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Comparison of Properties of Pine Scrim Lumber Made from Modified Scrim

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COMPARISON OF PROPERTIES OF PINE SCRIM LUMBER MADE FROM MODIFIED SCRIM

By

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COMPARISON OF PROPERTIES OF PINE SCRIM LUMBER

MADE FROM MODIFIED SCRIM

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In this study southern pine scrim was treated with low molecular weight melamine formaldehyde (MF), phenolic formaldehyde (PF), and furfuryl alcohol (FA) at different loadings and formed into 25-mm thick panels. Mechanical, dimensional and biological properties were evaluated.

Results showed that samples treated with 5% MF had the highest MOE, MOR and work to maximum load values (15.3 GPa, 54.2 MPa and 25.4 KJ/m^3, respectively), while those treated with 10% MF had the highest internal bond and edgewise toughness values of 390 kPa and 12 N•m, respectively. With respect to dimensional stability, samples treated with 20% FA had the lowest swelling value (ASE = 36.8%), and the lowest water absorption value (27.5%). Dynamic swelling test revealed much higher ASE value (> 45%) for furfurylated samples. As for termite resistance, both untreated and treated samples had little weight loss (1.10-1.56%), high visual rating (8-9.3/10), and 100% mortality in laboratory test.

DEDICATION

I would like to dedicate this work and pursuit of accomplishment to my mother, Yulan Wei, and wife, Rui Sun, for without their support and love, I would have chosen a different path. From the bottom of my heart, thank you

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

The wood modification industry developed rapidly in the past several decades. Research on wood modification began in the 1930s (Stamm and Seborg 1936; Goldstein and Dreher 1960) and can consist of physical and chemical modification. Physical modification focuses on thermal treatment which can control volume swelling by decreasing the hydroxyl groups of cellulose and hemicellulose (Seborg et al 1953; Kollmann and Schneider 1963; Stamm 1964; Kollmann and Fengel 1965; Burmester 1973; Giebeler 1983; Hillis 1984; Bourgois and Guyonnet 1988). Thermal treatment of wood can also enhance decay resistance, and contribute to uniform color change. (Kollmann et al 1975). However, there is a decrease in mechanical properties due to changes in chemical composition from the elevated temperature and duration of time. Exothermic decomposition of wood initiates at 273 ºC at which point hemicellulose starts to pyrolyze (Rowell et al 2009). Therefore, propositional temperatures for thermal treatment are between 160 ºC -260 ºC. Thermal treatment depends on factors including temperature, duration time, pressure, moisture content (MC), and species. For example, the optimum condition for pinewood is 160 ºC, 0.7MPa, and 20-30% MC (Burmester 1973). Alternatively, a low temperature but a long duration time can also break down the chemical bonds of wood (Shafizadeh and Chin 1976).

Chemical modification of wood can be defined as a process of bonding a reactive simple chemical to a reactive part of a cell wall polymer, with or without catalyst, to form a covalent bond between the two (Rowell 2006), which results in lowering of the cell-wall water holding capacity and the scrim saturation point (Kumar et al 1991; Militz 1991; Codd et al 1992). The essential requirement is that the reacting chemical should penetrate into the cell wall and react with the available hydroxyl groups of the cell-wall polymer, preferably in neutral or mild alkaline conditions at temperatures below 120 ºC. The major types of linkages formed by reaction with wood are ether, acetal, ester, etc., of which ester bonds are the weakest and are liable to acid or base attack (Kumar 1994). The chemicals could be in a liquid or gaseous phase.

Acetylation is a popular and commercial chemical modification method. Considerable studies have been conducted using not only solid wood, but also fibers, flakes and panels. It was first performed by Fuchs (1928). However, Tarkow (1945) first found decay resistance of acetylated balsa and first described the use of acetylation to stabilize wood from swelling and shrinking (Tarkow 1946). These properties were confirmed by many other researchers (Hon 1996; Evans et al 2000; Chang and Chang 2001; Larsson 2002; Hill et al 2005; Hill 2006). Detailed studies on the relationship between weight percentage gain (WPG) of active chemical ingredient and bio-resistance were then conducted. It was reported that decay and termite resistance were satisfactory at 6-20% WPG and 13-18% WPG, respectively (Kumar and Agrawal 1982; Kumar and

Kohli 1986; Videlov 1986; Imamura and Nishimoto 1986, 1987). The main chemical reaction in acetylation is esterification with accessible hydroxyl groups of wood cell wall components and anhydrides which include acetyl anhydride, butyric anhydride, phthalic anhydride and maleic anhydride (Goldstein et al 1961; Popper and Bariska 1975; Matsuda 1993). These treatments, however, yield by-products which are corrosive to metallic fasteners (Simonson and Rowell 2000). Researchers then focused on eliminating by-products and thus cyclic anhydride such as succinic anhydride and octenyl succinic anhydride, were used to avoid by-products (Hill and Mallon 1988). Recently, researchers also used vinyl acetate to react with wood and obtained expected outcomes (Jebrane and Sebe 2007). In addition, this novel method could easily remove the acetaldehyde by-product because its boiling point is low (21 ºC). Nevertheless, the impregnation of the acid into the wood would hydrolyze wood components (Oshima 1965); consequently, the strength of wood will be reduced compared to that of untreated one.

Impregnation with phenol formaldehyde (PF) resin was first introduced to treat wood in the 1930s (Stamm and Seborg, 1939). Hygroscopicity, shrinking and swelling, and susceptibility to biodeterioration were all reduced (Stamm and Baechler 1960). High mechanical strength was obtained at the same time (Stamm and Seborg 1939). PF resin was located mainly in the cell wall (Kumar 1994). A good decay resistance was reported at about 10% polymer loading in the cell wall (Furuno et al 1992). In further study researchers found that average weight of PF molecule affected the performance of impregnation (Ryu et al 1993). Low molecular weight (LMW) PF resin could easily

penetrate into the cell wall, playing a vital role in dimensional stability and decay resistance of wood; while medium and high molecular weight resin could only partially penetrate with most just deposited within the cell lumen, resulting in negligible contribution to dimensional stability and decay resistance (Furuno et al 2004). Ryu (1993) pointed out that molecular weight distribution and pH of the resin also contributed to the decay resistance. PF resin consisted exclusively of monomeric phenol alcohols with two or three reactive alcohol groups and that had lower alkalinities was less apt to decay. Similar to PF resin, water soluble melamine formaldehyde (MF) resin could be utilized to impregnate wood (Gindl et al 2003). The MF resin could penetrate into wood cell wall (Rapp et al 1999; Gindl et al 2002) and amorphous region of cellulose fibrils (Hua et al 1987a, b), forming covalent bonds with cellulose and lignin (Troughton and Chow 1968; Troughton 1969). MF resin itself is used as a decorative laminate because of its hardness. Improved surface hardness and MOE of wood products can also be obtained when impregnated with LMW MF resin (Gindl et al 2003). Decreased hygroscopicity and bio-deterioration were also reported (Minato et al 1993).

With the development of the adhesive industry, furfuryl alcohol (FA) was recognized as a substitute for phenol formaldehyde resins, and furfurylation of wood was then introduced by Stamm in the early 1950s. FA has a small size, which is preferable in order to penetrate into wood cell wall (Baysal and Osaki 2004). At that time, researchers' main interests were in durability towards acids and alkali, improved mechanical properties, dimensional stability, and biological durability (Dunlop and Peters 1942;

Goldstein 1955; Stamm 1964). Acetylation, PF, MF, and FA impregnation did not decrease the mechanical properties of wood, which were crucial for structural material. Improper use of some catalysts, however, was a major problem for furfurylation, since metallic and halogenic catalyst could reduce the strength of wood substrate (Anaya 1984, 1987). For example, zinc chloride, which was previously used as one catalyst, could dramatically degrade wood cellulose. Catalysts that contains metal and halogen elements did not have low mammalian toxicities (Lande et al 2004) and thus presented environmental concerns. Hence, cyclic carboxylic anhydrides, mainly maleic anhydride, were used as the main catalyst for furfurylation (Schneider 1995; Westin 1995; Westin et al 1996).

The methods mentioned above all used liquid chemicals. The liquid phase could cause some problems in penetration, which resulted from low pressure differential and high molecular weight of the chemicals. However, gaseous phase could avoid these drawbacks (Scheurch 1968), with much lower molecular weight and lower pressure differential requirements. Problems with liquid tension interfaces are also avoided. Barnes et al (1969) evaluated vapors of ethylene oxide and vinyl chloride as dimension stabilizing agents. Poor results were obtained with vinyl chloride, while ethylene oxide yielded high ASE values when using an oscillating pressure method. In addition, a lower chemical loading was needed with gaseous phase. Successful preservative treatment with trimethyl borate in the gaseous phase has been achieved for several composites (Barnes and Murphy 2006).

After decades of development in wood modification, the research system has become more sophisticated. There are four heat treatment processes (Thermowood, Plato, Retification, and OHT), one acetylation process (Titan wood), several impregnation processes such as Fibron and C-K composites in the USA, Permali in the UK, Dymonwood in Pakistan (Hill 2006), and two furfurylation processes (Kebony for hardwood and Visorwood for softwood) (Lande et al 2008), being commercialized in the wood products market. Researchers have shifted their interests to new treating processes and evaluating methods, and mechanisms of these treatments due to the advancement of equipment. The effects of acetylation have been proved to be not only have a bulking effect, but also a reaction kinetics that follow a diffusion model (Ramsden and Blake 1997). Hydroxyl groups in wood cell wall could interact with acetic groups (Papadopoulos and Hill 2002), resulting in a permanent dimensional stability for acetylated wood. However, the performance of acetylation was affected by the size of acetyl groups. If the size was larger than the wood pore size, then the acetyl groups could not access into the cell wall. Acetylated wood also had a diminished fire performance (Morozovs and Buksans 2009). The ignition time of acetylated ash wood was less than that of untreated one, while the extent of burning was larger than that of untreated one. After further studies on the mechanisms of decay resistance of acetylated wood, scientists found three possible mechanisms: a) modification of substrate such that prevent the enzymatic attack, b) bulking effect of covalently bonded acetyl groups (Forster et al 1997; Forster 1998), and c) physical blocking of cell wall micropores from enzyme

penetration (Hill 2002). Stamm and Baechler (1960) concluded that decay resistance was related to insufficient moisture content in cell wall because of anhydride substitution of accessible hydroxyl group, while Rowell (1983) proposed that the substrate was unrecognizable to enzymes initiated fungal agents. With further study, Hill (2009) argued that the mechanisms were depended on species. For some species, the decay resistance was a function of WPG, while for others it was a function of the extent of OH substitution. However, Hill (2009) generally preferred the insufficient MC mechanism. The relationship between reagent WPG and distribution of acetyl groups in wood cell wall has also been studied (Rowell 2006). It was reported that at low WPG, acetyl groups were mainly located in the S2 layer. With the increase in WPG, acetyl groups began to concentrate in the middle lamella (ML).

