent Thickness Swell
PF1 5 S NC	PF1 10 S NC	0.360	0.000	0.107	0.210	0.138
	PF1 20 S NC	-	-	0.000	0.001	0.000
	PF2 5 S NC	0.037	0.119	0.001	0.000	0.000
	Control	0.000	-	-	0.000	0.000
PF1 10 S C	PF1 10 S NC	0.013	0.046	0.362	0.362	0.421
	PF1 10 NS NC	0.000	0.004	0.022	0.078	0.051
	PF2 10 SC	0.009	0.870	0.000	0.589	0.000
	PF2 1 S NC	0.036	0.004	0.000	0.279	0.000
	TO 10 S C	0.001	0.002	0.000	0.000	0.000
	Control	0.045	-	-	0.000	0.000
PF 1 10 S NC	PF 1 10 NS NC	0.001	0.064	0.000	0.003	0.002
	PF1 20 S NC	-	-	0.003	0.003	0.002
	PF2 10 S NC	0.635	0.000	0.000	0.015	0.000
	PF 2 10 NS NC	0.000	0.436	0.001	0.001	0.000
	TO10 S NC	0.168	0.565	0.000	0.000	0.000
	Control	0.000	-	-	0.000	0.000
PF1 10 NS NC	PF2 10 NS NC	0.195	0.034	0.000	0.000	0.000
	Control	0.000	-	-	0.000	0.000
PF1 20 S NC	PF2 20 S NC	-	-	0.000	0.000	0.000
	AA 20 S NC	-	-	0.000	0.000	0.000
	Control	-	-	-	0.000	0.000
PF1 5 S NC HD	PF2 5 S NC HD	0.832	0.012	-	0.006	0.007
	PF1 5 S NC	0.020	0.000	-	0.003	0.653
	CONTROL	0.053	-	-	0.000	0.000
PF2 5 S NC	PF2 10 S NC	0.069	0.167	0.159	0.000	0.003
	PF2 20 S NC	0.533	0.000	0.000	0.000	0.000
	Control	0.000	-	-	0.003	0.001
PF2 10 S C	PF2 10 S NC	0.464	0.002	0.421	0.458	0.846
	PF2 10 NS NC	0.001	0.174	0.633	0.000	0.019
	TO 10 SC	0.071	0.000	0.019	0.000	0.000
	Control	0.000	-	-	0.000	0.000
PF 2 10 S NC	PF 2 10 NS NC	0.000	0.000	0.213	0.000	0.018
	PF2 20 S NC	0.116	0.000	0.000	0.000	0.003
	TO10 S NC	0.111	0.001	0.000	0.000	0.000
	Control	0.000	-	-	0.000	0.000
PF2 10 NS NC	Control	0.000	-	-	0.011	0.009
PF2 5 S NC HD	PF2 5 S NC	0.000	0.000	-	0.000	0.002
	CONTROL	0.006	-	-	0.000	0.000
PF2 20 S NC	AA 20 S NC	0.801	0.022	0.031	0.007	0.015
	Control	0.000	-	-	0.000	0.000
TO 10 S C	TO 10 S NC	0.149	0.056	0.006	0.002	0.007
	Control	0.000	-	-	0.143	0.116
TO 10 S NC	Control	0.000	-	-	0.050	0.183
AA 20 S NC	Control	0.000	-	-	0.000	0.000

**Table A.2.** Statistical P-values for all Studentized t-tests performed for comparisons made between values of different treatments. P-values smaller than 0.05 were considered statistically significant.

COMPARISONS		ASE Boil	Thickness Swell Boil	Percent Thickness Swell	WPG Potential	WPG
PF1 5 S NC	PF1 10 S NC	0.093	0.297	0.158	0.000	0.000
	PF1 20 S NC	0.000	0.000	0.000	0.000	0.000
	PF2 5 S NC	0.000	0.000	0.000	0.000	0.308
	Control	-	0.000	0.000	-	-
PF1 10 S C	PF1 10 S NC	0.607	0.786	0.680	0.064	0.474
	PF1 10 NS NC	0.071	0.046	0.055	0.466	0.864
	PF2 10 SC	0.002	0.003	0.003	0.060	0.015
	PF2 1 S NC	0.001	0.002	0.002	0.167	0.000
	TO 10 S C	0.000	0.000	0.000	0.000	0.464
Control	-	0.000	0.000	-	-	
PF 1 10 S NC	PF 1 10 NS NC	0.029	0.024	0.023	0.200	0.496
	PF1 20 S NC	0.000	0.000	0.000	0.000	0.000
	PF2 10 S NC	0.000	0.000	0.000	0.350	0.000
	PF 2 10 NS NC	0.001	0.001	0.001	0.436	0.000
	TO10 S NC	0.000	0.000	0.000	0.001	0.855
Control	-	0.000	0.000	-	-	
PF1 10 NS NC	PF2 10 NS NC	0.124	0.129	0.106	0.529	0.000
	Control	-	0.000	0.000	-	-
PF1 20 S NC	PF2 20 S NC	0.000	0.000	0.000	0.865	0.000
	AA 20 S NC	0.000	0.000	0.000	-	0.006
	Control	-	0.000	0.000	-	-
PF1 5 S NC HD	PF2 5 S NC HD	-	0.007	0.005	0.152	0.005
	PF1 5 S NC	-	0.013	0.128	0.003	0.033
	CONTROL	-	0.000	0.000	-	-
PF2 5 S NC	PF2 10 S NC	0.028	0.004	0.013	0.421	0.007
	PF2 20 S NC	0.000	0.000	0.000	0.000	0.000
	Control	-	0.000	0.000	-	-
PF2 10 S C	PF2 10 S NC	0.497	0.492	0.486	0.634	0.000
	PF2 10 NS NC	0.333	0.207	0.217	0.776	0.021
	TO 10 SC	0.000	0.000	0.000	0.000	0.001
	Control	-	0.000	0.000	-	-
PF 2 10 S NC	PF 2 10 NS NC	0.127	0.069	0.072	0.873	0.029
	PF2 20 S NC	0.000	0.002	0.002	0.000	0.000
	TO10 S NC	0.000	0.000	0.000	0.003	0.006
	Control	-	0.000	0.000	-	-
PF2 10 NS NC	Control	-	0.000	0.000	-	-
PF2 5 S NC HD	PF2 5 S NC	-	0.000	0.020	0.000	0.090
	CONTROL	-	0.000	0.000	-	-
PF2 20 S NC	AA 20 S NC	0.000	0.000	0.000	-	0.000
	Control	-	0.000	0.000	-	-
TO 10 S C	TO 10 S NC	0.002	0.001	0.005	0.864	0.881
	Control	-	0.100	0.076	-	-
TO 10 S NC	Control	-	0.016	0.132	-	-
AA 20 S NC	Control	-	0.000	0.000	-	-

**Table A.3.** Statistical P-values for all Studentized t-tests performed for comparisons made between values of different treatments. P-values smaller than 0.05 were considered statistically significant.

COMPARISONS		Normalized ASE Soak	Normalized ASE Boil	Chemical Retention	Irreversible Swelling Soak	Irreversible Swelling Boil
PF1 5 S NC	PF1 10 S NC	0.000	0.000	0.000	0.346	0.721
	PF1 20 S NC	0.000	0.000	0.000	0.262	0.903
	PF2 5 S NC	0.065	0.010	0.000	0.000	0.000
	Control	-	-	-	0.000	0.000
PF1 10 S C	PF1 10 S NC	0.223	0.631	0.331	0.789	0.452
	PF1 10 NS NC	0.348	0.102	0.773	0.001	0.000
	PF2 10 SC	0.065	0.573	0.000	0.555	0.345
	PF2 1 S NC	0.132	0.004	0.000	0.832	0.255
	TO 10 S C	0.000	0.000	0.004	0.000	0.010
	Control	-	-	-	0.000	0.005
PF 1 10 S NC	PF 1 10 NS NC	0.015	0.131	0.191	0.000	0.000
	PF1 20 S NC	0.000	0.000	0.031	0.124	0.719
	PF2 10 S NC	0.009	0.001	0.000	0.436	0.003
	PF 2 10 NS NC	0.447	0.834	0.000	0.000	0.000
	TO10 S NC	0.000	0.000	0.023	0.000	0.000
	Control	-	-	-	0.000	0.000
PF1 10 NS NC	PF2 10 NS NC	0.028	0.353	0.000	0.240	0.000
	Control	-	-	-	0.805	0.089
PF1 20 S NC	PF2 20 S NC	0.951	0.294	0.000	0.019	0.000
	AA 20 S NC	0.001	0.000	-	0.000	0.000
	Control	-	-	-	0.000	0.001
PF1 5 S NC HD	PF2 5 S NC HD	-	-	0.026	0.000	0.127
	PF1 5 S NC	-	-	0.145	0.015	0.142
	CONTROL	-	-	-	0.132	0.026
PF2 5 S NC	PF2 10 S NC	0.222	0.089	0.000	0.000	0.004
	PF2 20 S NC	0.011	0.001	0.002	0.000	0.000
	Control	-	-	-	0.072	0.949
PF2 10 S C	PF2 10 S NC	0.005	0.003	0.000	0.553	0.967
	PF2 10 NS NC	0.804	0.983	0.000	0.000	0.000
	TO 10 SC	0.004	0.000	0.000	0.000	0.046
	Control	-	-	-	0.001	0.047
PF 2 10 S NC	PF 2 10 NS NC	0.012	0.003	0.000	0.000	0.000
	PF2 20 S NC	0.000	0.000	0.000	0.630	0.000
	TO10 S NC	0.000	0.000	0.000	0.000	0.000
	Control	-	-	-	0.000	0.013
PF2 10 NS NC	Control	-	-	-	0.110	0.000
PF2 5 S NC HD	PF2 5 S NC	-	-	0.000	0.000	0.000
	CONTROL	-	-	-	0.000	0.001
PF2 20 S NC	AA 20 S NC	0.000	0.000	-	0.000	0.034
	Control	-	-	-	0.000	0.000
TO 10 S C	TO 10 S NC	0.018	0.010	0.768	0.508	0.013
	Control	-	-	-	0.000	0.569
TO 10 S NC	Control	-	-	-	0.000	0.001
AA 20 S NC	Control	-	-	-	0.000	0.000

**Table A.4.** Statistical P-values for all Studentized t-tests performed for comparisons made between values of different treatments. P-values smaller than 0.05 were considered statistically significant.

COMPARISONS		Thickness Recovery	Thickness Recovery Boil	% Thickness Swell	% Thickness Swell
PF1 5 S NC	PF1 10 S NC	0.588	0.690	0.000	0.000
	PF1 20 S NC	0.110	0.306	0.000	0.000
	PF2 5 S NC	0.000	0.000	0.026	0.004
	Control	0.000	0.000	-	-
PF1 10 S C	PF1 10 S NC	0.338	0.459	0.292	0.621
	PF1 10 NS NC	0.204	0.008	0.375	0.081
	PF2 10 SC	0.451	0.476	0.061	0.515
	PF2 1 S NC	0.433	0.197	0.228	0.007
	TO 10 S C	0.000	0.003	-	-
	Control	0.001	0.001	-	-
PF 1 10 S NC	PF 1 10 NS NC	0.003	0.003	0.023	0.100
	PF1 20 S NC	0.198	0.404	0.000	0.000
	PF2 10 S NC	0.001	0.001	0.021	0.001
	PF 2 10 NS NC	0.000	0.000	0.112	0.436
	TO10 S NC	0.000	0.000	-	-
	Control	0.000	0.000	-	-
PF1 10 NS NC	PF2 10 NS NC	0.001	0.114	0.008	0.599
	Control	0.001	0.131	-	-
PF1 20 S NC	PF2 20 S NC	0.006	0.001	0.691	0.519
	AA 20 S NC	0.000	0.000	-	-
	Control	0.000	0.000	-	-
PF1 5 S NC HD	PF2 5 S NC HD	0.000	0.968	-	-
	PF1 5 S NC	0.027	0.531	-	-
	CONTROL	0.001	0.000	-	-
PF2 5 S NC	PF2 10 S NC	0.001	0.002	0.329	0.139
	PF2 20 S NC	0.000	0.000	0.018	0.001
	Control	0.030	0.062	-	-
PF2 10 S C	PF2 10 S NC	0.001	0.001	0.007	0.003
	PF2 10 NS NC	0.000	0.000	0.700	0.708
	TO 10 SC	0.000	0.002	-	-
	Control	0.000	0.000	-	-
PF 2 10 S NC	PF 2 10 NS NC	0.001	0.001	0.005	0.002
	PF2 20 S NC	0.176	0.258	0.000	0.000
	TO10 S NC	0.000	0.000	-	-
	Control	0.001	0.002	-	-
PF2 10 NS NC	Control	0.480	0.952	-	-
PF2 5 S NC HD	PF2 5 S NC	0.000	0.000	-	-
	CONTROL	0.000	0.001	-	-
PF2 20 S NC	AA 20 S NC	0.000	0.000	-	-
	Control	0.001	0.001	-	-
TO 10 S C	TO 10 S NC	0.009	0.003	-	-
	Control	0.017	0.825	-	-
TO 10 S NC	Control	0.000	0.002	-	-
AA 20 S NC	Control	0.000	0.000	-	-

Table A.5. Calculated values for all replicates of each treatment.