The mechanism of furfurylation was considered to be the production of highly branched and cross-linked furan polymer bonds with cell wall components. Three types of reactions between furfuryl alcohol (FA) and wood substrate were demonstrated: homo-polymerization of FA, co-polymerization of FA and additives or wood extractive substances, and grafting of FA or polymerized FA to wood cell wall polymers (Foo and Hemingway 1985; Choura and Gandini 1996). A controversy was on whether or not were there covalent bonds between FA and wood cell walls. Earlier it was considered that FA only polymerized inside the wood and hindered water penetration into wood, acting as a physical barrier. Choura et al (1996) introduced five model compounds to investigate the polycondesation of FA. They showed that linear unconjugated oligomers were first

formed, followed by conjugated products after repetitive cycles which resulted in the loss of hydride ions and the deprotonation of the carbenium ions. Finally, cross linking between conjugated polymers and furan rings occured. On the other hand, Lande et al (2004) debated that covalent bonds existed between FA and wood cell wall by comparing the anti-shrink efficiencies (ASE) of PF resin and FA treated wood. He and his coworkers argued that the ASE of FA treated wood should be less than PF resin treated wood if there were only polymerization reactions inside wood, while the experiment results contradicted this theory, which strongly indicated the existence of covalent bonds. Later Nordstierna et al (2008) proved Lande's hypothesis using NMR spectroscopic techniques to analyze the products obtained from the reactions between three model compounds that resemble units of lignin and FA. NMR spectroscopy revealed that the degree of polymerization of FA and the amount of covalent bonds increased with the increase in time. They also proposed the mechanism of reactions between FA and lignin units as follow:

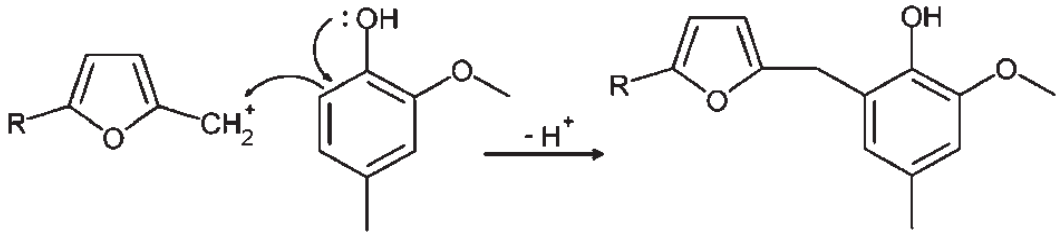

Figure 1.1 Mechanism of reactions between FA and lignin units (Lande et al 2008)

Similar attempts were made using ultraviolet (UV) spectroscopy, fluorescence spectroscopy, and confocal laser scanning microscopy (CLSM) on the basis of the brown color of furfurylated wood. Thygesen et al (2010) studied the fluorescence characteristics of furfurylated Scots pine using above techniques. He and his team treated different sizes of Scots pine solid wood with FA and then analyzed the samples using UV-visible spectroscopy, fluorescence spectroscopy, and confocal laser scanning microscopy, respectively. It was reported that fluorescent cured products were introduced into cell wall by furfurylation. More intense fluorescence was found in lignin-rich area of compound middle lamella (CML) than in the secondary cell wall. None to minor differences were found if the wood was treated with small FA oligomers.

The catalyst played an important role in the furfurylation treatment. In a fluorescence study (Thygesen et al 2010), where citric acid was utilized as the catalyst, a red-shift of the fluorescence was discovered with higher amounts of catalyst utilization, corresponding to an increased length of conjugated FA formed within the cell wall. Higher conjugation was observed for the poly FA formed within the lumen, which indicated restriction of poly FA formation by cell wall polymers. Baysal and Osaki (2004) tried to substitute acidic catalyst with borates on the idea of only minimally affecting the mechanical properties of furfurylated wood. FA-borate complex was found considerably improved the ASE of Japanese cedar and Scots pine by about 85%. At the same time, leachability significantly reduced, which indicated a linkage between active sites of FA

and boron after being cured. Termite resistance, however, was not influenced by the WPG of this FA, indicating the main contribution was likely residual boron.

Species was another factor that influenced the results of furfurylation. Scots pine, southern pine, and cedar were normally utilized for furfurylation treatment. New species such as maritime pine, Radiata pine, Norway spruce, and aspen have recently been tried. The treatability of maritime pine (*Pinus pinaster*) was determined in southern Europe (Esteves et al 2010). Boards measuring 1000 x 150 x 20 mm were treated with 70% FA. Average WPG of 38% was obtained. All properties improved considerably except the MOE: Equilibrium moisture content (EMC) decreased by more than 40% and ASE and hardness increased by 45% and 50%, respectively. Bio-durability increased significantly. The mass loss due to *Postia placenta* and *Coniophora puteana* decreased from 28.23% to 1.11% and from 5.69% to 0.78%, respectively.

Weight percent gain (WPG) is an important index for chemical modified wood products. WPG correlates to the properties such as decay resistance, hardness, dimensional stability, surface resistance to staining, and wear and scratching resistance. Traditionally, WPG was measured by weighing oven-dried samples before and after treatment. Near-infrared spectroscopy was used to determine WPG directly in a production flow-in-line (Venas and Rinnan 2008). This novel model was proved to be reasonable and stable with a root-mean-square error of prediction (RMSEP) value for the final prediction being 1.7±0.1 WPG with an R^2 of as high as 0.97 ± 0.01. With the development of instrument science and technology, bio-durability of furfurylated wood

can be measured, even quantified by advanced equipment. Verma and coworkers (2008) determined fungal activity in modified wood by micro-calorimetry and total esterase activity (TEA). It was believed that metabolism of fungi was related to the energy production which could be measured by micro-calorimetry, and to the total esterase activity which could be determined by the hydrolysis of fluorescein diacetate. Results confirmed the feasibility of the above methods to determine the fungal activity, of which the micro-calorimetry was the better one. Recently, Pilgard et al (2010a) applied quantitative real-time polymerase chain reaction (qPCR) to study the colonization of *Trametes versicolor* on treated wood. Samples of treated wood were ground and the DNA of *T. versicolor* was extracted and then quantified. Results showed that qPCR was the most sensitive assay for profiling microbial growth in their natural substrates, which could detect even minor changes of fungus in wood colonization. Coupled with other sophisticated methods such as microscopy, micro-calorimetry, qPCR was believed to be promising method for determining durability of modified wood products.

With the environmental concern, toxicity of chemical modified wood and their leachates was evaluated (Pilgard et al 2009). Vetter et al (2009) suggested a combination of adequate decay resistance and low ecotoxicity. They treated southern, scots, and radiata pines, and beech with 20%, 30%, and 40% solution of FA. A tiered approach was utilized to optimize the combination of durability and ecotoxicity. Results showed that an increase in WPG did not render a significant increase in ecotoxicity of leachates, indicating that there must be a sufficient polymerization of FA inside the furfurylated

wood and cross linking between wood cell wall and active sites of FA. Pilgard et al (2010b) used Microtox assay and Daphtox analysis to determine the ecotoxicity of radiata pine and Scots pine furfurylated by three different procedures. According to their findings, treating procedures, species, and even analysis methods affected the ecotoxicity. Vacuum drying was found better than kiln drying and steaming with respect to curing of FA, which resulted in a higher degree of polymerization and less production of leachates. The toxicity of radiata pine was more severe than that of Scots pine under the same level of treatment indicating that species should be taken into consideration when comparing the toxicity of furfurylated wood. This study also illustrated that the same analysis method should be used to compare the ecotoxicity of different treatment, since different apparatus had specific sensitivities, and error would occur if several methods were mixed.

The probable mechanism for impregnation of phenol formaldehyde (PF) resin was that formation of interlocks between ray tracheids and longitudinal tracheids resulted in dimensional stability (Wan and Kim 2008). Two kinds of low molecular weight (LWM) PF resin were used to impregnate southern pine, after which light microscopy, SEM, transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and confocal microscopy were combined to analyze the distribution of PF resin inside wood components. Results showed that possible path for PF resin penetration was from ray trachids, while not through the cell lumen or warty layers. Choong and Barnes (1969) reported that high dimensional stability was obtained when the chemical was impregnated by a diffusion process. Furuno et al (2004) applied bromine signal tracing

approach to analyze the penetration of PF resin. Three levels of molecular weight and five levels of concentration of m-bromophenol-formaldehyde resin were impregnated into Japanese cedar samples and then SEM, electron probe X-ray microanalysis were utilized to determine the distribution of the chemicals within wood cell wall. Results revealed that lower concentration of lower molecular weight PF resin could easily and fully penetrated into cell wall and form wall polymers, contributing to a higher dimensional stability. With an increase in molecular weight and concentration, more fractions of PF resin were found deposited in cell lumen, resulting in much lower dimensional stability.

To optimize the properties of PF resin impregnated wood, scientists have focused on process improvement. Shams et al (2004, 2005, and 2006) studied the effects of processing parameters, sodium chlorite treatment, steam pretreatment, and species on compressive deformation of LMW PF impregnated wood. Results with Japanese cedar (*Cryptomeria japonica*) showed that the higher solid content of PF resin rendered more softening of the cell wall, resulting a lower collapse-initiating stress. Detailed study of the relationship between collapse-initiating stress and Young's modulus in the radial direction demonstrated that higher concentration of PF resin acted as a plasticizer to lower the Young's modulus of cell wall perpendicular to the scrim direction, thus reducing the collapse stress. The stress-strain curves of PF resin impregnated wood at different preheating temperatures showed that lower preheating temperature yielded lower collapse-initiating stress. It was suggested that higher preheating temperature

caused the condensation of PF resin, which would diminish the role of resin as a plasticizer and cause an increase in Young's modulus of cell wall. Pressing speed played an important role in the production of Compreg wood. Lower speeds like 2 mm/min and 5 mm/min, are preferable with respect to the deformation, since wood was more viscous at lower speeds and easier to collapse. The same species was use to investigate the effect of sodium chlorite on deformation behavior. 2% aqueous sodium chlorite was used at 45 ºC to remove lignin. Lignin could agglutinate cells to form strong tissue (Oshima 1965). Hence, delignification could reduce the Young's modulus of cell wall, resulting in collapse of cell wall at low stress. High mechanical properties could be obtained at low pressure, when delignification was combined with pressure holding. This provides a promise future for industrial application. A similar process in which sodium chlorite treatment followed by sodium hydroxide treatment prior to conventional low molecular weight PF resin impregnation was investigated on Japanese cedar (Shams and Yana 2009). Results also showed that these pretreatment partially removed lignin, softened cell wall and consequently made it possible to compress wood composites at low pressure while did not compromise the mechanical strength. Combination of thermal modification and PF resin impregnation of Japanese cedar veneers were evaluated. Veneer samples were first through saturated steam of different temperatures (140-200 ºC) for a short time and then compressed at low pressure. Thermal modification even for a short time could degrade some fractions of hemicelluloses, lowering the Young's modulus of cells and making them possible to collapse at low pressure. Results confirmed that steam

pretreatment was feasible to facilitate compressive deformation of wood impregnated with LMW PF resin. Density, Young's modulus, and bending strength of the samples reached 1.09 g/cm^3, 20 GPa, and 207 MPa, respectively, when steam pretreated at 200 ºC for 10min. When studying the role of species on compressive deformation of impregnated wood, eight species of softwood and hardwood with diverse densities (0.23-0.71 g/cm^3) were selected. Microscopic details illustrated that density and anatomical structure contributed to the differences in deformation behavior among species, of which lower density was preferable for obtaining high strength at low pressure. The reason was that species with lower density had lower Young's modulus, thus obtaining better deformation behavior at low pressure. We can conclude that all the above improving approaches were related to decreasing the Young's modulus of primitive samples.

The microscopic principles of melamine formaldehyde (MF) impregnated wood has been investigated by UV microscopy, confocal Raman microscopy, electron energy loss spectroscopy (EELS), and other analytical instruments. Rapp et al (1999) used EELS to detect the concentrations of melamine in different locations of modified wood cell walls. EELS spectra of S2 layer of untreated wood, middle lamella (ML), S2, S3, resin filled lumen, and empty lumen of treated wood were studied. Two characteristic energy loss of carbon and nitrogen were found at 284 eV and 402 eV, respectively. Data revealed an average of 20% (S2) to 30% (S3) of melamine inside the wood cell wall. An interesting finding was that the S3 and ML contained more melamine than the S2 layer, which was not expected based on the penetration gradient of resin. The reason might be

related to the different fractions of lignin in each layer which was believed to be easier to penetrate than holocellulose because of the chemical structure differences. Gindl et al (2003) applied UV microscopy and two models to study the role of MF on mechanical properties of spruce. According to the composite modulus model, melamine inside the cell lumen (less than 2%) was found not responsible for the strength increase, while melamine modified cell wall was. The density increment due to MF modification was mainly related to the concentration of MF in cell wall (12.5%, weight based), which was estimated on the basis of Beer Lambert's law (Scott et al 1969). A combination of UV and Raman microscopy was utilized to study the MF inside the wood cell wall (Gierlinger et al 2005). Spruce heartwood was immersed with melamine and methanol to a weight ratio of 1:1. After that, samples of specific sizes were prepared for UV and Raman microscopy. Results showed that triazine-ring nitrogen had a characteristic vibration band that could be used to determine the concentration of MF inside cell wall. Both approaches concluded that about 11% of MF resin was in the wood cell wall. Raman microscopy, however, was better than UV microscopy in that a sharper melamine peak could be detected.

Process of MF impregnation has been improved for the purposes of obtaining better wood properties. Inoue et al (1993) treated sugi (*Cryptmeria japonica*) with different concentrations of MF resin. Recovery rate and surface hardness were evaluated after treatment. Results showed that wood with higher WPG could retain compressed state in severer conditions, indicating a better dimensional stability. The same trend was

found for surface hardness, when wood was compressed for the same level, higher WPG rendered higher hardness, and vice versa. Gindl et al (2003) treated European larch, Scots pine, and Norway spruce with MF resin. Different pre-drying approaches, concentrations of MF resin, contents of extractives, and immersion time were used to optimize the properties of end products. Initial moisture content (MC) was reported to affect WPG of MF resin, of which higher initial MC facilitated the uptake of MF resin. There was, however, no difference in WPG when the duration time was long enough (20h in this study). Another finding was that lower concentration of MF resin yielded a higher uptake, twice as much for 25% solution compared with that of 55%-60% solution. Finally, extractive content played an important role in resin uptake, since it could reduce the wettability of wood and make it difficult for the movement of resin. Hence, an extractive removal process was recommended before MF resin impregnation on extractive abundant wood species.

The exact mechanisms of these treatments are still not well known. Researchers can only give some possible reasons for improved durability of heat treated wood, such as hydrophobic character, chemical modification and extractive, but they are not sure which one is the exact reason. There are also diverse opinions on the behavior of acetylation. It was reported that acetylation only had a bulking effect (Hill and Jones 1999), but others argued that acetic anhydride could react with hydroxyl groups (Ramsden and Blake 1997). It is unknown what molecular weight of phenol and melamine formaldehyde resin is optimal to react sufficiently with wood cell wall in

impregnation treatment. As for furfurylation, it was shown that FA could form covalent bonds with lignin components (Nordstierna et al 2008). Nevertheless, such a reaction was not shown for wood lignin in situ (Thygesen et al 2010). Hence, further studies on the mechanisms need to be done.

The objectives of the study were to determine:

1) The dimensional and mechanical properties of modified wood and PSL made with modified scrim;

2) The effectiveness of modification treatments on the termite resistance;

3) The optimum treatment level for each modification treatment;

4) The differences of the performance among these three treatments;

5) The relationship between dimensional stability and mechanical and biological properties.

CHAPTER II

MATERIALS AND METHODS

Scrimming Procedure

Twenty-five small-dimension southern pine (*Pinus* spp.) logs were donated by a local lumber manufacturer (Liberty Post & Barn Pole, Inc, PO Box 985, Bristol, FL 32321; R & L Post Co., 330 Conner Road, Preston, MS 39354). The logs were 2.4 m long, with diameters less than 150 mm. The logs were transported to the Timtek Building at MSU and stored under water until scrimming, as shown in Figures 2.1.

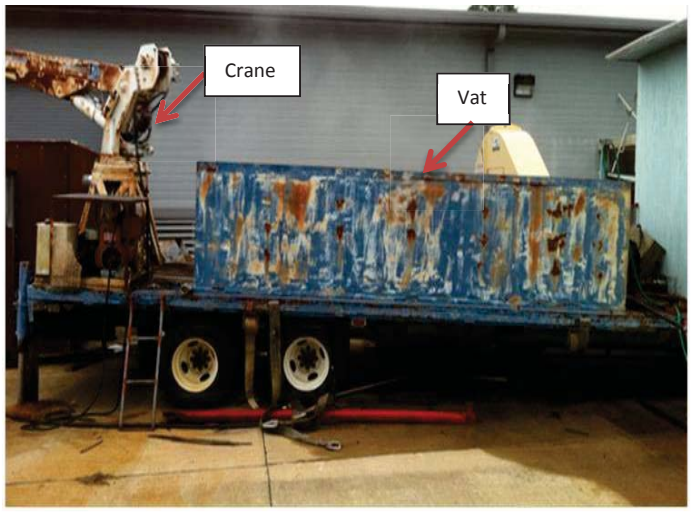

Figure 2.1 Log soaking tank

Before crushing, the logs were heated until the temperature of the center reached 80 ºC for at least 24 h. The purpose of this step was to soften the logs and make them easy to crush. Heated logs were then transferred to the scrim line where they were crushed and reduced to scrim. Details of the scrim line and process can be found at http://www.cfr.msstate.edu/timtek/index.asp. The line consists of one large crush roller and six scrimming heads, as shown in Figure 2.2. Logs crushed into scrim bundles were sent through scrim rollers in multiple passes until scrim of the appropriate size (thickness < 0.7 cm) and quality was obtained.

Figure 2.2 PSL scrim line.

When the scrimming was completed, the thickness of scrim was less than 8 mm. In addition, fine and short scrim was mixed with the long scrim bundles shown in Figure 2.3, since they could fill in the voids between large scrim and make the density distribution of panels more even.

Figure 2.3 Typical scrim bundles obtained in the scrimming process

As illustrated in Figures 2.4a, b, scrim bundles were laid evenly on trays (a) and put in the dryer (b) for pre-drying. Less than 10 kg of scrim was laid on each tray to make sure all scrim was dried evenly and had a MC less than 15%. Natural air was used in the

dryer. The pre-set temperature and time for drying period were 80 ºC and 4 min/kg of scrim, respectively.

The dryer could hold up to two stacks of trays of scrim, with eight layers in each tray, seven kg of scrim for each layer.

Figure 2.4 Drying of scrim bundles.

The pre-dried scrim was then cooled down and cut into lengths of 860 mm which was the size of panel to be made later. After that scrim was stored in a purpose built storage bin for later chemical treatment (Figure 2.5).

Figure 2.5 Scrim storage basket

Chemical Treatment

Citric acid and furfuryl alcohol (98% concentration) were purchased from Fisher Scientific. Melamine formaldehyde (MADURIT™ MW 840 75% WA) was donated by INEOS Melamines LLC (730-B Worcester Street Springfield, MA 01151, USA), and phenol formaldehyde polymer was donated by Arclin (475 North 28th Street, Springfield OR 97477, USA). All chemicals were in liquid phase, except the citric acid, which was a powder.

The treating equipment consisted of a vacuum/pressure cylinder, a solution mix tank, a 1200 x 330 x 330 mm metal treating pan, and a treating basket with dimensions of

1118 x 320 x 292 mm which was specially constructed to accommodate the metal treating pan (Figure 2.6).

During the chemical treatment process, scrim was first weighed and then loaded in the treating basket and covered with a lid. Four aluminum weights were put on top of the lid to ensure that all scrim was covered by the chemical solution all time during the treatment. When the scrim loading process was finished, the treating pan was pushed into the treating cylinder and a full cell treatment cycle was used to treat the wood. The cycle consisted of a vacuum at 85 kPa for 30 min, after which the chemical solution was pulled into the treating pan under vacuum. The cylinder was vented to atmospheric pressure after all solution was pulled into the pan by vacuum. An air pressure of 1.03 MPa was applied and held for 60 min. When the cycle was finished, the scrim was taken out of the treating cylinder and drained for an hour. Then treated scrim was weighed and solution uptake was calculated on a weight-weight basis. Treatment solutions were prepared by dilution with water to yield the desired solution strengths. With FA solutions 1.0% citric acid was included as a catalyst. Treatment data are shown in Table 2.1.

Table 2.1 Scrim treatment data sheet

Chemical	Solution %	Panel					Resin blended /solid content %	Density of southern pine scrim kg /m^3	Solution uptake kg /m^3	Solution/ scrim	Loading (w/w)	Active ingredient consumed kg	Oven-dry Scrim consumed kg
		Dimension mm			Specific Gravity/ od base kg /m^3	Weight kg							
		L	W	T									
FA	20%	860	860	25	750	14.26	10%	512	640	1.25	0.25	2.59	10.37
FA	30%	860	860	25	750	14.26	10%	512	640	1.25	0.375	3.54	9.43
FA	40%	860	860	25	750	14.26	10%	512	640	1.25	0.5	4.32	8.65
PF	5%	860	860	25	750	14.26	10%	512	640	1.25	0.0625	0.76	12.20
PF	10%	860	860	25	750	14.26	10%	512	640	1.25	0.125	1.44	11.53
PF	15%	860	860	25	750	14.26	10%	512	640	1.25	0.1875	2.05	10.92
MF	5%	860	860	25	750	14.26	10%	512	640	1.25	0.0625	0.76	12.20
MF	10%	860	860	25	750	14.26	10%	512	640	1.25	0.125	1.44	11.53
MF	15%	860	860	25	750	14.26	10%	512	640	1.25	0.1875	2.05	10.92
PF	15%	860	860	25	750	14.26	0%	512	640	1.25	0.1875	2.25	12.01
MF	15%	860	860	25	750	14.26	0%	512	640	1.25	0.1875	2.25	12.01
Control	0%	860	860	25	750	14.26	10%	512	0	0	0	0.00	12.96

Figure 2.6 Treating cylinder

Treated scrim was cured in a Blue M oven. The curing parameters for both PF and MF resin impregnated scrim was 50 ºC drying for 24 h, and 103 ºC curing for 20 h, while for furfurylated ones the curing process was air drying for 4 h, 103 ºC curing in sealed aluminum foil for 16 h, and 103 ^{0}C post drying for 8h. After curing, the oven dry weight of scrim was obtained to confirm the previous deduced WPG of active ingredient. The calculated initial oven dry weight was calculated by the moisture content formula:

$$W_{od} = W_{mc}/ (1+mc) \quad (2.1)$$

where W_{od} = oven dry weight of untreated scrim (g); W_{mc} = weight of untreated scrim at current moisture content g; and mc = the measured decimal moisture content of untreated scrim.

Panel Producing Process

Cured scrim was then resinated. Scrim treated with different chemicals and concentrations were aligned on the trays separately and labeled with steel tags. Another type of phenol formaldehyde resin (Specialty Engineered Wood Adhesive GP 585D09, 50%, Georgia-Pacific) was used as the adhesive. The resin was diluted with water, in which 21.85 kg of raw PF resin was injected in a 120 liter plastic drum. Then 46.4 kg of water was mixed into the drum and the mixture stirred with a wooden paddle. Then 0.9 kg 5% sodium hydroxide solution was put into the drum during stirring to make the PF resin dissolve in water. The final concentration of the resin solution was 16% resin solids. Diluted PF resin was sprayed on the scrim by a spray pipe powered by a small motor (Figure 2.7). The resin was sprayed row by row to make it evenly distributed among the scrim. A second drying was applied using the same dryer and conditions as was used in pre-dry process.

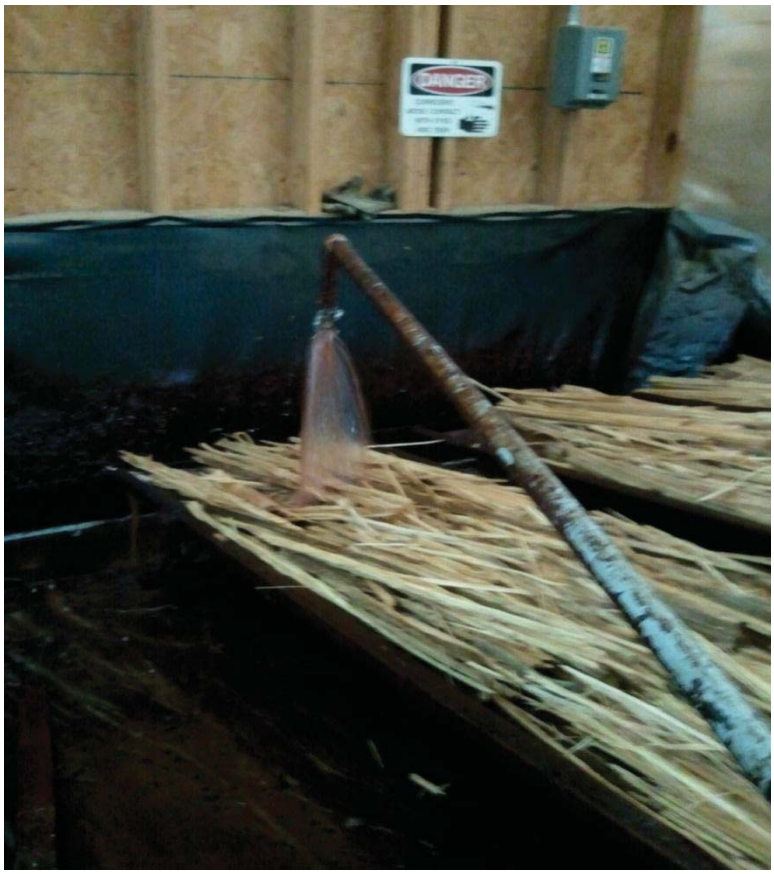

Figure 2.7 Application of resin

Before producing panels, the scrim was subjected to another drying process to bring the final MC down to 2-4%. This was achieved by the continuous electric dryer as shown in Figure 2.8. The advantage of this dryer was that a more uniform MC distribution could be obtained within scrim. Scrim was fed in by a belt conveyer at 4.5 min/kg scrim and drying temperature was 113 ºC.