Samples	Increase in MOE	Increase MOE/WPG	ASE Soak	Thickness Swell Soak, mm	Thickness Swell Soak, %	ASE Boil
Control	187.1%	-	-	1.100	45.1%	-
Control	210.2%	-	-	1.410	56.6%	-
Control	190.8%	-	-	0.937	38.3%	-
Control	229.5%	-	-	0.900	36.4%	-
Control	208.9%	-	-	0.620	25.4%	-
Control	182.6%	-	-	0.953	38.6%	-
Control	193.0%	-	-	0.860	35.1%	-
Control	230.2%	-	-	0.917	38.0%	-
Control	221.7%	-	-	0.563	23.2%	-
Control	228.4%	-	-	0.707	29.7%	-
PF1 5 S NC	152.5%	0.410	49.7%	0.443	18.2%	61.5%
PF1 5 S NC	125.8%	0.459	53.8%	0.430	17.9%	66.4%
PF1 5 S NC	165.0%	0.487	56.7%	0.387	16.0%	68.4%
PF1 5 S NC	169.0%	0.472	62.7%	0.317	13.3%	70.1%
PF1 5 S NC	184.1%	0.528	46.7%	0.473	19.8%	66.1%
PF1 5 S NC	177.3%	0.520	57.5%	0.350	15.7%	73.4%
PF1 5 S NC	178.3%	0.390	55.1%	0.367	16.0%	71.7%
PF1 5 S NC	181.1%	0.663	75.5%	0.197	8.8%	71.5%
PF1 5 S NC	125.4%	0.395	78.2%	0.180	7.3%	76.3%
PF1 5 S NC	126.6%	0.259	77.6%	0.197	8.1%	80.4%
PF1 10 S NC	155.6%	0.130	73.3%	0.217	8.9%	77.7%
PF1 10 S NC	183.2%	0.196	83.6%	0.137	5.7%	81.7%
PF1 10 S NC	129.1%	0.135	56.1%	0.420	17.1%	63.5%
PF1 10 S NC	137.5%	0.159	60.5%	0.340	14.0%	70.8%
PF1 10 S NC	143.8%	0.123	64.4%	0.333	13.6%	71.9%
PF1 10 S NC	160.2%	0.154	71.3%	0.263	10.9%	76.2%
PF1 10 S NC	163.4%	0.134	65.2%	0.313	12.7%	76.3%
PF1 10 S NC	146.4%	0.140	75.1%	0.227	9.2%	78.2%
PF1 10 S NC	125.8%	0.104	65.9%	0.310	12.5%	75.1%
PF1 10 S NC	151.8%	0.092	75.0%	0.220	8.9%	75.9%
PF1 20 S NC	-	-	84.6%	0.143	5.6%	88.7%
PF1 20 S NC	-	-	68.4%	0.247	9.7%	75.2%
PF1 20 S NC	-	-	78.9%	0.197	7.9%	83.9%
PF1 20 S NC	-	-	98.1%	0.007	0.3%	93.7%
PF1 20 S NC	-	-	80.1%	0.183	7.5%	81.8%
PF1 20 S NC	-	-	96.1%	0.013	0.5%	92.0%
PF1 20 S NC	-	-	92.2%	0.067	2.7%	91.6%
PF1 20 S NC	-	-	86.6%	0.130	5.2%	84.9%
PF1 20 S NC	-	-	66.3%	0.317	12.6%	77.5%
PF1 20 S NC	-	-	91.7%	0.030	1.2%	91.9%
PF1 10 S C	176.0%	0.128	45.7%	0.500	20.4%	47.3%
PF1 10 S C	124.1%	0.090	72.9%	0.237	10.1%	67.8%
PF1 10 S C	216.3%	0.283	74.7%	0.207	9.0%	76.2%
PF1 10 S C	213.2%	0.221	76.5%	0.287	12.1%	78.8%
PF1 10 S C	172.3%	0.182	78.6%	0.173	7.2%	79.9%
PF1 10 S C	195.8%	0.210	72.7%	0.237	9.8%	78.9%
PF1 10 S C	224.4%	0.212	70.2%	0.257	10.7%	60.5%
PF1 10 S C	182.5%	0.186	75.2%	0.207	8.6%	77.8%
PF1 10 S C	141.4%	0.137	83.1%	0.123	5.3%	80.5%
PF1 10 S C	178.4%	0.155	71.7%	0.247	10.2%	79.4%

Table A.6. Calculated values for all replicates of each treatment.

Samples	Thickness Swell Boil, mm	Thickness Swell Boil	WPG P	WPG	ASE Soak Normalized	ASE Boil Normalized
Control	2.247	92.2%	-	-3.4%	-	-
Control	2.277	91.4%	-	-2.7%	-	-
Control	1.887	77.2%	-	-3.2%	-	-
Control	1.680	67.9%	-	-4.1%	-	-
Control	2.003	82.2%	-	-3.2%	-	-
Control	1.843	74.6%	-	-3.3%	-	-
Control	1.763	71.9%	-	-3.2%	-	-
Control	1.867	77.3%	-	-3.4%	-	-
Control	1.270	52.3%	-	-3.7%	-	-
Control	1.773	74.5%	-	-3.6%	-	-
PF1 5 S NC	0.723	29.7%	9.6%	3.7%	13.4	16.5
PF1 5 S NC	0.593	24.7%	7.0%	2.7%	19.6	24.2
PF1 5 S NC	0.583	24.2%	9.5%	3.4%	16.8	20.2
PF1 5 S NC	0.523	21.9%	9.4%	3.6%	17.5	19.6
PF1 5 S NC	0.600	25.1%	8.8%	3.5%	13.4	18.9
PF1 5 S NC	0.430	19.3%	9.2%	3.4%	16.9	21.5
PF1 5 S NC	0.467	20.4%	9.7%	4.6%	12.1	15.7
PF1 5 S NC	0.453	20.3%	8.2%	2.7%	27.6	26.1
PF1 5 S NC	0.437	17.7%	9.3%	3.2%	24.7	24.1
PF1 5 S NC	0.357	14.7%	9.9%	4.9%	15.9	16.4
PF1 10 S NC	0.407	16.7%	17.1%	12.0%	6.1	6.5
PF1 10 S NC	0.303	12.7%	13.6%	9.3%	9.0	8.8
PF1 10 S NC	0.690	28.0%	16.4%	9.5%	5.9	6.7
PF1 10 S NC	0.520	21.5%	15.1%	8.6%	7.0	8.2
PF1 10 S NC	0.540	22.0%	18.2%	11.7%	5.5	6.2
PF1 10 S NC	0.437	18.1%	17.0%	10.4%	6.9	7.3
PF1 10 S NC	0.440	17.9%	18.6%	12.2%	5.3	6.2
PF1 10 S NC	0.407	16.6%	15.2%	10.5%	7.2	7.5
PF1 10 S NC	0.470	18.9%	17.3%	12.1%	5.4	6.2
PF1 10 S NC	0.447	18.1%	23.9%	16.5%	4.6	4.6
PF1 20 S NC	0.197	7.7%	27.2%	19.5%	4.3	4.5
PF1 20 S NC	0.407	16.0%	37.4%	27.1%	2.5	2.8
PF1 20 S NC	0.283	11.3%	41.6%	26.8%	2.9	3.1
PF1 20 S NC	0.083	3.4%	32.9%	22.1%	4.4	4.2
PF1 20 S NC	0.317	12.9%	31.5%	23.4%	3.4	3.5
PF1 20 S NC	0.100	4.1%	31.8%	24.6%	3.9	3.7
PF1 20 S NC	0.113	4.5%	27.1%	20.9%	4.4	4.4
PF1 20 S NC	0.263	10.5%	29.7%	22.2%	3.9	3.8
PF1 20 S NC	0.397	15.8%	36.3%	22.6%	2.9	3.4
PF1 20 S NC	0.130	5.2%	30.8%	20.4%	4.5	4.5
PF1 10 S C	1.013	41.3%	16.1%	13.7%	3.3	3.4
PF1 10 S C	0.583	25.0%	16.3%	13.8%	5.3	4.9
PF1 10 S C	0.387	16.9%	13.3%	7.6%	9.8	10.0
PF1 10 S C	0.383	16.1%	16.2%	9.7%	7.9	8.1
PF1 10 S C	0.343	14.3%	15.7%	9.5%	8.3	8.4
PF1 10 S C	0.360	14.9%	15.8%	9.3%	7.8	8.4
PF1 10 S C	0.773	32.3%	15.6%	10.6%	6.6	5.7
PF1 10 S C	0.387	16.0%	15.3%	9.8%	7.7	7.9
PF1 10 S C	0.290	12.5%	14.4%	10.3%	8.0	7.8
PF1 10 S C	0.363	15.0%	14.4%	11.5%	6.2	6.9

Table A.7. Calculated values for all replicates of each treatment.