Figure 2.8 Electric dryer

Electrically dried scrim was then laid in a forming box (Figure 2.9) immediately to prevent moisture reabsorption from the atmosphere. Two metal caul plates were located on both ends of the box to hold the scrim, and both plates were sprayed with non-stick spray. During the forming process, all scrim was laid straight in the box, and short fine scrim, as mentioned previously was used to fill the voids. Ties were also applied to tie up the scrim to prevent edge losses and minimize density variation during pressing.

Figure 2.9 Forming box used in scrim layup

The formed scrim mat was transferred to a Dieffenbacher one meter laboratory press with Pressman controls to make 860 x 860 x 25 mm panels. The pressing temperatures were 188 ºC and 187 ºC for the upper and bottom press platen, respectively, at holding pressure of 5 MPa. Closure time was 30 sec, pressing time was 1020 sec, and decompression was 55 sec. The movement and time intervals of the platen were shown in the following chart:

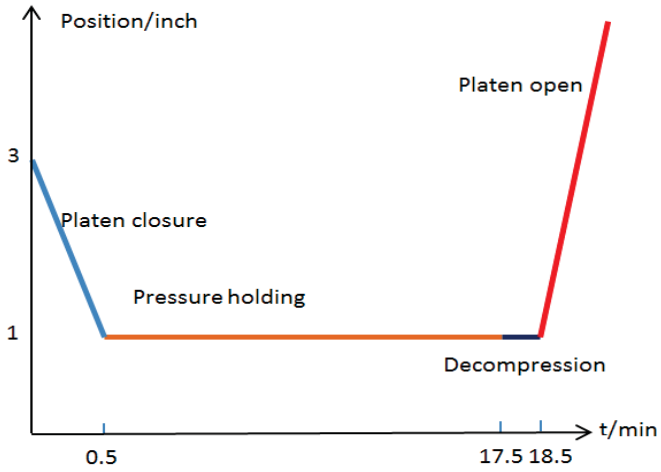

Figure 2.10 Press diagram

During pressing, scrim treated with 15% PF and 15% MF solutions were not resinated. These panels did not bond properly and were not evaluated. When the pressing phase was done, panels were pulled off of the caul plates and cooled down for 24 h (Figure 2.11). Edges were then trimmed as they were low density and could not be utilized. Panels were labeled according to different treatment, and then transferred into a conditioning chamber (20 ºC, 65% relative humidity) for 7 days. After that panels were cut into samples and returned to the conditioning cabinet until tested. The cutting diagram is shown in Figure 2.12. According to the diagram, 100 mm wide strip perpendicular to the grain was ripped for thickness swelling tests. A 50 mm wide strip parallel to the grain was ripped for internal bond test, while 25 mm wide strips parallel to the longitudinal direction of the scrim were cut for bending test. Then 20 mm wide strips parallel to the grain were cut for toughness test.

Figure 2.11 Hot pressed panel

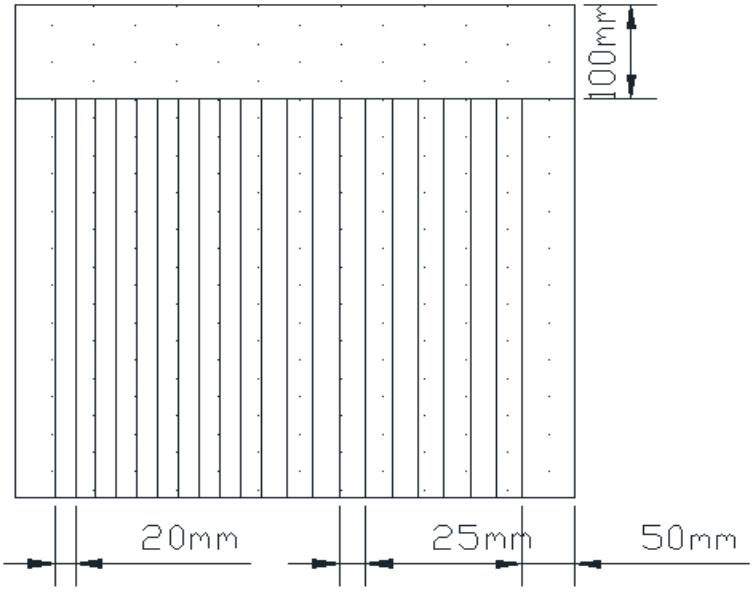

Figure 2.12 Sample cutting diagram

Property Testing Phase

Static Bending and Shear Strength

In this study, bending strength, internal bond, toughness, thickness swelling, tangential swelling and termite tests for both treated and untreated PSL were conducted according to ASTM standard D4761 (2005), D1037 (2006), D143 (2007), D1037 (2006), D143 (2007) and AWPA E1-09 (2010), respectively. Shear strength of samples treated with 30% FA was evaluated using ASTM D143 (2007). All mechanical tests were completed in the mechanical testing lab at Forest Products Department, Mississippi State University. The testing machines in the study consisted of Table top A and Satec™ mechanical testing machine (Instron, 825 University Ave, Norwood, MA 02062-2643), which were both connected to Blue Hill operating software. According to ASTM D4761 (2005), for edge-wise (loading direction parallel to the panel surface) bending, the span depth ratio was 17:1 yielding a sample dimension for bending tests of 480 x 25 x 25 mm, with a span of 430 mm. By virtue of the restriction of panel dimension, dimension for thickness swelling and tangential swelling could not comply with the standard, and was chosen as 100 x 100 x 25 mm. Sizes for the other tests strictly followed the standards. Sample numbers (Table 2.2) varied because of density distribution of different panels.

Table 2.2 Replications by test for samples tested in the study[1]

Treatment / Item	Control	P5	P10	P15	M5	M10	M15	F20	F30	F40
Bending test	10	14	13	10	14	14	14	12	12	12
Internal bond	10	10	10	10	12	11	12	10	10	10
Toughness	20	20	20	20	20	20	20	20	20	20
Thickness swelling and tangential swelling	4	4	4	4	4	4	4	4	4	4
Termite test	5	5	-	-	5	-	-	-	5	-

[1] (P5-samples treated with 5% PF solution, P10-samples treated with 10% PF solution, P15-samples treated with 15% PF solution, M5- samples treated with 5% MF solution, M10- samples treated with 10% MF solution, M15- samples treated with 15% MF solution, F20- samples treated with 20% FA solution, F30- samples treated with 30% FA solution, F40- samples treated with 40% FA solution.)

According to ASTM D4761 (2005) bending edge-wise test, two-point loading was used with two equal transverse concentrated loads spaced equidistant from the supports, to determine bending properties. The loading speed was 2.5 mm/min. Samples and test setup are illustrated in Figures 2.13 and 2.14, respectively.

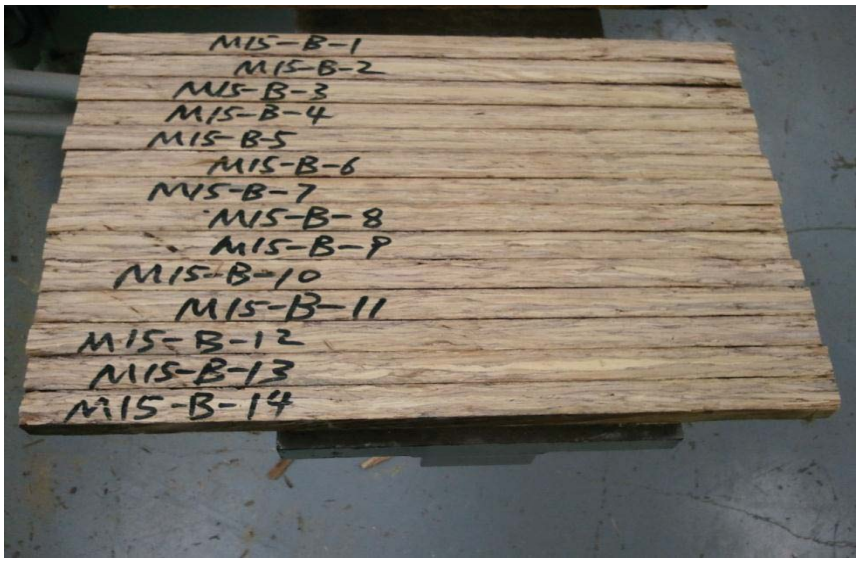

Figure 2.13 Samples for bending test

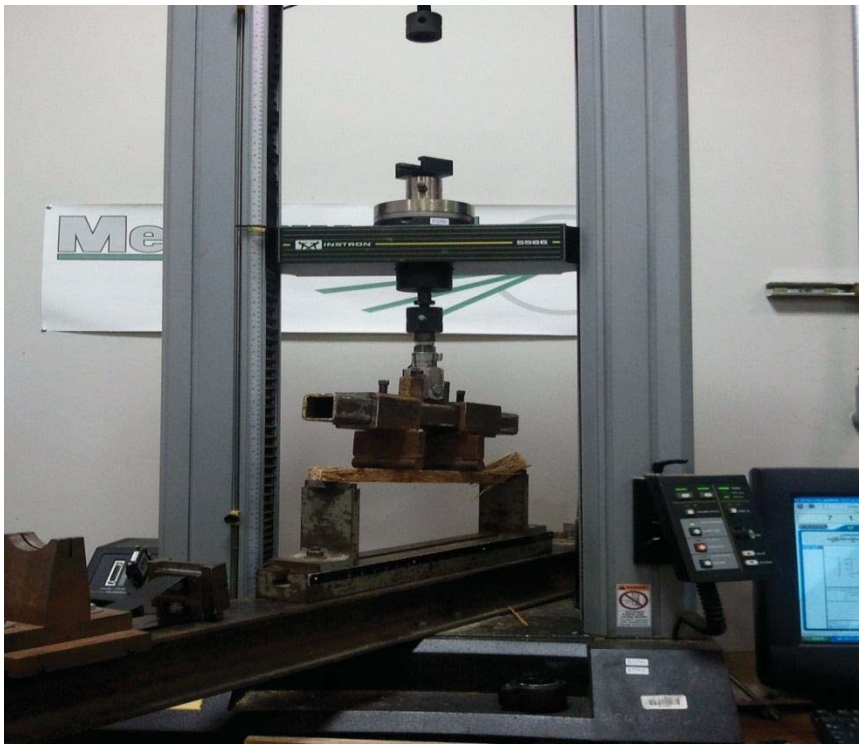

Figure 2.14 Bending test setup

In order to analyze the bending strength of PSL, shear strength of samples treated with 30% FA solution was tested. According to ASTM D143 (2007), the dimension of the shear area should be 50 x 50 mm. Since the thickness of all panels was 25 only mm, modification of sample dimension was made with a shear area of nominal 25 x 25 mm. Shear strength on two orthogonal surfaces was evaluated. In Figure 2.15, the sample was tested for shear strength perpendicular to panel surface is shown.