Samples	Chem. Retention	Irreversible Swelling Soak	Irreversible Swelling Boil	Thickness Recovery Soak	Thickness Recovery Boil	Inc. In Density
Control	-	54.9%	33.9%	19.9%	24.4%	127.1%
Control	-	60.9%	38.1%	28.9%	30.6%	123.0%
Control	-	34.0%	16.1%	11.3%	11.1%	126.4%
Control	-	32.4%	10.3%	10.7%	7.4%	120.2%
Control	-	61.9%	16.2%	13.2%	11.9%	128.5%
Control	-	43.6%	21.0%	14.5%	14.3%	120.7%
Control	-	31.4%	21.2%	9.9%	13.7%	122.7%
Control	-	31.1%	22.5%	10.2%	14.6%	127.8%
Control	-	2.6%	0.6%	1.6%	2.3%	128.3%
Control	-	32.5%	23.4%	8.0%	14.2%	130.6%
PF1 5 S NC	38.6%	9.8%	13.2%	1.9%	3.9%	147.8%
PF1 5 S NC	39.4%	11.4%	6.8%	1.9%	2.2%	144.3%
PF1 5 S NC	35.7%	0.2%	0.8%	0.3%	0.7%	153.2%
PF1 5 S NC	38.0%	0.0%	0.0%	0.0%	0.0%	152.1%
PF1 5 S NC	39.5%	0.6%	0.0%	0.2%	0.4%	154.1%
PF1 5 S NC	37.1%	0.0%	0.0%	0.0%	0.0%	166.5%
PF1 5 S NC	47.0%	0.0%	0.0%	0.0%	0.0%	169.4%
PF1 5 S NC	33.4%	0.0%	0.0%	0.0%	0.0%	177.0%
PF1 5 S NC	34.1%	0.0%	0.0%	0.1%	0.5%	137.7%
PF1 5 S NC	49.5%	0.0%	0.0%	0.0%	0.0%	148.1%
PF1 10 S NC	70.3%	8.3%	0.0%	0.0%	0.1%	164.8%
PF1 10 S NC	68.8%	0.0%	0.0%	0.0%	0.0%	157.1%
PF1 10 S NC	58.2%	26.8%	8.3%	1.8%	2.4%	155.2%
PF1 10 S NC	57.4%	0.4%	0.0%	0.8%	0.0%	157.5%
PF1 10 S NC	64.1%	0.0%	5.5%	0.0%	1.7%	158.9%
PF1 10 S NC	61.0%	0.0%	0.0%	0.0%	0.0%	158.4%
PF1 10 S NC	65.9%	3.2%	0.9%	0.0%	0.4%	161.0%
PF1 10 S NC	69.1%	0.0%	0.0%	0.0%	0.7%	158.0%
PF1 10 S NC	70.0%	14.1%	0.0%	0.0%	0.2%	161.7%
PF1 10 S NC	68.8%	0.0%	0.0%	0.0%	0.2%	162.7%
PF1 20 S NC	71.8%	0.0%	0.0%	0.0%	0.0%	160.9%
PF1 20 S NC	72.6%	4.5%	24.3%	0.0%	2.6%	184.4%
PF1 20 S NC	64.4%	0.0%	0.0%	0.0%	0.0%	184.3%
PF1 20 S NC	67.2%	0.0%	0.0%	0.0%	0.0%	181.1%
PF1 20 S NC	74.2%	0.0%	0.0%	0.0%	0.0%	178.6%
PF1 20 S NC	77.5%	0.0%	0.0%	0.0%	0.0%	191.2%
PF1 20 S NC	77.4%	0.0%	0.0%	0.0%	0.0%	178.0%
PF1 20 S NC	74.7%	0.0%	0.0%	0.0%	0.0%	185.0%
PF1 20 S NC	62.2%	0.0%	0.0%	0.0%	0.0%	174.1%
PF1 20 S NC	66.1%	0.0%	0.0%	0.0%	0.0%	173.3%
PF1 10 S C	85.6%	44.9%	36.6%	7.9%	12.5%	162.9%
PF1 10 S C	84.9%	0.0%	7.6%	0.5%	2.2%	184.4%
PF1 10 S C	57.5%	0.0%	0.0%	0.0%	0.4%	178.5%
PF1 10 S C	59.8%	0.0%	0.0%	0.0%	0.0%	160.6%
PF1 10 S C	60.5%	0.0%	0.0%	0.0%	0.0%	163.3%
PF1 10 S C	59.2%	0.0%	0.0%	0.0%	0.0%	160.1%
PF1 10 S C	68.0%	0.0%	0.0%	0.0%	0.1%	164.1%
PF1 10 S C	64.0%	0.0%	0.0%	0.0%	0.0%	158.4%
PF1 10 S C	72.0%	0.0%	0.0%	0.0%	0.3%	179.7%
PF1 10 S C	80.0%	23.1%	0.0%	2.4%	0.0%	161.3%

Table A.8. Calculated values for all replicates of each treatment.

Samples	Increase in MOE	Increase MOE/WPG	ASE Soak	Thickness Swell Soak, mm	Thickness Swell Soak, %	ASE Boil
PF1 10 NS NC	110.4%	0.125	84.8%	0.153	6.0%	64.2%
PF1 10 NS NC	113.6%	0.097	70.6%	0.293	11.6%	32.0%
PF1 10 NS NC	107.6%	0.102	87.3%	0.133	5.4%	78.5%
PF1 10 NS NC	122.5%	0.110	79.1%	0.200	8.0%	31.1%
PF1 10 NS NC	155.7%	0.153	85.2%	0.143	6.1%	78.8%
PF1 10 NS NC	100.8%	0.093	80.5%	0.190	8.0%	73.0%
PF1 10 NS NC	88.5%	0.075	81.9%	0.177	7.1%	66.2%
PF1 10 NS NC	126.6%	0.105	85.9%	0.120	5.1%	71.4%
PF1 10 NS NC	112.1%	0.097	81.9%	0.160	6.3%	45.0%
PF1 10 NS NC	139.7%	0.161	87.5%	0.113	4.5%	57.6%
PF1 5 S NC HD	-	-	-	0.173	11.0%	-
PF1 5 S NC HD	-	-	-	0.137	9.3%	-
PF1 5 S NC HD	-	-	-	0.247	17.7%	-
PF1 5 S NC HD	430.5%	0.488	-	0.170	11.9%	-
PF1 5 S NC HD	474.5%	0.257	-	0.213	15.8%	-
PF1 5 S NC HD	381.0%	0.519	-	0.277	18.6%	-
PF1 5 S NC HD	-	-	-	0.140	8.8%	-
PF1 5 S NC HD	208.4%	0.236	-	0.213	13.3%	-
PF1 5 S NC HD	247.9%	0.255	-	0.177	11.0%	-
PF1 5 S NC HD	-	-	-	0.130	8.5%	-
PF1 10 Uncomp.	10.5%	0.004	-	0.097	1.6%	-
PF1 10 Uncomp.	20.5%	0.007	-	0.047	0.8%	-
PF1 10 Uncomp.	13.1%	0.005	-	0.030	0.5%	-
PF1 10 Uncomp.	15.4%	0.008	-	0.123	2.1%	-
PF1 10 Uncomp.	12.0%	0.005	-	0.110	1.8%	-
PF1 10 Uncomp.	20.7%	0.010	-	0.093	1.6%	-
PF1 10 Uncomp.	10.0%	0.006	-	0.057	0.9%	-
PF1 10 Uncomp.	21.1%	0.007	-	0.053	0.9%	-
PF1 10 Uncomp.	13.0%	0.004	-	0.097	1.5%	-
PF1 10 Uncomp.	10.3%	0.004	-	0.053	0.9%	-
PF2 5 S NC	92.1%	0.169	42.4%	0.573	22.7%	45.7%
PF2 5 S NC	145.5%	0.326	29.9%	0.685	27.5%	40.6%
PF2 5 S NC	169.4%	0.500	46.1%	0.500	20.7%	59.8%
PF2 5 S NC	128.0%	0.300	42.2%	0.580	22.8%	51.6%
PF2 5 S NC	120.2%	0.664	60.1%	0.410	16.2%	51.4%
PF2 5 S NC	135.7%	0.477	32.0%	0.687	26.6%	44.3%
PF2 5 S NC	113.6%	0.267	46.9%	0.523	20.8%	55.8%
PF2 5 S NC	78.7%	0.209	47.3%	0.530	20.8%	55.2%
PF2 5 S NC	172.5%	0.453	20.7%	0.822	31.6%	42.5%
PF2 5 S NC	149.6%	0.222	45.7%	0.530	20.8%	55.8%
PF2 10 S NC	107.3%	0.148	54.6%	0.450	18.6%	59.9%
PF2 10 S NC	133.9%	0.232	43.0%	0.437	18.2%	63.6%
PF2 10 S NC	136.5%	0.217	43.9%	0.517	21.3%	50.9%
PF2 10 S NC	154.0%	0.299	52.0%	0.503	20.7%	52.7%
PF2 10 S NC	172.3%	0.345	29.8%	0.603	24.9%	45.9%
PF2 10 S NC	175.2%	0.215	51.7%	0.497	20.6%	58.5%
PF2 10 S NC	179.5%	0.362	42.5%	0.470	19.3%	59.0%
PF2 10 S NC	171.4%	0.382	52.8%	0.447	18.6%	61.2%
PF2 10 S NC	160.3%	0.274	54.3%	0.500	20.3%	55.8%
PF2 10 S NC	150.0%	0.300	52.3%	0.437	17.7%	60.2%

Table A.9. Calculated values for all replicates of each treatment.

Samples	Thickness Swell Boil, mm	Thickness Swell Boil	WPG P	WPG	ASE Soak Normalized	ASE Boil Normalized
PF1 10 NS NC	0.713	28.1%	14.1%	8.8%	9.6	7.3
PF1 10 NS NC	1.387	54.8%	18.4%	11.8%	6.0	2.7
PF1 10 NS NC	0.413	16.6%	16.3%	10.5%	8.3	7.5
PF1 10 NS NC	1.393	56.0%	17.2%	11.1%	7.1	2.8
PF1 10 NS NC	0.387	16.4%	14.6%	10.2%	8.4	7.7
PF1 10 NS NC	0.510	21.5%	15.5%	10.9%	7.4	6.7
PF1 10 NS NC	0.680	27.2%	16.8%	11.8%	7.0	5.6
PF1 10 NS NC	0.527	22.2%	16.3%	12.0%	7.2	6.0
PF1 10 NS NC	1.093	43.3%	16.9%	11.6%	7.1	3.9
PF1 10 NS NC	0.830	33.0%	11.8%	8.7%	10.1	6.6
PF1 5 S NC HD	0.327	20.8%	13.9%	7.3%	-	-
PF1 5 S NC HD	0.313	21.3%	14.9%	7.8%	-	-
PF1 5 S NC HD	0.477	34.2%	13.3%	8.7%	-	-
PF1 5 S NC HD	0.410	28.6%	13.8%	8.8%	-	-
PF1 5 S NC HD	0.400	29.6%	10.5%	18.5%	-	-
PF1 5 S NC HD	0.450	30.2%	11.3%	7.3%	-	-
PF1 5 S NC HD	0.340	21.3%	11.5%	7.1%	-	-
PF1 5 S NC HD	0.517	32.2%	10.9%	8.8%	-	-
PF1 5 S NC HD	0.427	26.6%	11.7%	9.7%	-	-
PF1 5 S NC HD	0.347	22.6%	9.2%	6.8%	-	-
PF1 10 Uncomp.	0.117	1.9%	24.7%	25.9%	-	-
PF1 10 Uncomp.	0.063	1.0%	27.3%	28.2%	-	-
PF1 10 Uncomp.	0.047	0.8%	25.7%	25.8%	-	-
PF1 10 Uncomp.	0.150	2.5%	18.3%	19.2%	-	-
PF1 10 Uncomp.	0.107	1.7%	24.7%	25.1%	-	-
PF1 10 Uncomp.	0.117	2.0%	19.6%	20.0%	-	-
PF1 10 Uncomp.	0.087	1.4%	16.4%	17.4%	-	-
PF1 10 Uncomp.	0.077	1.2%	27.6%	28.9%	-	-
PF1 10 Uncomp.	0.053	0.9%	29.4%	30.0%	-	-
PF1 10 Uncomp.	0.060	1.0%	25.1%	26.5%	-	-
PF2 5 S NC	1.107	43.8%	17.9%	5.5%	7.8	8.4
PF2 5 S NC	1.185	47.6%	20.0%	4.5%	6.7	9.1
PF2 5 S NC	0.753	31.2%	16.2%	3.4%	13.6	17.7
PF2 5 S NC	0.983	38.7%	20.9%	4.3%	9.9	12.1
PF2 5 S NC	0.977	38.5%	12.5%	1.8%	33.2	28.4
PF2 5 S NC	1.150	44.6%	14.1%	2.8%	11.3	15.6
PF2 5 S NC	0.883	35.1%	16.4%	4.3%	11.0	13.1
PF2 5 S NC	0.920	36.1%	15.4%	3.8%	12.6	14.7
PF2 5 S NC	1.208	46.5%	16.9%	3.8%	5.4	11.2
PF2 5 S NC	0.887	34.9%	20.8%	6.7%	6.8	8.3
PF2 10 S NC	0.720	29.7%	18.8%	7.3%	7.5	8.2
PF2 10 S NC	0.643	26.8%	16.2%	5.8%	7.4	11.0
PF2 10 S NC	0.943	38.8%	16.1%	6.3%	7.0	8.1
PF2 10 S NC	0.903	37.2%	13.7%	5.1%	10.1	10.2
PF2 10 S NC	1.037	42.8%	15.3%	5.0%	6.0	9.2
PF2 10 S NC	0.753	31.3%	19.5%	8.1%	6.3	7.2
PF2 10 S NC	0.753	31.0%	14.9%	5.0%	8.6	11.9
PF2 10 S NC	0.710	29.5%	15.2%	4.5%	11.8	13.6
PF2 10 S NC	0.840	34.1%	16.3%	5.9%	9.3	9.5
PF2 10 S NC	0.737	29.9%	16.3%	5.0%	10.5	12.1

Table A.10. Calculated values for all replicates of each treatment.

Samples	Chem. Retention	Irreversible Swelling Soak	Irreversible Swelling Boil	Thickness Recovery Soak	Thickness Recovery Boil	Inc. In Density
PF1 10 NS NC	62.7%	60.1%	37.0%	2.7%	9.2%	141.1%
PF1 10 NS NC	63.9%	66.5%	44.5%	6.3%	19.8%	152.1%
PF1 10 NS NC	64.4%	33.4%	22.6%	1.4%	3.6%	150.8%
PF1 10 NS NC	64.5%	56.2%	46.9%	3.6%	19.7%	160.7%
PF1 10 NS NC	69.6%	6.0%	9.7%	0.6%	1.7%	174.9%
PF1 10 NS NC	70.1%	30.9%	20.6%	1.8%	4.1%	167.3%
PF1 10 NS NC	70.1%	25.4%	23.0%	1.6%	5.3%	158.3%
PF1 10 NS NC	73.8%	13.4%	16.3%	0.7%	3.2%	170.3%
PF1 10 NS NC	68.3%	52.7%	41.0%	2.6%	14.3%	153.4%
PF1 10 NS NC	73.5%	62.9%	37.9%	2.2%	11.0%	142.8%
PF1 5 S NC HD	52.4%	27.1%	0.4%	1.5%	0.5%	245.9%
PF1 5 S NC HD	52.4%	3.1%	0.0%	0.3%	0.1%	275.3%
PF1 5 S NC HD	65.2%	26.6%	12.4%	2.0%	1.7%	303.3%
PF1 5 S NC HD	63.7%	34.8%	15.0%	1.6%	1.7%	289.4%
PF1 5 S NC HD	175.5%	35.0%	13.2%	2.0%	1.5%	360.3%
PF1 5 S NC HD	64.8%	33.3%	7.7%	2.5%	1.5%	266.1%
PF1 5 S NC HD	61.7%	26.2%	8.5%	1.4%	1.3%	237.5%
PF1 5 S NC HD	80.6%	36.3%	18.1%	2.3%	3.3%	232.9%
PF1 5 S NC HD	83.2%	25.4%	37.7%	1.2%	4.6%	249.0%
PF1 5 S NC HD	73.9%	42.6%	37.3%	1.5%	4.1%	270.8%
PF1 10 Uncomp.	105.0%	23.1%	0.0%	-	-	25.5%
PF1 10 Uncomp.	103.3%	0.0%	0.0%	-	-	24.4%
PF1 10 Uncomp.	100.5%	0.0%	0.0%	-	-	21.8%
PF1 10 Uncomp.	104.5%	0.0%	5.3%	-	-	18.2%
PF1 10 Uncomp.	101.5%	0.0%	1.0%	-	-	22.4%
PF1 10 Uncomp.	102.1%	0.0%	1.3%	-	-	19.5%
PF1 10 Uncomp.	106.1%	0.0%	0.0%	-	-	17.3%
PF1 10 Uncomp.	104.7%	0.0%	0.0%	-	-	24.8%
PF1 10 Uncomp.	101.9%	0.0%	0.0%	-	-	25.7%
PF1 10 Uncomp.	105.3%	0.0%	0.0%	-	-	22.6%
PF2 5 S NC	30.5%	27.4%	22.0%	6.7%	9.9%	134.5%
PF2 5 S NC	22.3%	30.1%	25.1%	7.7%	10.7%	137.1%
PF2 5 S NC	20.9%	7.6%	4.0%	2.3%	2.4%	146.7%
PF2 5 S NC	20.5%	21.1%	17.9%	5.0%	7.1%	135.1%
PF2 5 S NC	14.5%	28.1%	16.9%	5.1%	7.5%	133.9%
PF2 5 S NC	20.2%	41.9%	29.1%	11.2%	12.7%	127.9%
PF2 5 S NC	26.0%	17.2%	13.2%	4.3%	5.5%	135.1%
PF2 5 S NC	24.5%	26.9%	22.6%	6.2%	8.7%	125.7%
PF2 5 S NC	22.5%	39.4%	36.1%	13.1%	15.9%	128.2%
PF2 5 S NC	32.4%	19.8%	19.4%	4.5%	6.9%	143.9%
PF2 10 S NC	38.7%	9.9%	9.2%	2.0%	3.2%	152.7%
PF2 10 S NC	35.6%	6.4%	3.5%	1.3%	1.5%	152.8%
PF2 10 S NC	38.9%	11.1%	11.5%	2.5%	4.3%	151.3%
PF2 10 S NC	37.7%	12.4%	20.7%	2.5%	7.0%	144.9%
PF2 10 S NC	32.8%	13.9%	16.1%	3.3%	5.8%	150.0%
PF2 10 S NC	41.7%	3.6%	6.2%	0.9%	2.3%	147.8%
PF2 10 S NC	33.3%	6.9%	7.7%	1.9%	2.9%	148.9%
PF2 10 S NC	29.5%	0.0%	3.0%	0.4%	1.3%	151.9%
PF2 10 S NC	36.0%	14.4%	13.0%	2.3%	4.3%	145.0%
PF2 10 S NC	30.7%	0.5%	2.5%	0.7%	1.6%	149.8%

**Table A.11.** Calculated values for all replicates of each treatment.

Samples	Increase in MOE	Increase MOE/WPG	ASE Soak	Thickness Swell Soak, mm	Thickness Swell Soak, %	ASE Boil
TO 10 S C	101.2%	0.083	25.4%	0.777	30.8%	27.6%
TO 10 S C	159.5%	0.149	11.9%	0.900	36.1%	13.5%
TO 10 S C	149.3%	0.138	63.0%	0.357	14.8%	24.4%
TO 10 S C	173.5%	0.130	8.5%	0.913	36.8%	12.1%
TO 10 S C	147.0%	0.118	28.8%	0.727	29.6%	37.0%
TO 10 S C	101.6%	0.109	30.5%	0.697	28.3%	26.2%
TO 10 S C	55.4%	0.060	27.7%	0.707	29.0%	41.2%
TO 10 S C	94.2%	0.092	21.2%	0.770	31.2%	34.1%
TO 10 S C	64.4%	0.067	18.1%	0.793	32.3%	5.4%
TO 10 S C	147.1%	0.103	7.6%	0.900	36.6%	2.4%
TO 10 S NC	147.4%	0.242	18.3%	0.843	32.4%	13.8%
TO 10 S NC	123.0%	0.215	-20.3%	1.240	48.1%	-9.2%
TO 10 S NC	129.9%	0.202	23.7%	0.783	29.9%	16.2%
TO 10 S NC	133.1%	0.079	-42.1%	1.483	56.3%	-27.9%
TO 10 S NC	136.6%	0.109	-39.6%	1.487	55.4%	-20.2%
TO 10 S NC	134.9%	0.089	-45.9%	1.617	57.6%	-18.7%
TO 10 S NC	148.4%	0.132	27.8%	0.800	30.3%	26.6%
TO 10 S NC	155.8%	0.195	-1.8%	1.140	40.0%	7.0%
TO 10 S NC	153.1%	0.085	-5.4%	1.100	41.6%	-6.1%
TO 10 S NC	142.1%	0.145	1.1%	1.057	38.4%	-10.4%
AA 20 S NC	145.8%	0.075	47.6%	0.510	20.2%	-33.0%
AA 20 S NC	130.8%	0.068	38.9%	0.607	23.7%	-38.8%
AA 20 S NC	144.5%	0.072	39.8%	0.587	23.5%	-31.1%
AA 20 S NC	154.9%	0.076	40.2%	0.597	23.6%	-34.8%
AA 20 S NC	158.4%	0.078	46.9%	0.530	20.8%	-31.2%
AA 20 S NC	132.8%	0.067	44.0%	0.550	22.0%	-42.7%
AA 20 S NC	154.8%	0.076	61.4%	0.387	15.5%	-22.2%
AA 20 S NC	138.5%	0.072	48.7%	0.493	19.7%	-27.8%
AA 20 S NC	115.6%	0.056	76.8%	0.217	8.6%	-50.0%
AA 20 S NC	123.9%	0.058	60.8%	0.398	15.6%	-17.3%

Table A.12. Calculated values for all replicates of each treatment.

Samples	Thickness Swell Boil, mm	Thickness Swell Boil	WPG P	WPG	ASE Soak Normalized	ASE Boil Normalized
TO 10 S C	1.577	62.5%	12.5%	12.2%	2.1	2.3
TO 10 S C	1.873	75.2%	11.0%	10.7%	1.1	1.3
TO 10 S C	1.570	65.1%	11.5%	10.8%	5.8	2.3
TO 10 S C	1.850	74.5%	10.5%	13.3%	0.6	0.9
TO 10 S C	1.360	55.4%	12.9%	12.5%	2.3	3.0
TO 10 S C	1.570	63.8%	10.9%	9.3%	3.3	2.8
TO 10 S C	1.227	50.3%	15.4%	9.2%	3.0	4.5
TO 10 S C	1.347	54.6%	13.8%	10.2%	2.1	3.3
TO 10 S C	1.973	80.4%	9.5%	9.6%	1.9	0.6
TO 10 S C	2.050	83.3%	10.4%	14.3%	0.5	0.2
TO 10 S NC	1.847	70.9%	10.6%	6.1%	3.0	2.3
TO 10 S NC	2.380	92.4%	9.3%	5.7%	-3.6	-1.6
TO 10 S NC	1.810	69.0%	18.7%	6.4%	3.7	2.5
TO 10 S NC	2.797	106.1%	15.0%	16.9%	-2.5	-1.6
TO 10 S NC	2.703	100.7%	10.0%	12.5%	-3.2	-1.6
TO 10 S NC	2.793	99.5%	12.5%	15.2%	-3.0	-1.2
TO 10 S NC	1.620	61.4%	9.7%	11.3%	2.5	2.4
TO 10 S NC	2.197	77.0%	8.0%	8.0%	-0.2	0.9
TO 10 S NC	2.347	88.7%	14.6%	17.9%	-0.3	-0.3
TO 10 S NC	2.513	91.3%	11.8%	9.8%	0.1	-1.1
AA 20 S NC	2.760	109.5%	-	19.6%	2.4	-1.7
AA 20 S NC	2.910	113.8%	-	19.4%	2.0	-2.0
AA 20 S NC	2.760	110.5%	-	20.1%	2.0	-1.5
AA 20 S NC	2.813	111.1%	-	20.4%	2.0	-1.7
AA 20 S NC	2.793	109.4%	-	20.3%	2.3	-1.5
AA 20 S NC	2.940	117.8%	-	19.8%	2.2	-2.2
AA 20 S NC	2.583	103.9%	-	20.4%	3.0	-1.1
AA 20 S NC	2.687	107.2%	-	19.3%	2.5	-1.4
AA 20 S NC	3.183	125.8%	-	20.6%	3.7	-2.4
AA 20 S NC	2.515	98.4%	-	21.2%	2.9	-0.8

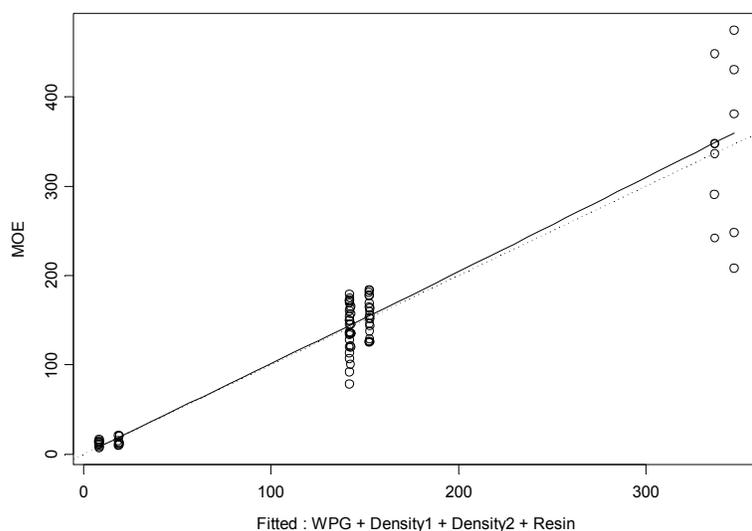
**Table A.13.** Calculated values for all replicates of each treatment.