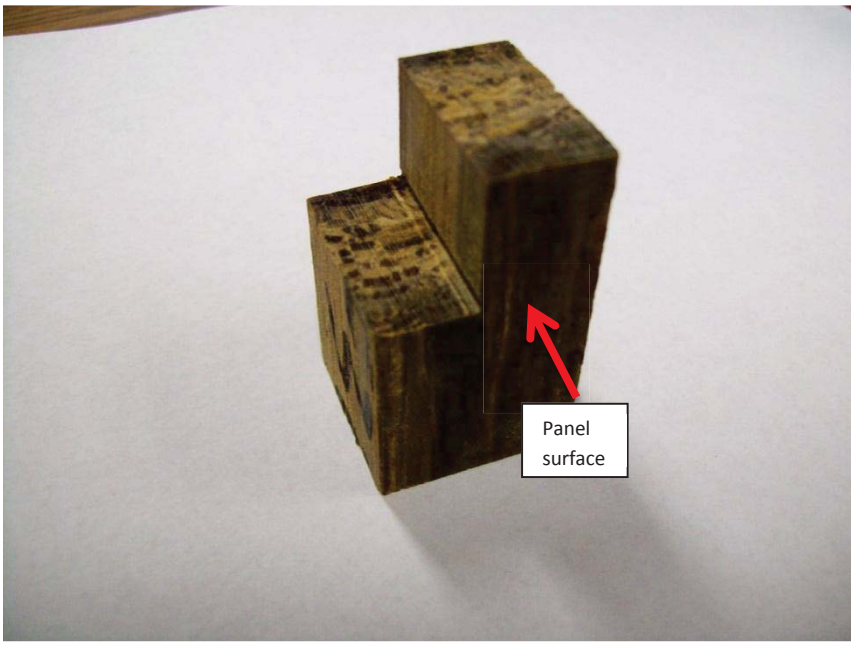

Figure 2.15 Sample for shear test

Figure 2.16 Shear test setup

Shear strength samples were tested in Satec™ mechanical testing machine. The sample was loaded in the center area to prevent uneven force distribution. After the test, shear strength of the two orthogonal surfaces was analyzed.

Toughness

Toughness test was conducted in compliance with ASTM D143. Samples numbered from 1 to 10 in each group were tested in a position where panel surface was parallel to the load direction, while those numbered from 11 to 20 were tested in a position where panel surface was perpendicular to the force direction. During each test, the pendulum was located in position 5, and the initial anger was 30^{o}. The gauge was returned to zero before each test. Finally, toughness value was calculated using the

formula listed in the standard (ASTM 2007). Toughness samples are shown in Figure 2.17 while the toughness testing machine is shown in Figure 2.18.

Figure 2.17 Samples for toughness test

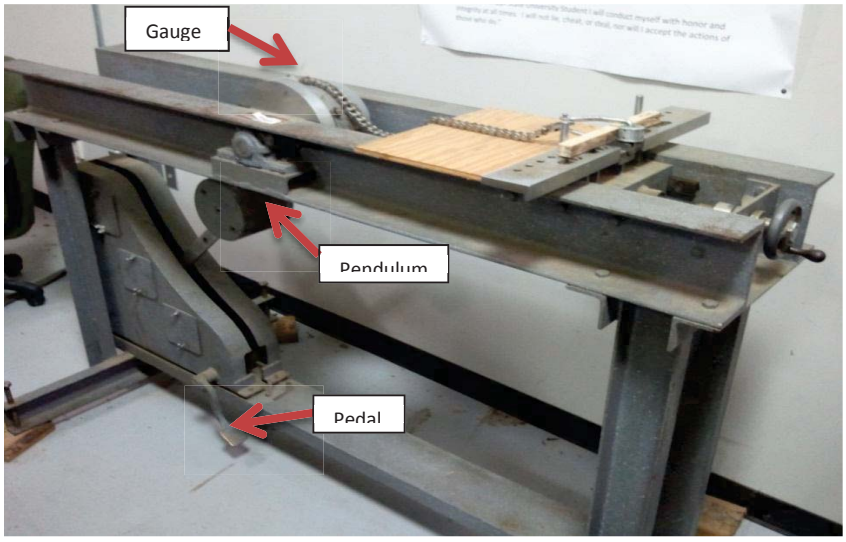

Figure 2.18 Toughness test

Internal Bond and Density Profile

Samples (Figure 2.19) for internal bond (IB) test were first subject to X-ray scanning for density profile along the thickness direction (Figure 2.20). Then glued with aluminum blocks for IB test in accordance with standard ASTM D1037 (2006).

Figure 2.19 Samples for internal bond test

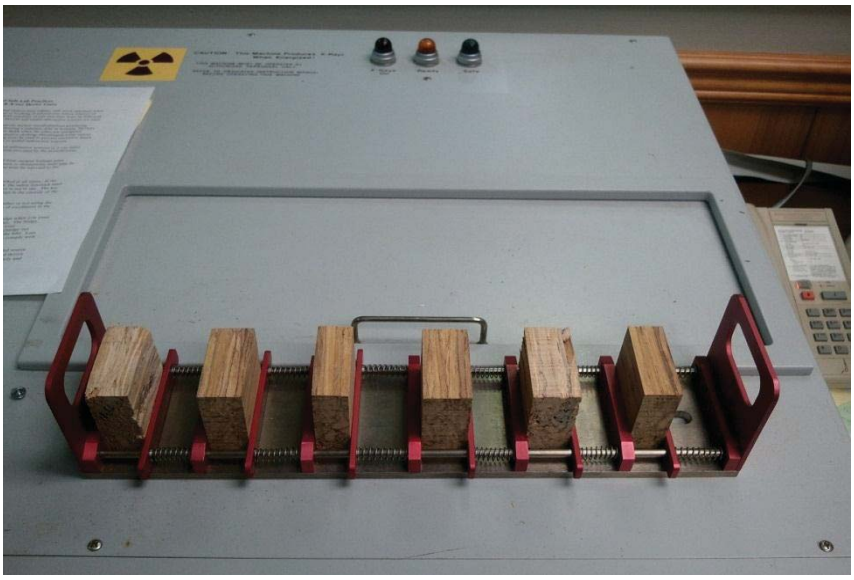

Figure 2.20 QMS density profiler

Figure 2.21 Internal bond test

Thickness Swelling

As for thickness swelling and tangential swelling study, samples with dimensions of 100 x 100 x 25 mm (Figure 2.22) were conditioned (20 ºC, 65% relative humidity) and weighed, then thickness, width, and length were measured by a caliper (accuracy 0.01 mm). The thickness of each sample was measured at three points along the grain direction and three points across the grain direction. All measured points were marked for later measurement. Then all samples were put into a water bath for 24 h, as shown in Figure 2.23. Weights were utilized to assure that all samples were submerged under water during the 24-h period. Samples were then measured again at the same points.

Figure 2.22 Samples for thickness swelling and tangential swelling

.

Figure 2.23 Thickness swelling and tangential swelling testing pool

Dynamic Swelling

Dynamic swelling was included in this study in addition to the thickness swelling test. Samples of nominal 25 x 25 x 25 mm were prepared from untreated and treated PSL and southern pine solid wood. Samples were cut from the remnants of the static bending tests. For each group, dynamic swelling of four replicates of both along the thickness direction and across the long dimension of the scrim perpendicular to the board faces was determined. Each five-hour cycle consisted of 60 readings, with one reading every five minutes. The test setup is shown in Figure 2.24.

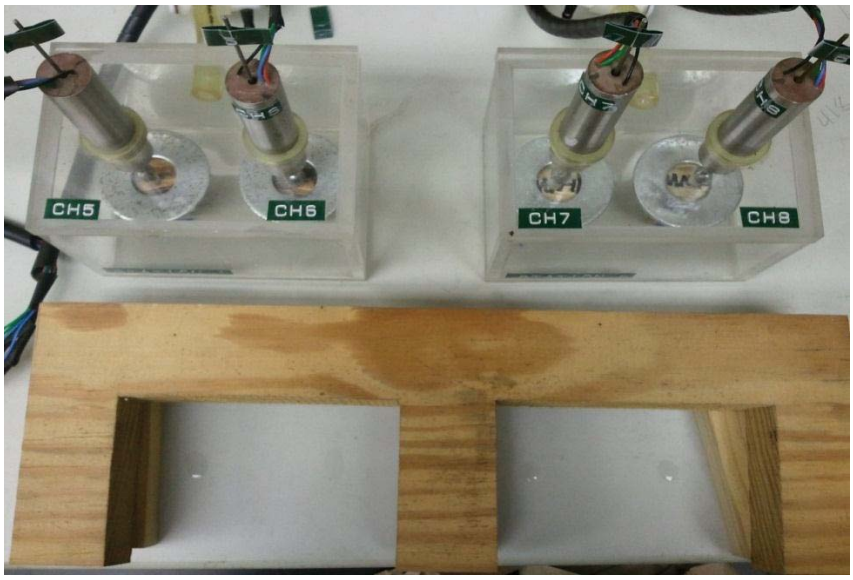

Figure 2.24 Experimental setup for the dynamic swelling test

Before setting up the program, eight samples with initially measured dimensions and weights were input into each of the four stations. Then washers were put on the top of each sample to prevent them from floating. After that, each station was covered by a lid holding LVDT transducers. Finally, deionized water was injected into the stations to assure all samples were submerged under water. When each cycle was completed, samples were removed and dimensions and weights were measured again. Data were automatically recorded via a computer.

Termite Testing

Because of a limited quantity of termites, only samples from the best mechanical properties in each chemical treatment group plus an untreated group were tested. Testing was done in accordance with AWPA Standard E1 (2010). For this test 140 grams of sand

and 15 mL deionized water were placed into sterilized jars and allowed to set over night. Samples were put into jars the next day, followed by adding 1 g of termites (*Reticulitermes flavipes* Kollar) on the sand while avoiding direct contact with the wood sample. All jars were moved into a conditioning cabinet at 27.8 ºC for 28 days. A control jar with no samples or termites was also put into the cabin to monitor the moisture loss during the study to assure termites did not die from loss of moisture. The control jar was weighed at one week interval. The experimental procedure is shown in Figures 2.25 to 2.28.

Figure 2.25 Termite test samples into jars

Figure 2.26 Termites-with only few soldiers

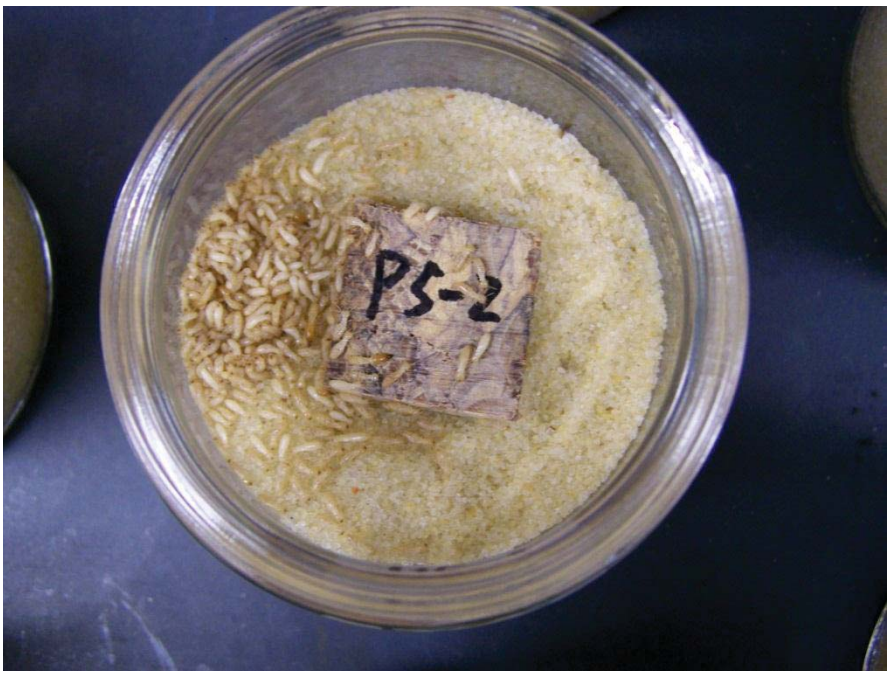

Figure 2.27 Insert termites into jar

Figure 2.28 Conditioning for 28 days

Mechanical Property Evaluation for Southern Pine Solid Wood

For comparison, 60 southern pine solid wood samples (Figure 2.29), 25x 25x 406 mm (radial, tangential, longitudinal) were tested. They were divided into six groups of equal weight distribution. One served as the control group. The others were then treated with 5 and 15% melamine solution, 5 and 15% phenol formaldehyde solution, and 20% furfuryl alcohol solution, using the same procedures as were used in PSL treatment. Then both treated and untreated samples were conditioned in the chamber with a constant 20 ºC and 65% relative humidity until constant weight was achieved. Finally, all samples were subject to bending test according to ASTM D143 (2007) with a span of 355 mm.

Load was applied on the tangential surface nearest the pith. Center point loading was utilized, as shown in Figure 2.30.

Figure 2.29 Southern pine solid wood

Figure 2.30 Bending test-center point loading

Data Analysis

All data obtained from each test were analyzed using statistical analysis software (SAS 2009). Analysis of variance (ANOVA) was conducted and Tukey's Studentized Range (HSD) Test with a confidence interval of 95% (α=0.05), was used to analyze the significant differences between groups. Tukey's Studentized Range Test results were adopted since it was a more conservative estimator.

CHAPTER III

RESULTS AND DISCUSSION

The solution uptake and weight percent gain (WPG) on a dry wood basis is shown in Table 3.1.

Table 3.1 Solution uptake for treated scrim

Chemical	Concentration %	Scrim MC %	Solution uptake % wt/wt	WPG active ingredient oven-dry basis %
PF	5	8.70	140	7.60
PF	10	8.20	150	16.27
PF	15	8.20	148	24.00
PF	15	8.20	150	24.28
MF	5	10.39	140	7.69
MF	10	10.39	135	14.92
MF	15	9.95	144	23.72
MF	15	9.96	138	22.84
FA	20	8.75	149	32.34
FA	30	8.75	140	45.80
FA	40	8.75	147	64.11

Scrim used for chemical treatment was air-dried, with MC from 8.2 to 10.4 %. It was observed that the solution uptake was around 140% for all chemicals, and the consequential WPG of active ingredient increased in proportion to the increase of solution concentration. Compared to the target solution/scrim ratio, which was 125%, the uptake shown in Table 3.1 was higher. The actual WPG calculated after curing was illustrated in Table 3.2.

Comparing Table 3.2 with Table 3.1, it could be concluded that the calculated WPG after curing agreed with the one deduced from solution uptake for both PF and MF impregnated scrim. However, for furfurylated scrim, there were significant differences between those two WPGs. The reason was that during curing phase, most of the furfuryl alcohol evaporated, since this chemical was unstable at high temperature. According to Hadi et al (2005) and Lande et al (2004), aluminum foil was used when curing, and high WPG was obtained. The same procedure was applied in this research. However, only low WPG was obtained. It seems aluminum foil could not prevent furfuryl alcohol from evaporating. Further studies utilizing catalysts to accelerate interaction between furfuryl alcohol and wood polymers should be studied.

Table 3.2 Calculated WPG after curing

Chemical	Concentration %	Scrim MC %	WPG active ingredient oven-dry basis %
PF	5	8.70	7.88
PF	10	8.20	17.72
PF	15	8.20	23.48
PF	15	8.20	22.66
MF	5	10.39	7.94
MF	10	10.39	15.15
MF	15	9.95	19.04
MF	15	9.96	18.26
FA	20	8.75	6.35
FA	30	8.75	7.70
FA	40	8.75	8.18

ANOVA Results

Data were compared between treated and untreated samples, and between differently treated samples, as shown in Table 3.3. Since we were unable to bond unresinated scrim treated with 15% PF and 15% MF solutions, these groups were not included in the analysis. ANOVA analysis indicated significant differences for all properties of PSL at 95% confidence interval, while no significant differences were observed for MOE and MOR between treated and control southern pine solid wood, with P-values of 0.513 and 0.920, respectively.

Table 3.3 ANOVA results

Variable	R^2	F-value	P-value
PSL-MOE	0.77	12.39	<.0001
PSL-MOR	0.84	22.22	<.0001
PSL-WML	0.63	9.73	<.0001
PSL-IB	0.62	10.66	<.0001
PSL-Toughness Parallel to grain	0.59	6.29	<.0001
PSL-Toughness Perpendicular to grain	0.63	7.75	<.0001
PSL-Water absorption	0.98	109.75	<.0001
PSL-Tangential swelling	0.89	16.91	<.0001
PSL-Thickness swelling along the grain	0.75	5.56	0.0006
PSL-Thickness swelling perpendicular to the grain	0.95	39.48	<.0001
PSL-dynamic swelling	0.92	31.64	<.0001
Solid wood-MOE	0.07	0.86	0.5134
Solid wood-MOR	0.03	0.28	0.9199
Solid wood-MOR	0.23	3.21	0.0131

Mechanical Properties

Bending Properties

As is shown in Table 3.4, there is a large variation for MOR and WML. Several factors could result in this large property variation, such as scrim size, density distribution, resin consolidation.

Table 3.4 Mean bending properties for both treated and control groups

Variable	WPG (%)	MOE (MPa)	COV %	MOR (MPa)	COV %	Work To Max Load (KJ/m3)	COV %
M5	7.94	15320.77A	25.15	54.22A	31.80	25.39A	35.25
F30	7.70	15146.29A	23.61	47.87AB	28.11	17.60B	41.40
M15	19.04	13784.70AB	20.82	38.43BCD	31.43	14.17BCD	38.50
M10	15.15	13657.05AB	32.18	39.18BCD	43.12	17.30BC	58.83
F40	8.18	12782.68ABC	25.74	33.19CDE	38.29	11.41BCD	50.99
P15	23.48	11262.58BC	27.23	27.44E	35.81	10.71BCD	39.65
F20	6.35	10904.87C	39.34	40.01BC	44.87	15.56BCD	55.67
Control	0.00	10717.38C	25.60	29.61DE	27.23	9.61D	40.99
P5	7.88	10381.36C	26.46	28.80E	40.41	13.38BCD	49.09
P10	17.72	10330.71C	20.25	26.65E	41.08	10.44CD	50.32

Panel density had an important effect on wood strength. In this study, Panel density was controlled by the press program as a control factor (Figure 3.1). Density uniformity was further confirmed by the ANOVA test as no significant difference in density was observed between treated and control groups.

Table 3.4 shows that samples treated with MF and 30% and 40% FA were better than control group with respect to MOE, while those treated with PF and 20% FA had almost the same value for MOE as compared to the control group. On the basis of ANOVA test, however, samples treated with all three levels of MF and 30% FA had significantly higher MOE than control group (significance level is α=0.05 here and in all other studies), while the MOE for samples treated with other levels of chemicals were not significantly different from control group. For MOR, all treatment levels of MF and FA

were stronger than the control group (Table 3.4), while all three levels of PF were lower but statistically equal to the control group. Only samples treated with 5% MF, and 20%, 30% FA had significantly higher MOR values than the control group. Samples treated with other levels of chemicals were not significantly different compared to controls. Work to maximum load in bending (WML) is an ability to absorb shock with some permanent deformation and more or less injury to a specimen (FPL 2010). As shown in Table 3.4, all treated groups had higher work values than controls but only 5%, 10% MF and 30% FA had significant higher WML values than controls. It was obvious that furnish treated with 5% MF performed best with respect to MOE, MOR, and WML.

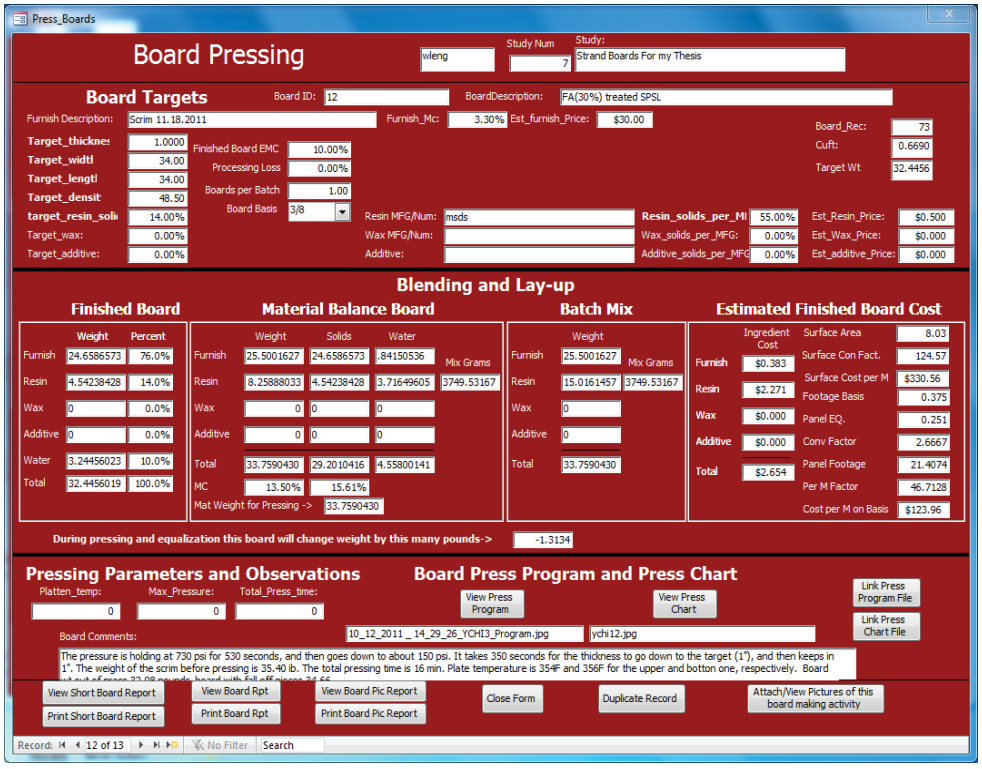

Figure 3.1 Chart of press study

According to Stamm and Seborg (1939), PF treated wood should have great mechanical properties, while in this study, opposite results were observed. The molecular weight of the resin might be a possible reason. As pointed out by Furuno et al (2004), lower concentrations of lower molecular weight PF resin could easily and fully penetrated into cell wall and form wall polymers. With an increase in molecular weight and solids content, more fractions of PF resin were found deposited in cell lumen. The PF resin used in this research has a molecular weight of 1300-1400, much higher compared with 350 and 451, which were studied by Wan and Kim (2008). In this study since all densities were not significantly different, more resin may be going into the cell lumen which means lower proportion in the cell wall, resulting in weaker mechanical properties. Another reason for the weak strength might be a combining effect of curing thermal treatment and PF treatment.

Results obtained for MF impregnation and furfurylation performed as expected. The molecular weight of both of MF and FA was so low that they could easily access the cell wall, thus improved the strength of the furnish (Gindl et al 2003; Baysal and Osaki 2004).

Internal Bond and Density Profile

The internal bond properties of both controls and treated samples are shown in Table 3.5. A typical shape of rupture for an IB test is shown in Figure 3.2. As illustrated in Figure 3.4, all treated samples had better IB property than controls. Statistically

speaking, all treated samples had significant higher IB values than controls except for those treated with 10 and 15% PF solutions. As is known, internal bond is related to resin type/content, sample density and element geometry (Dai et al 2007). In this research, resin type/content, and pressing parameters were the same for each panel. Element geometry and density could not be control as the same for each because of the variation in scrim size and geometry. According to the output from QMS density profile system (Figure 3.3), the density profile of controls varied significantly through thickness direction. The loss of bonding strength could start from the weakest point, which would be the lowest density region. Dai et al (2008) reported that de-bonding was attributed to the low density area, and then shifted to higher density area as a result of subsequent load concentration. Thus, controls group had the lowest mean IB value although the average density was in the medium density range. It was unexpected that IB strength for panels treated with 10% and 15% PF solutions were not significantly higher than that of controls. The density profiles for both of them were uniform through thickness direction, and average densities were much higher than those treated with 5% PF solution, as shown in Figure 3.3. Possible reasons could be scrim size and geometry with larger scrim size leading to less interfacial contact surfaces and many more voids among scrim, thus lower IB strength was obtained. In order to find detailed reasons for this phenomenon, microscopic techniques should be applied to determine if rupture was due to resin failure. An analysis comparing the pressing parameters and density profiles with IB values and failure modes could be useful.