Samples	Chem. Retention	Irreversible Swelling Soak	Irreversible Swelling Boil	Thickness Recovery Soak	Thickness Recovery Boil	Inc. In Density
TO 10 S C	97.5%	97.6%	30.6%	20.9%	18.8%	134.7%
TO 10 S C	97.2%	100.0%	53.6%	33.4%	32.1%	150.6%
TO 10 S C	94.5%	100.0%	16.2%	13.9%	10.1%	147.0%
TO 10 S C	127.4%	83.3%	19.8%	25.3%	14.0%	159.2%
TO 10 S C	97.0%	46.0%	0.0%	13.0%	0.0%	140.6%
TO 10 S C	85.7%	89.4%	31.5%	20.9%	17.5%	149.5%
TO 10 S C	59.8%	50.3%	0.0%	12.8%	1.6%	145.1%
TO 10 S C	74.4%	58.8%	34.6%	15.8%	17.4%	158.0%
TO 10 S C	101.4%	100.0%	11.6%	32.0%	11.3%	144.5%
TO 10 S C	137.1%	100.0%	44.1%	34.6%	31.4%	163.1%
TO 10 S NC	57.4%	64.2%	12.9%	20.4%	11.2%	134.1%
TO 10 S NC	61.3%	95.5%	36.9%	41.9%	32.1%	133.4%
TO 10 S NC	34.4%	75.5%	33.8%	21.7%	22.3%	144.1%
TO 10 S NC	112.8%	100.0%	59.1%	57.0%	55.9%	162.2%
TO 10 S NC	125.3%	97.6%	61.8%	50.0%	57.5%	147.0%
TO 10 S NC	121.4%	96.3%	59.7%	58.7%	61.9%	140.1%
TO 10 S NC	116.7%	63.2%	33.8%	17.0%	20.2%	140.5%
TO 10 S NC	99.7%	95.8%	44.0%	40.9%	36.2%	124.3%
TO 10 S NC	122.5%	94.4%	49.0%	37.3%	40.6%	159.8%
TO 10 S NC	82.9%	100.0%	60.2%	42.8%	54.2%	130.7%
AA 20 S NC	-	100.0%	86.4%	38.7%	73.6%	169.5%
AA 20 S NC	-	100.0%	86.1%	49.4%	77.8%	170.8%
AA 20 S NC	-	100.0%	88.1%	47.0%	75.4%	170.1%
AA 20 S NC	-	100.0%	87.6%	48.6%	77.8%	170.8%
AA 20 S NC	-	100.0%	87.2%	42.5%	74.4%	171.6%
AA 20 S NC	-	100.0%	87.2%	45.9%	74.2%	183.9%
AA 20 S NC	-	100.0%	82.7%	27.3%	63.8%	175.4%
AA 20 S NC	-	100.0%	88.1%	34.0%	73.4%	167.8%
AA 20 S NC	-	100.0%	48.0%	16.3%	47.5%	166.0%
AA 20 S NC	-	100.0%	79.4%	21.7%	60.3%	179.1%

## Appendix B: Multiple Linear Regression Output

**Table B.1** Extra sums of squares F-test for models with all densities.

Extra Sums of Squares F-Test for Models with All Densities						
Testing	Reduced	df	Full	DF	F-Stat	P-Value
Density	501336	2	105995	76	141.7327	0
WPG	105998	1			0.002151	0.96313
Resin	108152	1			1.546601	0.21745



**Figure B.1.** Multiple linear regression curve for MOE vs WPG, Density and resin type. Plotted for all density levels.

### Full Model For All Density Levels

\*\*\* Linear Model \*\*\*

```
Call: lm(formula = MOE ~ WPG + RESIN + Denisty1 + Denisty1.1, data =
MOE.Density.stats, na.action = na.exclude)
```

Residuals:

```
    Min       1Q   Median       3Q      Max
-138.6  -8.587   2.124  12.76  127.4
```

Coefficients:

```
            Value Std. Error  t value Pr(>|t|)
(Intercept)  7.2290   23.3690    0.3093  0.7579
          WPG   0.0447    0.9206    0.0485  0.9614
          RESIN 10.4562    8.4088    1.2435  0.2175
          Denisty1 134.3626  16.9809    7.9126  0.0000
          Denisty1.1 329.1619  21.7716   15.1189  0.0000
```

Residual standard error: 37.35 on 76 degrees of freedom

Multiple R-Squared: 0.879  
 F-statistic: 138.1 on 4 and 76 degrees of freedom, the p-value is 0

Analysis of Variance Table

Response: MOE

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
WPG	1	372416.7	372416.7	267.0267	0.0000000
RESIN	1	2423.5	2423.5	1.7377	0.1913901
Denisty1	1	76545.1	76545.1	54.8837	0.0000000
Denisty1.1	1	318795.5	318795.5	228.5798	0.0000000
Residuals	76	105995.6	1394.7		

### Reduced Model Testing Density for all density levels

Call: lm(formula = MOE ~ WPG + RESIN, data = MOE.Density.stats, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-121.3	-43.61	-17.4	21.14	284.9

Coefficients:

	Value	Std. Error	t value	Pr(> t )
(Intercept)	231.5057	16.9951	13.6219	0.0000
WPG	-8.3676	1.0961	-7.6339	0.0000
RESIN	11.0579	18.0079	0.6141	0.5410

Residual standard error: 80.17 on 78 degrees of freedom

Multiple R-Squared: 0.4278

F-statistic: 29.16 on 2 and 78 degrees of freedom, the p-value is 3.499e-010

Analysis of Variance Table

Response: MOE

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
WPG	1	372416.7	372416.7	57.94215	0.0000000
RESIN	1	2423.5	2423.5	0.37706	0.5409661
Residuals	78	501336.2	6427.4		

### Reduced Model Testing Resin for all density levels

\*\*\* Linear Model \*\*\*

Call: lm(formula = MOE ~ Denisty1 + Denisty1.1 + WPG, data = MOE.Density.stats, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-132.9	-11.15	-0.3811	14.23	133.1

Coefficients:

	Value	Std. Error	t value	Pr(> t )
(Intercept)	12.7748	23.0207	0.5549	0.5806
Denisty1	133.1122	17.0111	7.8250	0.0000
Denisty1.1	328.4390	21.8409	15.0378	0.0000
WPG	0.0310	0.9237	0.0335	0.9733

Residual standard error: 37.48 on 77 degrees of freedom

Multiple R-Squared: 0.8766

F-statistic: 182.3 on 3 and 77 degrees of freedom, the p-value is 0

Analysis of Variance Table

Response: MOE

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Denisty1	1	5087.1	5087.1	3.6218	0.0607652
Denisty1.1	1	762935.7	762935.7	543.1797	0.0000000
WPG	1	1.6	1.6	0.0011	0.9733404
Residuals	77	108152.1	1404.6		

### Reduced Model Testing WPG for all density levels

\*\*\* Linear Model \*\*\*

Call: lm(formula = MOE ~ Denisty1 + Denisty1.1 + RESIN, data = MOE.Density.stats, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-138.7	-8.663	2.001	12.54	127.5

Coefficients:

	Value	Std. Error	t value	Pr(> t )
(Intercept)	8.2681	9.2885	0.8901	0.3762
Denisty1	133.6939	9.8519	13.5703	0.0000
Denisty1.1	328.3540	13.9327	23.5671	0.0000
RESIN	10.4513	8.3536	1.2511	0.2147

Residual standard error: 37.1 on 77 degrees of freedom

Multiple R-Squared: 0.879

F-statistic: 186.5 on 3 and 77 degrees of freedom, the p-value is 0

Analysis of Variance Table

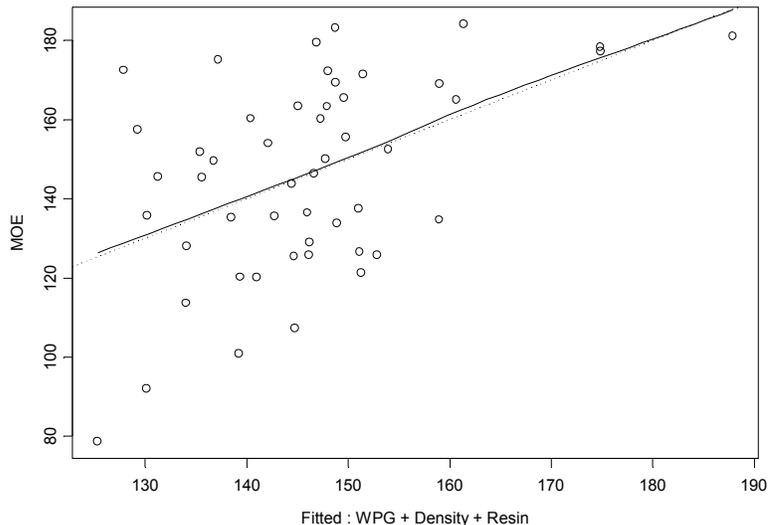
Response: MOE

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Denisty1	1	5087.1	5087.1	3.6954	0.0582628
Denisty1.1	1	762935.7	762935.7	554.2137	0.0000000
RESIN	1	2154.8	2154.8	1.5653	0.2146796
Residuals	77	105998.9	1376.6		

**Table B.2.** Extra sums of squares F-test for models with only standard densities.

Extra Sums of Squares F-Test for Models with only standard Densities							
Testing	Reduced	df	Full	DF	F-Stat	P-Value	
Density	28001		1	23134	46	9.677617	0.00321
WPG	27026		1			7.738912	0.00781
Resin	23377		1			0.483185	0.49049



**Figure B.2.** Multiple linear regression output for MOE vs WPG, Density and Resin type. Plotted only for standard densities.

### Full Model For Standard Density Samples

\*\*\* Linear Model \*\*\*

Call: `lm(formula = MOE ~ Density + WPG + RESIN, data = MOE.Density.stats.for.Standard.densities, na.action = na.exclude)`

Residuals:

Min	1Q	Median	3Q	Max
-46.64	-18.62	2.317	15.74	44.6

Coefficients:

	Value	Std. Error	t value	Pr(> t )
(Intercept)	0.8419	46.5369	0.0181	0.9856
Density	1.0712	0.3444	3.1107	0.0032
WPG	-2.7044	0.9722	-2.7818	0.0078
RESIN	4.8646	7.0034	0.6946	0.4908

Residual standard error: 22.43 on 46 degrees of freedom

Multiple R-Squared: 0.2361

F-statistic: 4.739 on 3 and 46 degrees of freedom, the p-value is 0.005803

Analysis of Variance Table

Response: MOE

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Density	1	1621.08	1621.084	3.22327	0.0791696
WPG	1	5286.08	5286.083	10.51054	0.0022110
RESIN	1	242.66	242.658	0.48249	0.4907919
Residuals	46	23134.85	502.932		

## Reduced Model Testing DENSITY for standard density samples

\*\*\* Linear Model \*\*\*

Call: lm(formula = MOE ~ WPG + RESIN, data =  
MOE.Density.stats.for.Standard.densities, na.action = na.exclude)

Residuals:

	Min	1Q	Median	3Q	Max
	-64.01	-16.82	2.029	21.59	37.26

Coefficients:

	Value	Std. Error	t value	Pr(> t )
(Intercept)	144.0547	7.3925	19.4866	0.0000
WPG	-0.3652	0.6706	-0.5446	0.5886
RESIN	12.7495	7.1057	1.7943	0.0792

Residual standard error: 24.41 on 47 degrees of freedom

Multiple R-Squared: 0.07539

F-statistic: 1.916 on 2 and 47 degrees of freedom, the p-value is 0.1585

Analysis of Variance Table

Response: MOE

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
WPG	1	365.15	365.149	0.612897	0.4376262
RESIN	1	1918.05	1918.049	3.219413	0.0792033
Residuals	47	28001.48	595.776		

## Reduced Model Testing WPG for standard density samples

\*\*\* Linear Model \*\*\*

Call: lm(formula = MOE ~ Density + RESIN, data =  
MOE.Density.stats.for.Standard.densities, na.action = na.exclude)

Residuals:

	Min	1Q	Median	3Q	Max
	-53.19	-17.67	1.681	16.58	40

Coefficients:

	Value	Std. Error	t value	Pr(> t )
(Intercept)	90.3499	35.9503	2.5132	0.0155
Density	0.3302	0.2334	1.4150	0.1636
RESIN	11.8055	6.9972	1.6872	0.0982

Residual standard error: 23.98 on 47 degrees of freedom

Multiple R-Squared: 0.1076

F-statistic: 2.833 on 2 and 47 degrees of freedom, the p-value is 0.06893

Analysis of Variance Table

Response: MOE

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Density	1	1621.08	1621.084	2.819098	0.09978604
RESIN	1	1636.88	1636.878	2.846564	0.09819647
Residuals	47	27026.72	575.037		

## Reduced Testing RESIN for standard density samples

\*\*\* Linear Model \*\*\*

Call: lm(formula = MOE ~ WPG + Density, data =  
MOE.Density.stats.for.Standard.densities, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-47.16	-16.82	3.038	15.4	43.88

Coefficients:

	Value	Std. Error	t value	Pr(> t )
(Intercept)	-8.6164	44.2546	-0.1947	0.8465
WPG	-2.9450	0.9034	-3.2600	0.0021
Density	1.1578	0.3192	3.6266	0.0007

Residual standard error: 22.3 on 47 degrees of freedom

Multiple R-Squared: 0.2281

F-statistic: 6.943 on 2 and 47 degrees of freedom, the p-value is 0.00228

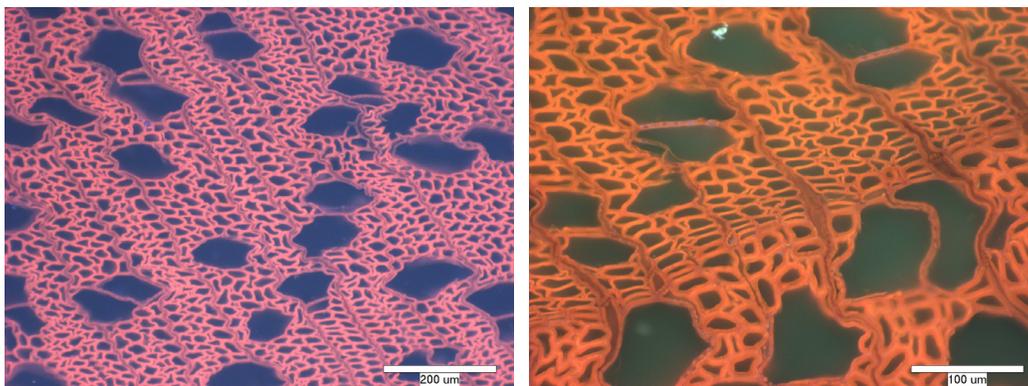
Analysis of Variance Table

Response: MOE

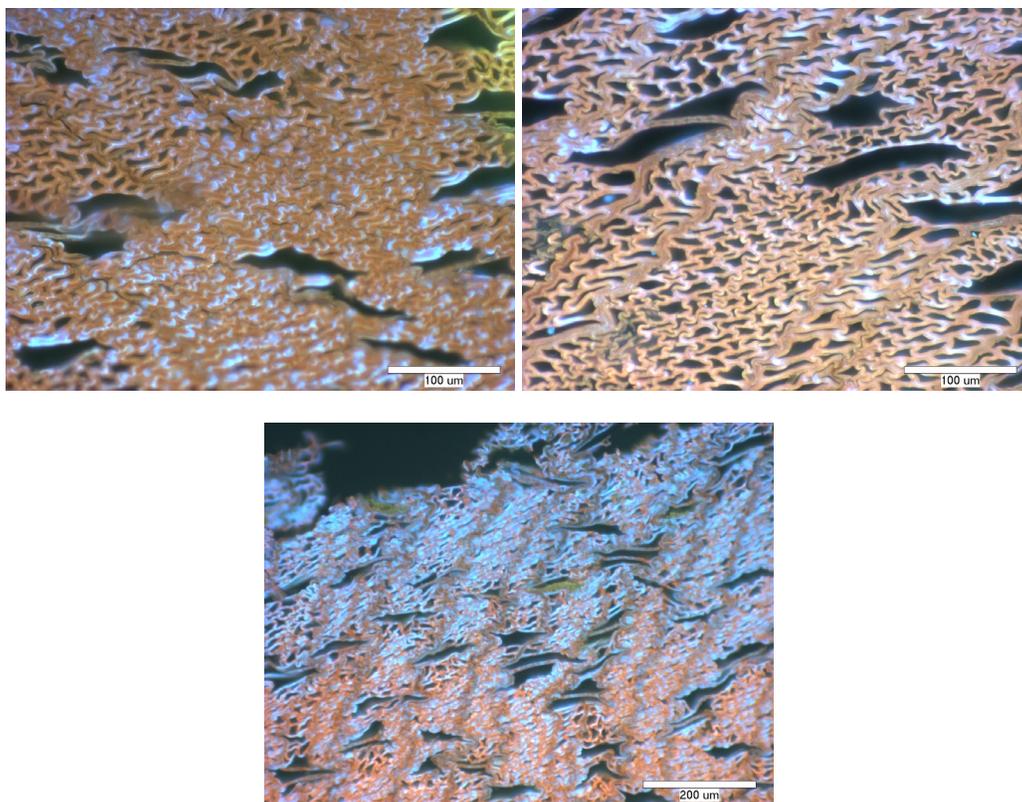
Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
WPG	1	365.15	365.149	0.73413	0.3958971
Density	1	6542.02	6542.017	13.15259	0.0007048
Residuals	47	23377.51	497.394		

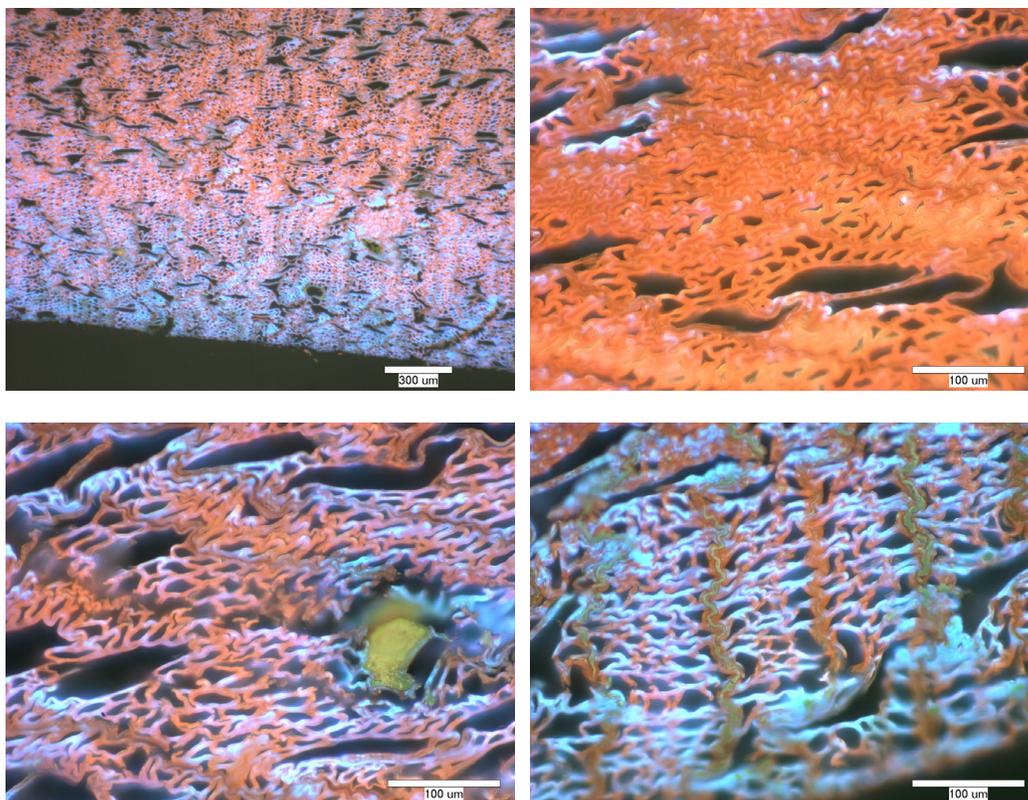
### Appendix C: Additional Microscopy Images



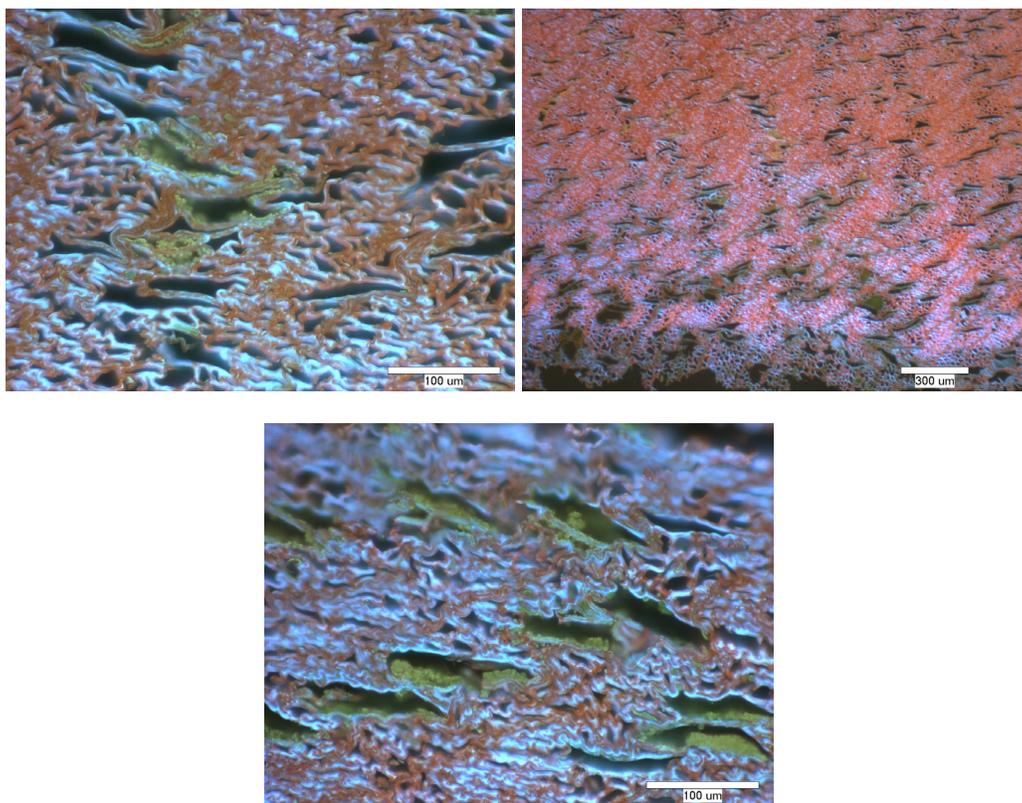
**Figure C.1.** Unmodified control sample.control



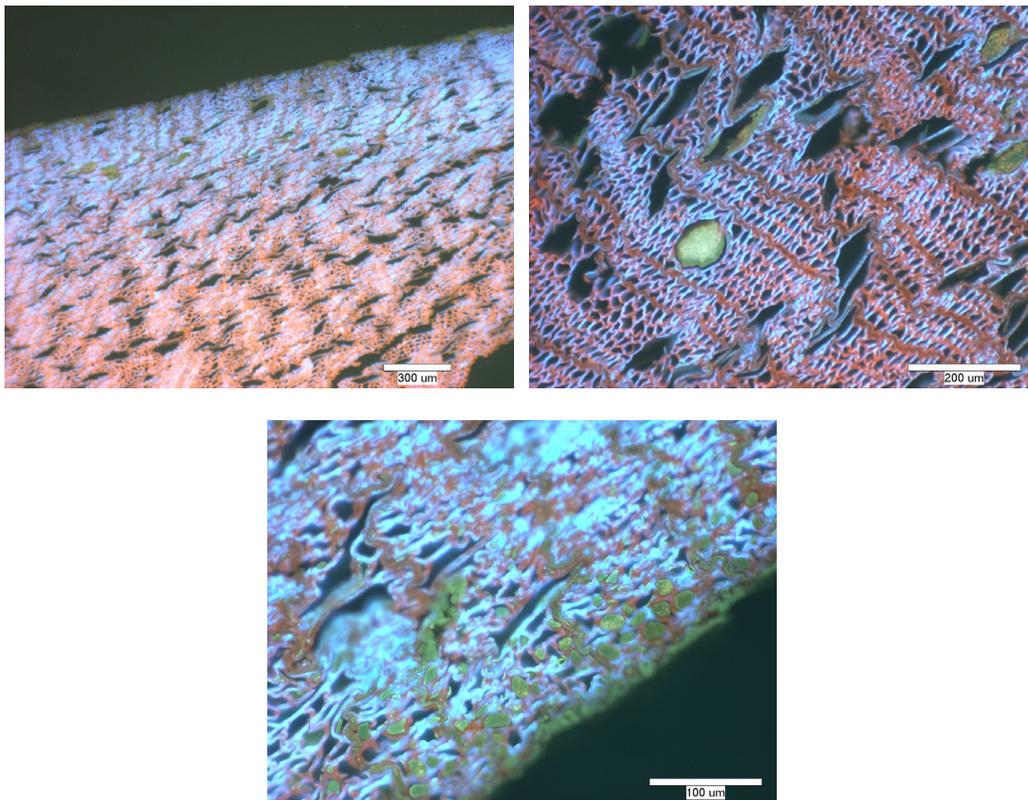
**Figure C.2.** Sample PF1 5 S NC. Impregnated with PF1 resin at 5% concentration and processed with steam and without conditioning.