Figure 3.2 Typical rupture failure for IB test

Table 3.5 Internal bond mean values

Variable	Mean kPa	COV %
Control	76.19	30.16
P5	238.45	56.16
P10	134.35	38.02
P15	180.74	35.65
M5	320.62	39.71
M10	389.21	37.96
M15	210.63	39.86
F20	263.51	43.01
F30	340.18	48.89
F40	303.90	32.48

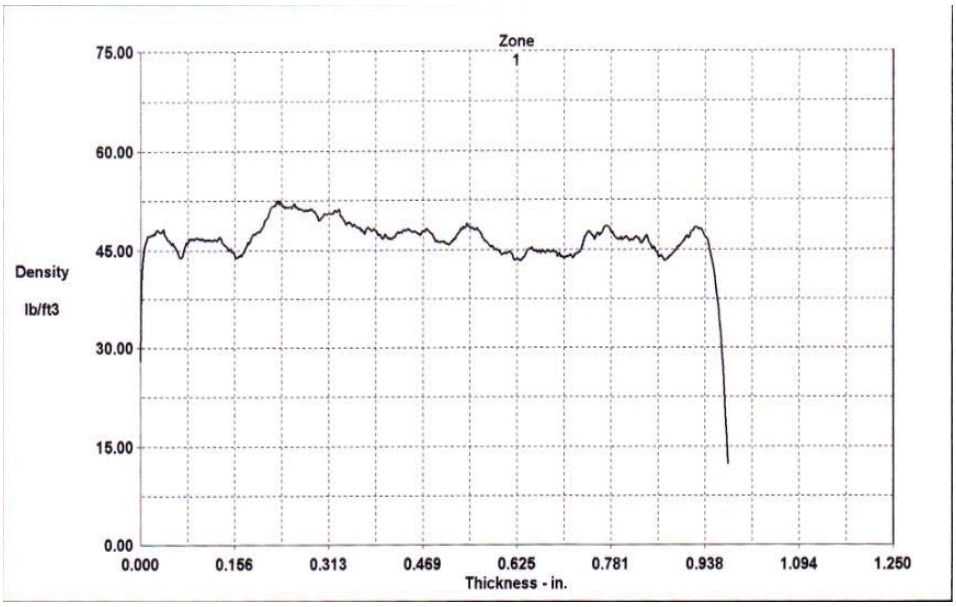

Figure 3.3 QMS density profile for samples treated with PF resin

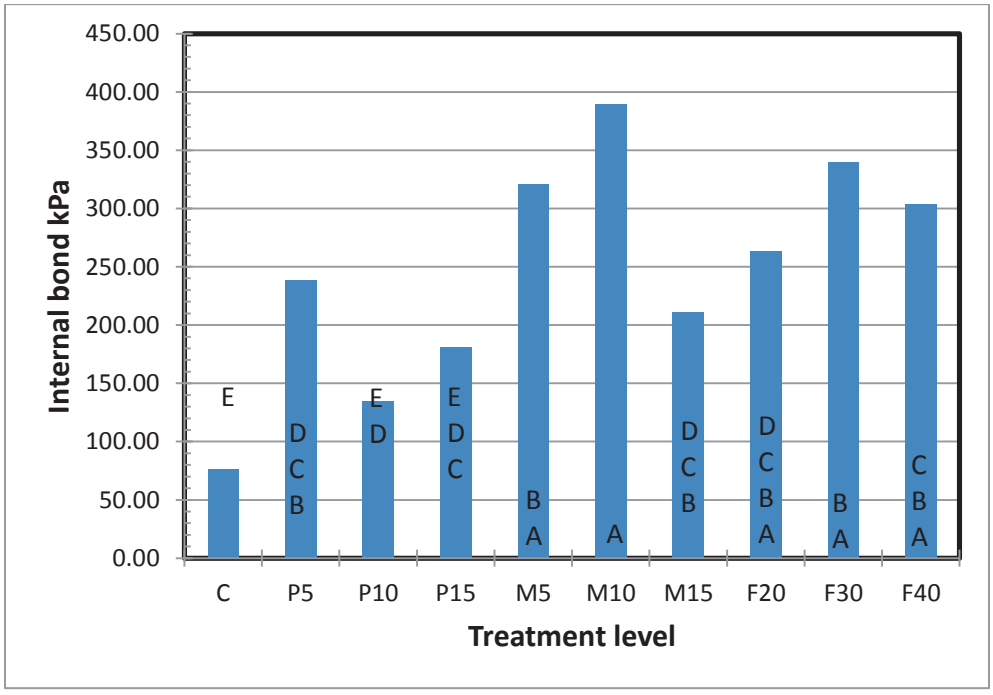

Figure 3.4 Internal bond (Means without a common letter are significantly different one from another at p = 0.05)

Toughness

There was a large variation in toughness (Table 3.6). Statistical analysis confirmed that only samples treated with 10% MF solution had a significantly higher toughness value than controls with load direction parallel to panel surface, while samples treated with 5% PF, and 5 and 10% MF solutions had significantly better toughness properties than controls for load direction perpendicular to panel surface. There was some randomness in toughness in both force directions within each group. The large variation of toughness was also reported by Gerhards (1968) and in the Wood Handbook (FPL 2010), with a coefficient of variation (COV) around 30%. Toughness is a most sensitive mechanical property, which can vary sample by sample because of uneven density distribution, differences in resin coverage, annual rings, moisture content, and even chemical modification of wood furnish (Gagan and Mclain 1983). A typical toughness fracture is shown in Figure 3.5.

Figure 3.5 Toughness fracture

Table 3.6 Toughness properties for treated and control groups

	Force direction parallel to the panel surface			Force direction perpendicular to the panel surface		
Variable	Mean (N·m)	Standard deviation	COV %	Mean (N·m)	Standard deviation	COV %
M10	11.95A	5.41	45.28	9.04AB	2.93	32.35
P5	11.16AB	3.15	28.24	10.47A	2.50	23.84
P15	9.54ABC	2.34	24.57	7.23BCD	1.69	23.32
F30	8.96ABC	2.15	24.01	7.60BCD	2.17	28.62
M5	8.63BC	3.61	41.83	9.10AB	3.04	33.43
C	8.37BC	1.76	21.03	5.84CD	1.76	30.20
F20	7.89C	1.00	12.70	5.73D	1.44	25.09
M15	6.89C	2.44	35.33	7.13BCD	1.79	25.12
P10	6.75C	1.39	20.59	8.32ABC	1.75	21.00
F40	6.71C	1.60	23.86	6.99BCD	1.39	19.96

Effect of Treatment Level

Phenol Formaldehyde (PF) Solution

Bending properties as a function of WPG for the PF resin are shown in Figure 3.6. According to the equations in Figure 3.6, WPG had no effect on bending properties. The curves are essentially flat. Samples treated with 5% and 10% PF solution had no differences in MOE, while those treated with 15% PF solution had a slightly higher MOE. As for MOR, samples from furnish treated with the lowest level of PF solution performed best, followed by those treated with 15% and 10% PF solution. The same trend was obtained for WML. This might be because that higher concentration of PF resin acts as a plasticizer lowering the Young's modulus of cell wall (Shams et al 2005). For the molecular weight PF in this study, furnish treated with 5% PF solution is suggested.

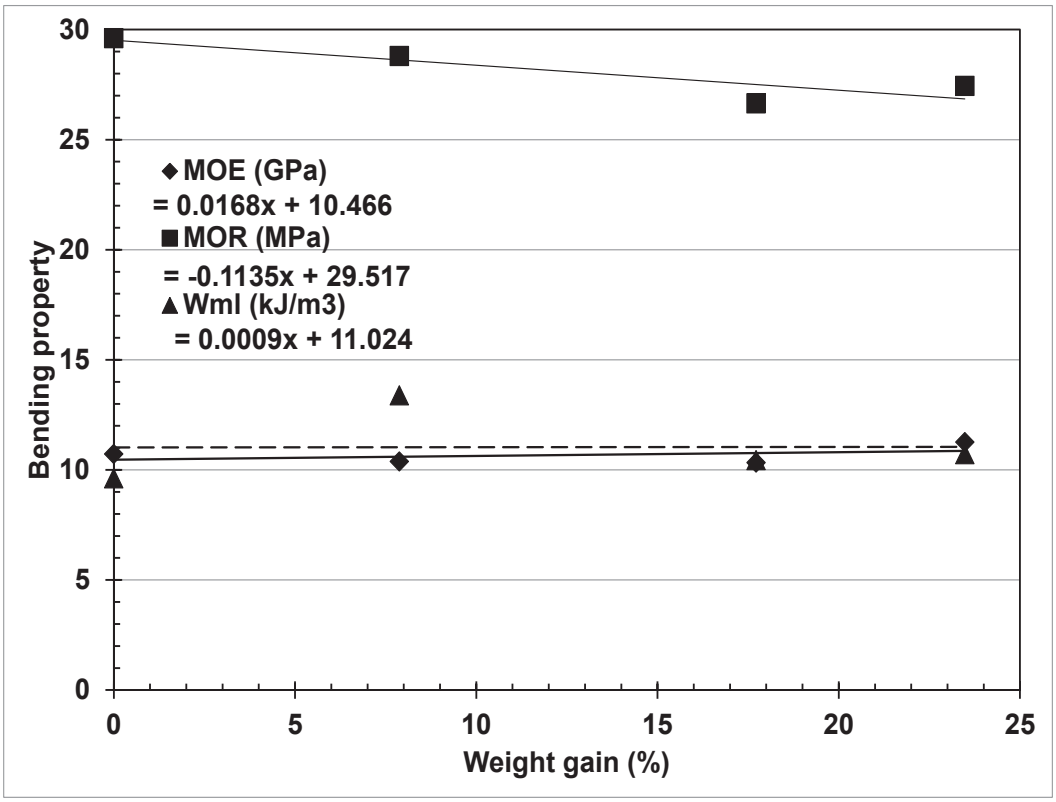

Figure 3.6 Bending properties for PF-treated samples

Melamine Formaldehyde (MF) Solution

PSL made with furnish treated with 5% MF solution had the highest MOE value, followed by that treated with 15% and 10% MF solution (Figure 3.7). MOR and WML had inversely proportional relation to the increase of WPG. This could be explained by the fact that when the concentration went above 10%, excess MF deposited only in cell lumen, playing little role in strength of the PSL. This result was coincided with that found by Inoue et al (1993). Furnish treated with 5% MF solution is recommended based on this study.

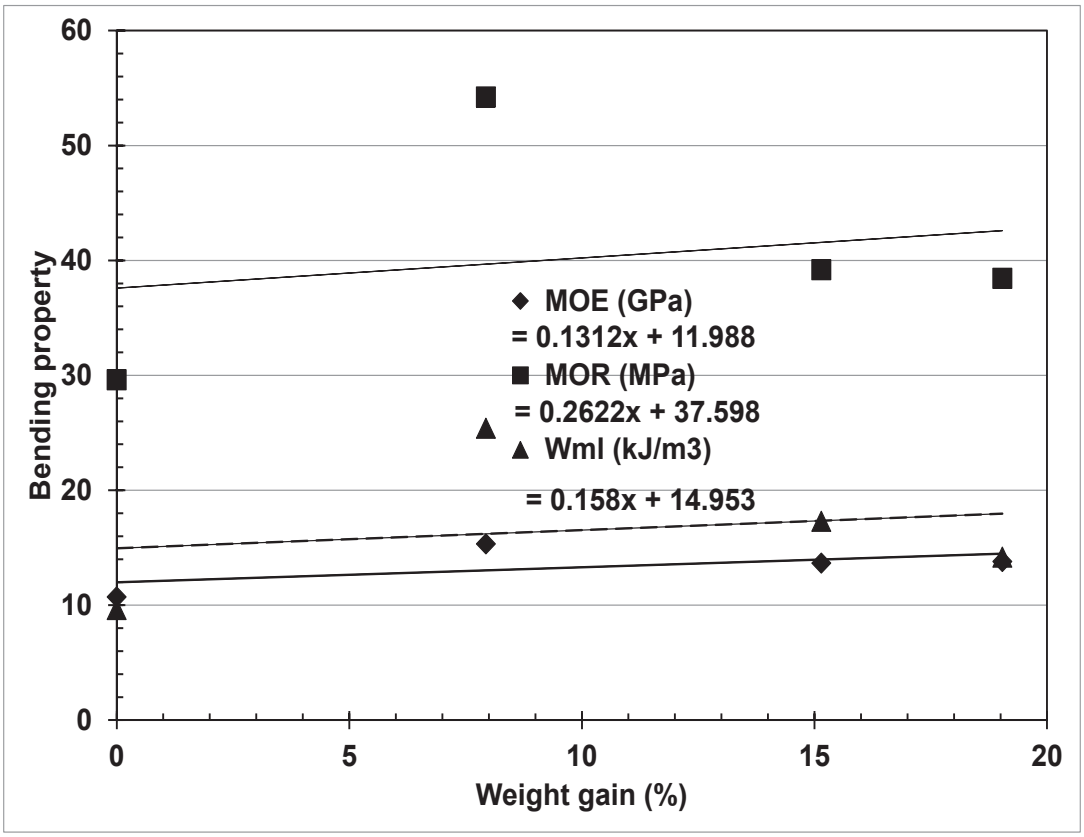

Figure 3.7 Bending properties for MF-treated samples

Furfuryl Alcohol (FA) Solution

During the furfurylation treatment, the uptake of solutions was similar as in both PF and MF impregnation. However, when scrim went through the curing process, most of furfuryl alcohol vaporized, resulting in much less WPG. It appeared that aluminum foil could not prevent furfuryl alcohol from vaporizing. Curves for MOE, MOR, and WML showed that the trend was different from that for PF and MF impregnated samples, of which samples treated with 30% furfuryl alcohol solution had better strength than the other concentrations. According to Epmeier et al (2004), MOE was not of significantly