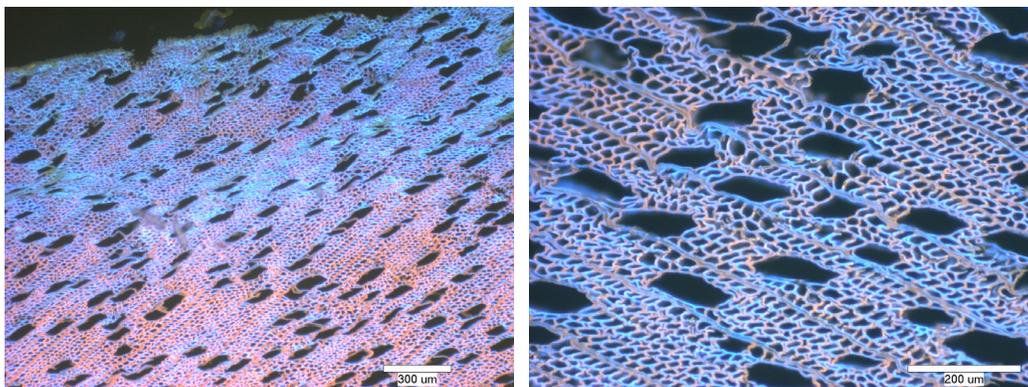
**Figure C.3.** Sample PF1 10 S NC. Impregnated with PF1 resin at 10% concentration and processed with steam and without conditioning.



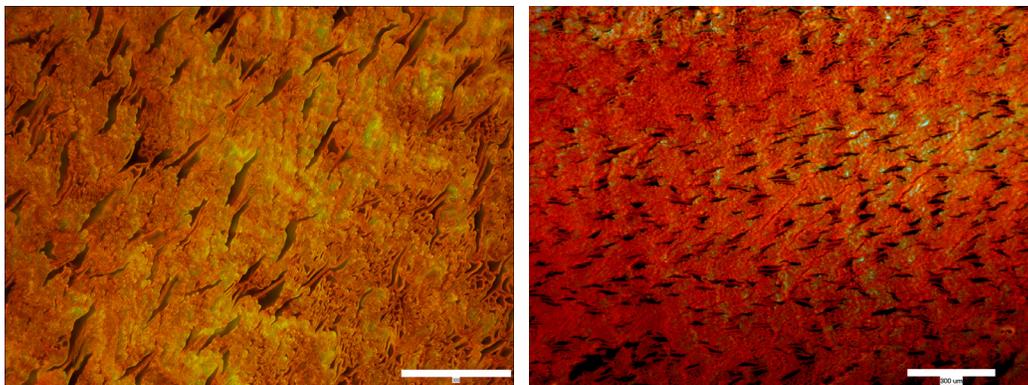
**Figure C.4.** Sample PF1 20 S NC. Impregnated with PF1 resin at 20% concentration and processed with steam and without conditioning.



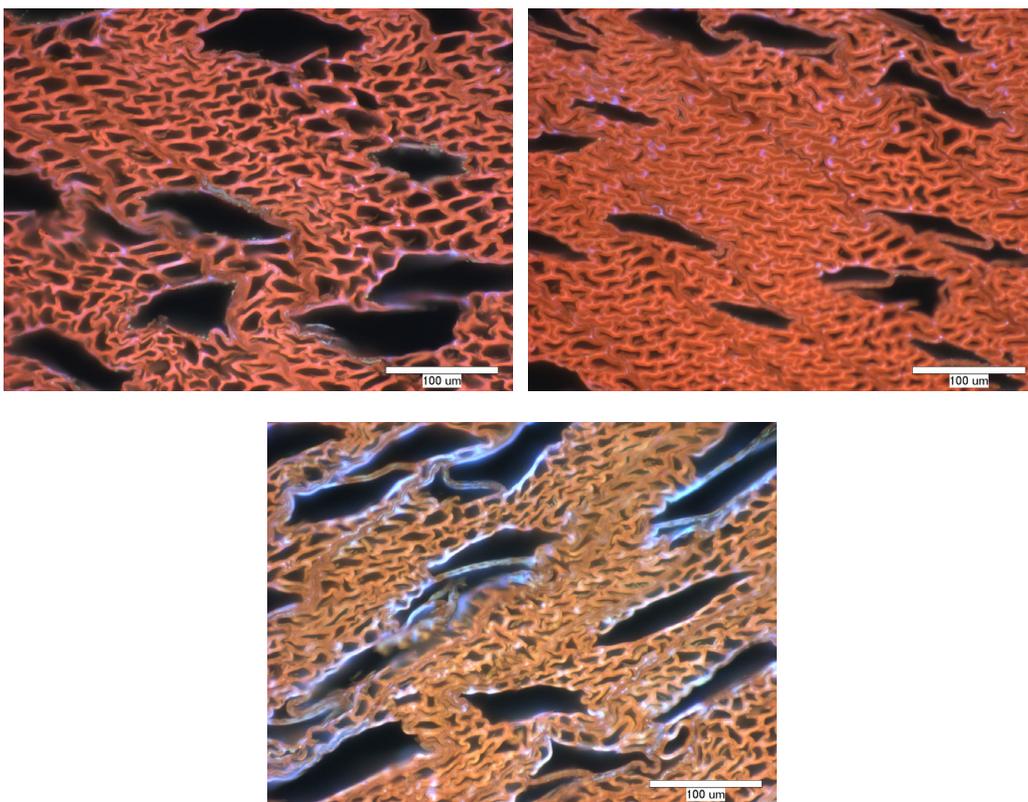
**Figure C.5.** Sample PF1 10 S C. Impregnated with PF1 resin at 10% concentration and processed with steam and with conditioning.



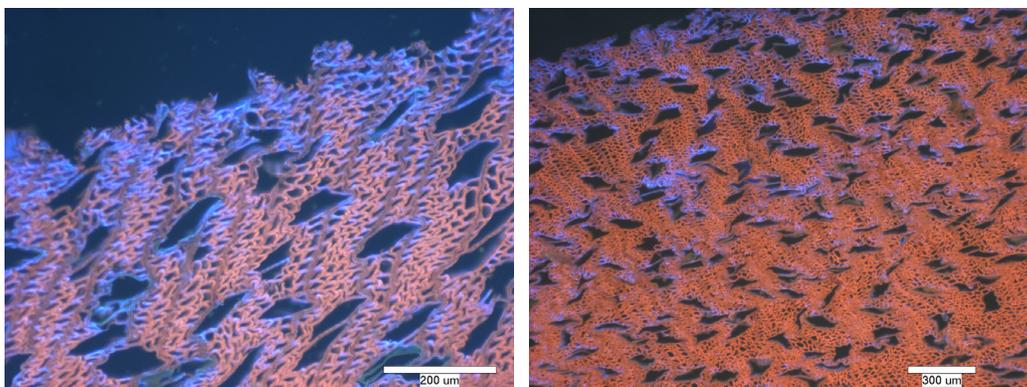
**Figure C.6.** Sample PF1 10 NS NC. Impregnated with PF1 resin at 10% concentration and processed without steam and without conditioning.



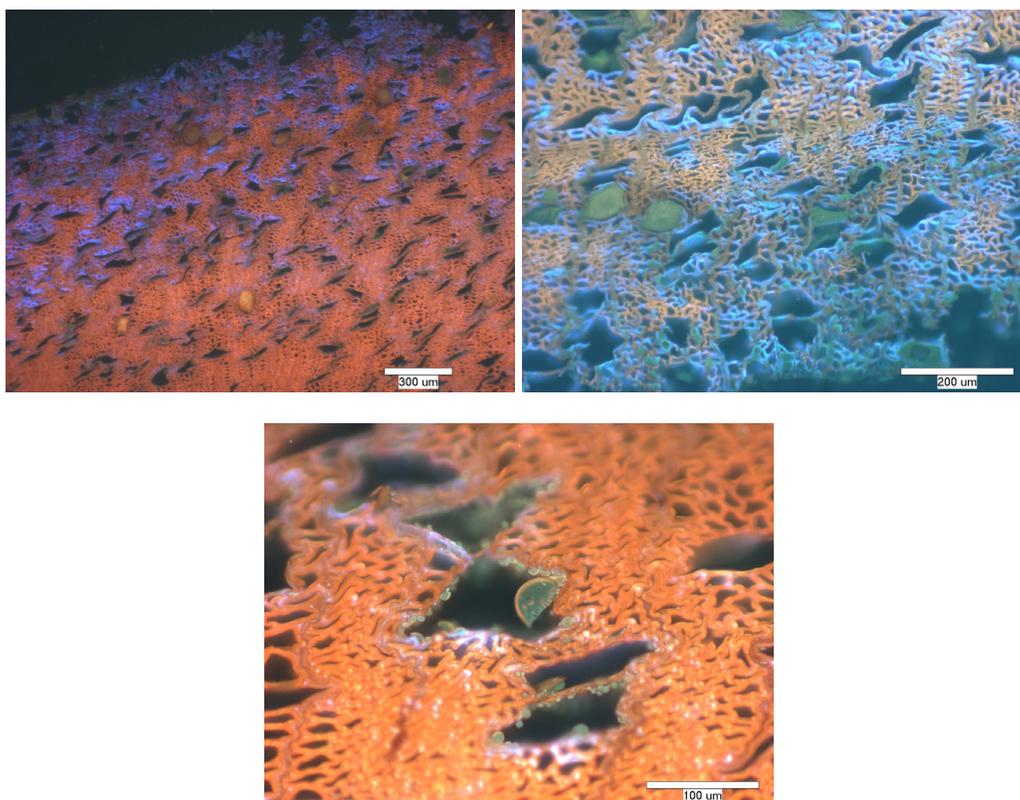
**Figure C.7.** Sample PF1 5 S NC HD. Impregnated with PF1 resin at 5% concentration and processed with steam and without conditioning. Compressed to a higher final density.



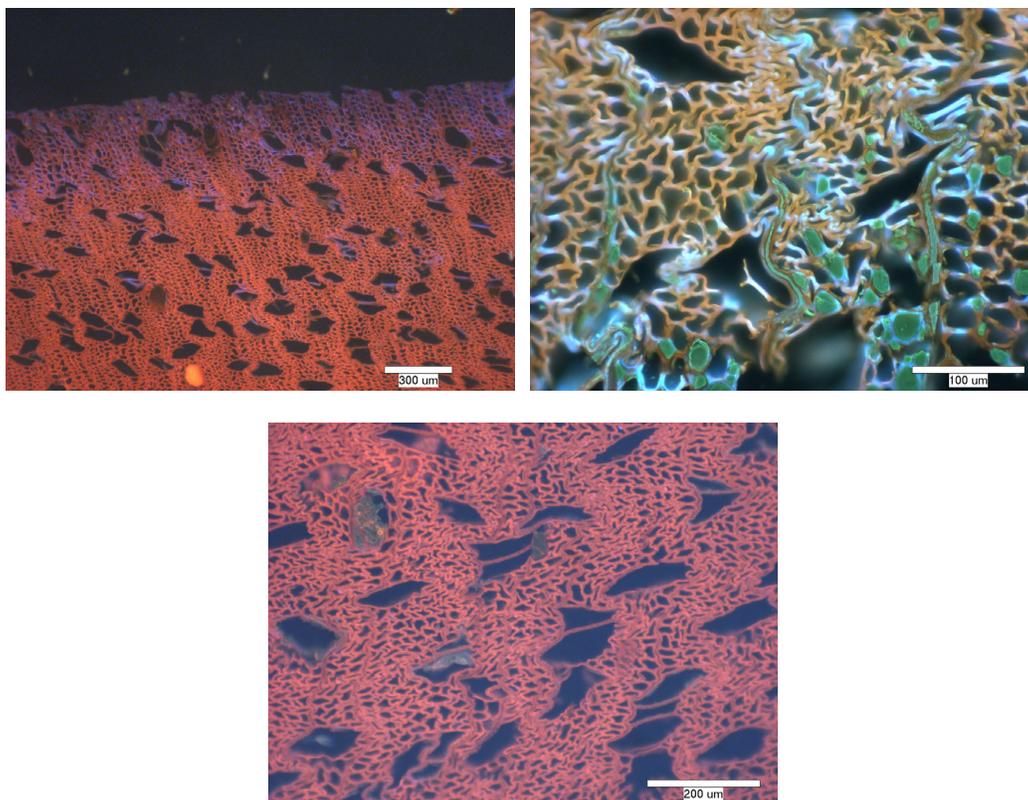
**Figure C.8.** Sample PF2 5 S NC. Impregnated with PF2 resin at 5% concentration and processed with steam and without conditioning.



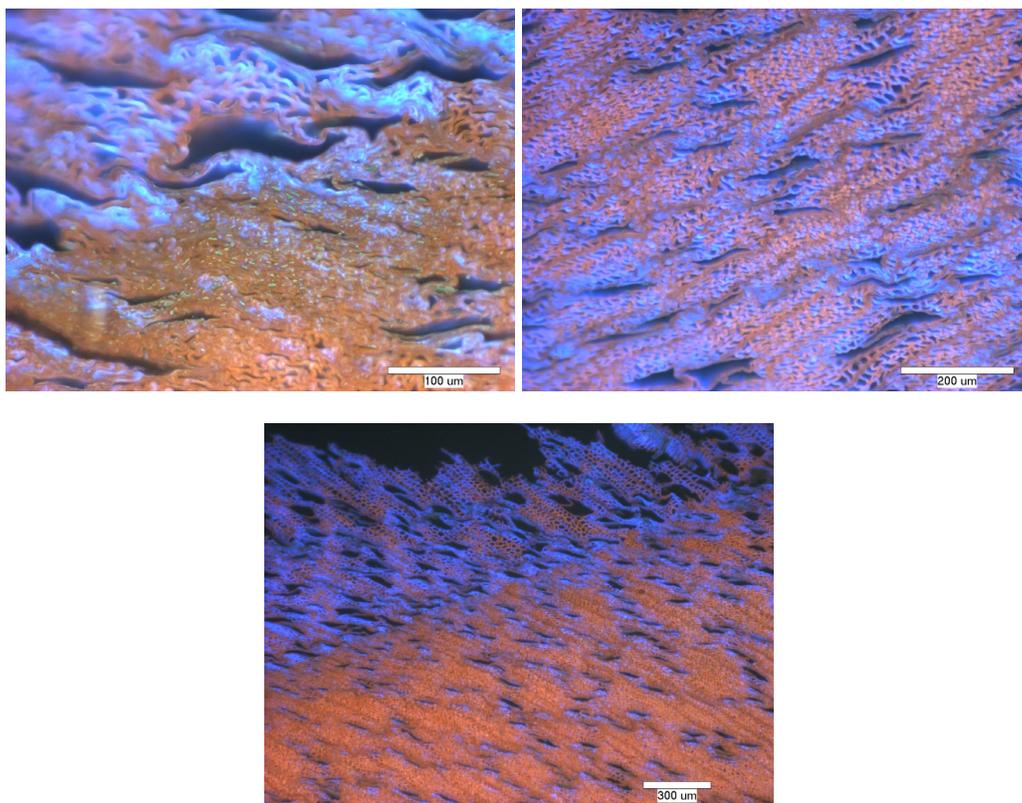
**Figure C.9.** Sample PF2 10 S NC. Impregnated with PF2 resin at 10% concentration and processed with steam and without conditioning.



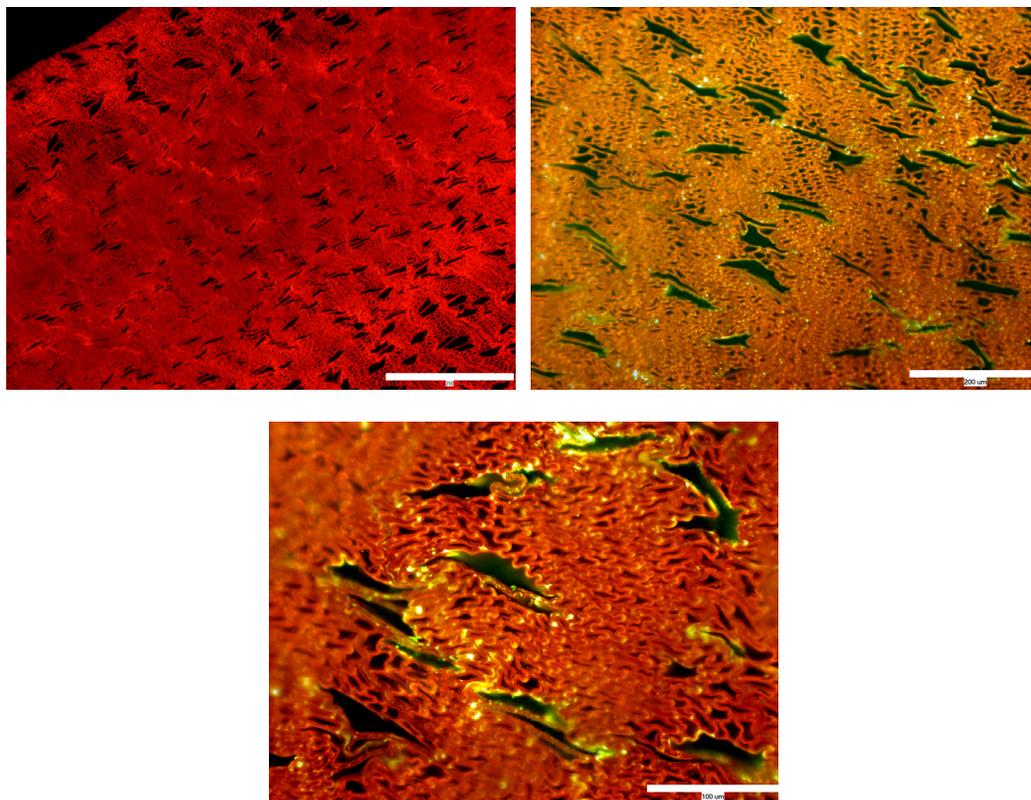
**Figure C.10.** Sample PF2 20 S NC. Impregnated with PF2 resin at 20% concentration and processed with steam and without conditioning.



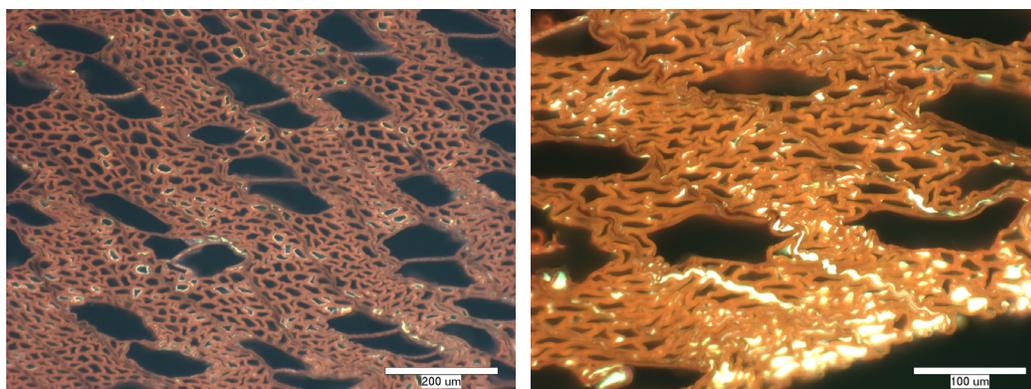
**Figure C.11.** Sample PF2 10 S C. Impregnated with PF2 resin at 10% concentration and processed with steam and with conditioning.



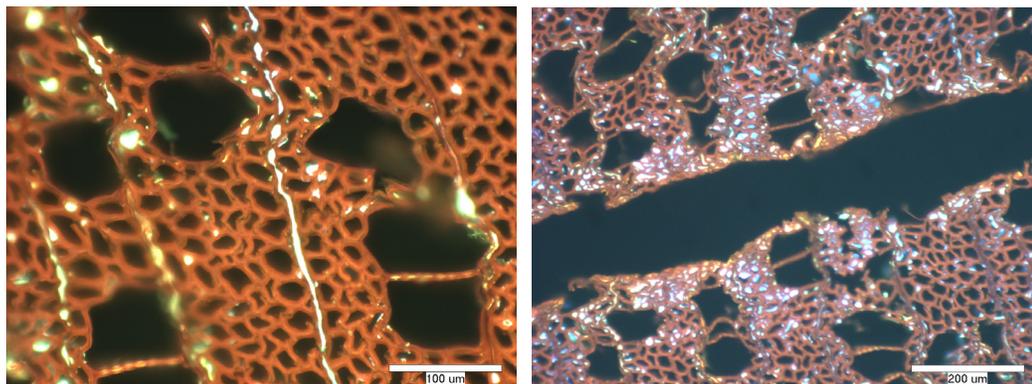
**Figure C.12.** Sample PF2 10 NS NC. Impregnated with PF2 resin at 10% concentration and processed without steam and without conditioning.



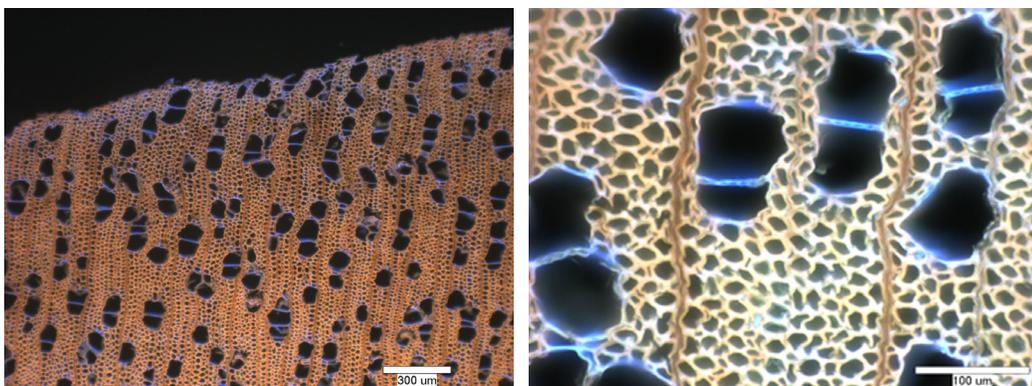
**Figure C.13.** Sample PF2 5 S NC HD. Impregnated with PF2 resin at 5% concentration and processed with steam and without conditioning. Compressed to a higher final density.



**Figure C.14.** Sample TO 10 S C. Impregnated with tung oil at 10% concentration and processed with steam and conditioning.



**Figure C.15.** Sample TO 10 S NC. Impregnated with tung oil at 10% concentration and processed with steam and without conditioning.



**Figure C.16.** Sample AA 20 S NC. Impregnated with acetic anhydride to achieve a final WPG of approximately 20% and processed with steam and without conditioning.