different between furfurylated and untreated wood, and high WPG could lead to a decrease in bending strength, A 75% decrease and 57% decrease for WPG of 48% and 70%, respectively, were reported by Epmeier et al (2004) and Lande et al (2004b). However, in this study, strength of furfurylated samples was better than untreated one. This finding means low WPG of FA could contribute positively to mechanical properties. Samples treated with 30% FA solution yielded the best results. Figure 3.6 to 3.8 showed the best property enhancement for each treatment had a WPG of around 8%. This is probably related to cell wall accessibility. Further study should be taken to investigate this case.

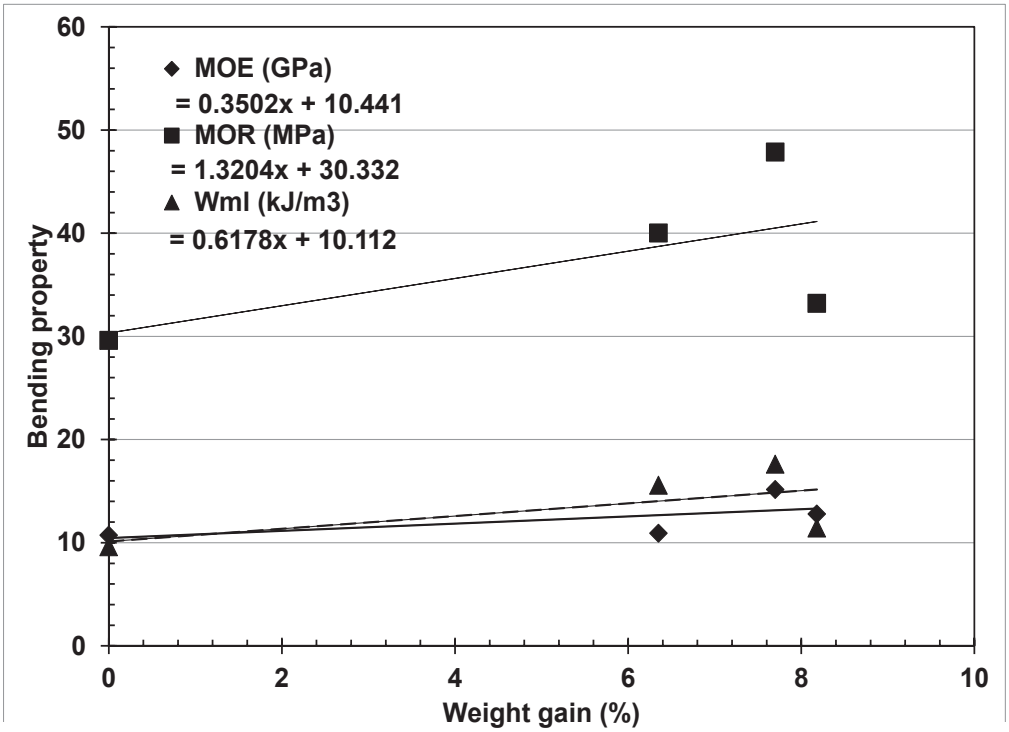

Figure 3.8 Bending properties for FA-treated samples

Strength Property Analysis

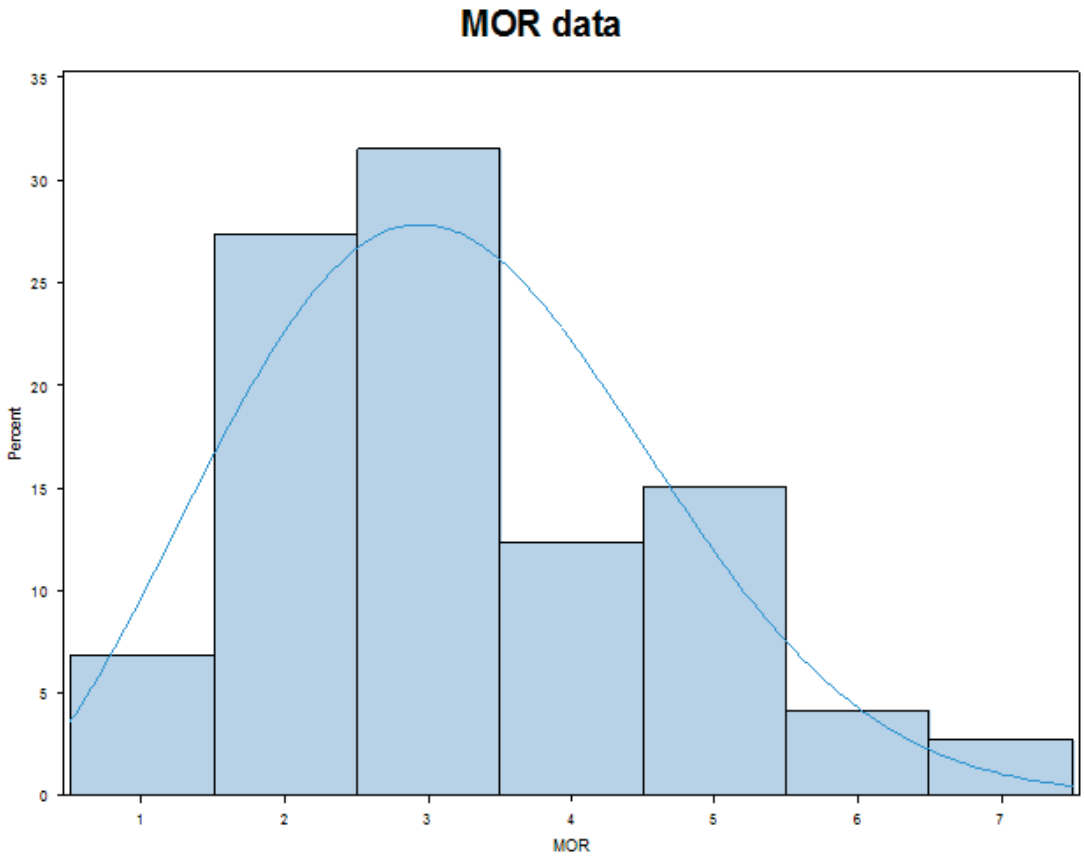

Figure 3.9 Weibull distribution of data for MOR (Shear failure)

According to the strength property analysis, the maximum normal stress $\sigma_{x\,max}$ is:

$$\sigma xmax = 12PLh / 6bh^3 = 34P / A \quad (3\text{-}1)$$

where:

P= loading force N,

h= thickness mm,

b= width mm,

A= area of cross section for PSL mm^2,

L= span mm.

and the maximum shear stress is:

$$\tau yx\ max = \tau xy\ max = Ph^2 / 8I = 12Ph^3 / 8bh^3 = 3P / 2A \quad (3\text{-}2)$$

where:

I= moment of inertia mm^4.

Then the ratio of the maximum normal stress to the maximum shear stress is

$$\sigma xmax / \tau xy\ max \approx 22.67 \quad (3\text{-}3)$$

According to Table 3.7, shear strength should be used for samples of shear failure, thus fracture strength of samples with shear failure mode was recalculated utilizing equation 3-2, and a univariate procedure was run to test the data distribution. Results showed that data fitted Weibull distribution, with P-values of 0.097 and 0.181 for Cramer-von Mises test and Anderson-Darling test, respectively. Moreover, fracture strength of those with tension failure was also through univariate procedure, and Weibull distribution was obtained, with P-values of > 0.250 and > 0.250 for Cramer-von Mises test and Anderson-Darling test, respectively.

Table 3.7 Failure mode sortation

Treatment	Shear failure Number	Tension failure Number
Control	7	2
P5	6	8
P10	7	6
P15	9	1
M5	11	3
M10	8	6
M15	9	5
F20	4	8
F30	5	7
F40	7	5
Percentage %	58.9	41.1

Finally, modified MOR values were tabulated in Table 3.8 according to the failure mode.

Table 3.8 Strength properties of samples (sorted according to failure mode)

Variable	MOR Mean (Shear failure mode) (MPa)	MOR Standard deviation	COV %	MOR Mean (Tension failure mode) (MPa)	MOR Standard deviation	COV %	MOR (tension failure mode) /MOR (Shear failure) ratio
Control	1.34	0.39	28.92	28.48	9.86	34.61	21.32
P5	1.28	0.51	40.07	23.49	11.65	49.61	18.29
P10	1.37	0.22	15.84	21.84	14.57	66.72	15.96
P15	1.19	0.45	38.23	27.99	-	-	23.52
M5	2.45	0.70	28.34	49.31	25.11	50.92	20.09
M10	1.51	0.69	45.49	45.35	17.80	39.26	30.05
M15	1.61	0.53	32.73	41.58	12.80	30.78	25.79
F20	1.74	0.97	56.04	40.09	16.92	42.21	23.08
F30	2.13	0.74	34.50	47.10	11.56	24.55	22.10
F40	1.19	0.45	37.67	42.69	10.13	23.73	35.98

As shown in Table 3.8, the coefficient of variation was high. This may be because of a small sample size and variation of material properties. The ratio of MOR (tension failure mode) to MOR (shear failure) ranged from 15.96 to 35.98. According to equation 3-3, the ratio of maximum normal stress to maximum shear stress was 22.67. The higher ratio of MOR (tension failure mode) to MOR (shear failure) than that of maximum

normal stress to maximum shear stress was caused by the variation of shear strength within each treatment group. For MOR (tension failure mode) to MOR (shear failure) ratios lower than that of maximum normal stress to maximum shear stress, the reason for the tension failure was that weak point(s) of tension strength existed along the cross section, which differed from the theoretical model of linear relationship as equation 3-1. For example, with samples treated with 30% FA, the tension failure was not at the outmost surface but at the inside layer, as shown in figure 3.10. The sample looked intact after bending test, thus fracture must happened somewhere inside. This meant that both shear and tension stress did not reach their maximum values. Hence, variation of properties between different layers was obvious from this example. Detailed investigation of fracture mode using microscopic means should be conducted to verify this assumption in the future.

Figure 3.10 Sample treated with 30% FA after tension failure (Looks intact outside, inside layer broken)

The relationship between residual and predicted MOR for both failure mode is shown in Figures 3.11 and 3.12. Both of the shapes looked random, however, with some outliers, of which the lowest outlier was from samples treated with 10% PF, while those higher outlier were from furnish treated with 30% FA, 10% MF, and 5% MF, respectively. The reason for extreme low MOR might be low resin content and low density at failure area, etc., while for extreme high MOR, the reason might be perfect bonding of scrim and low moisture content. These outliers should not be removed until exact reasons are determined, then the decision to remove or not could be made. Sometimes the cause of the high outliers might lead to an improvement of product properties.

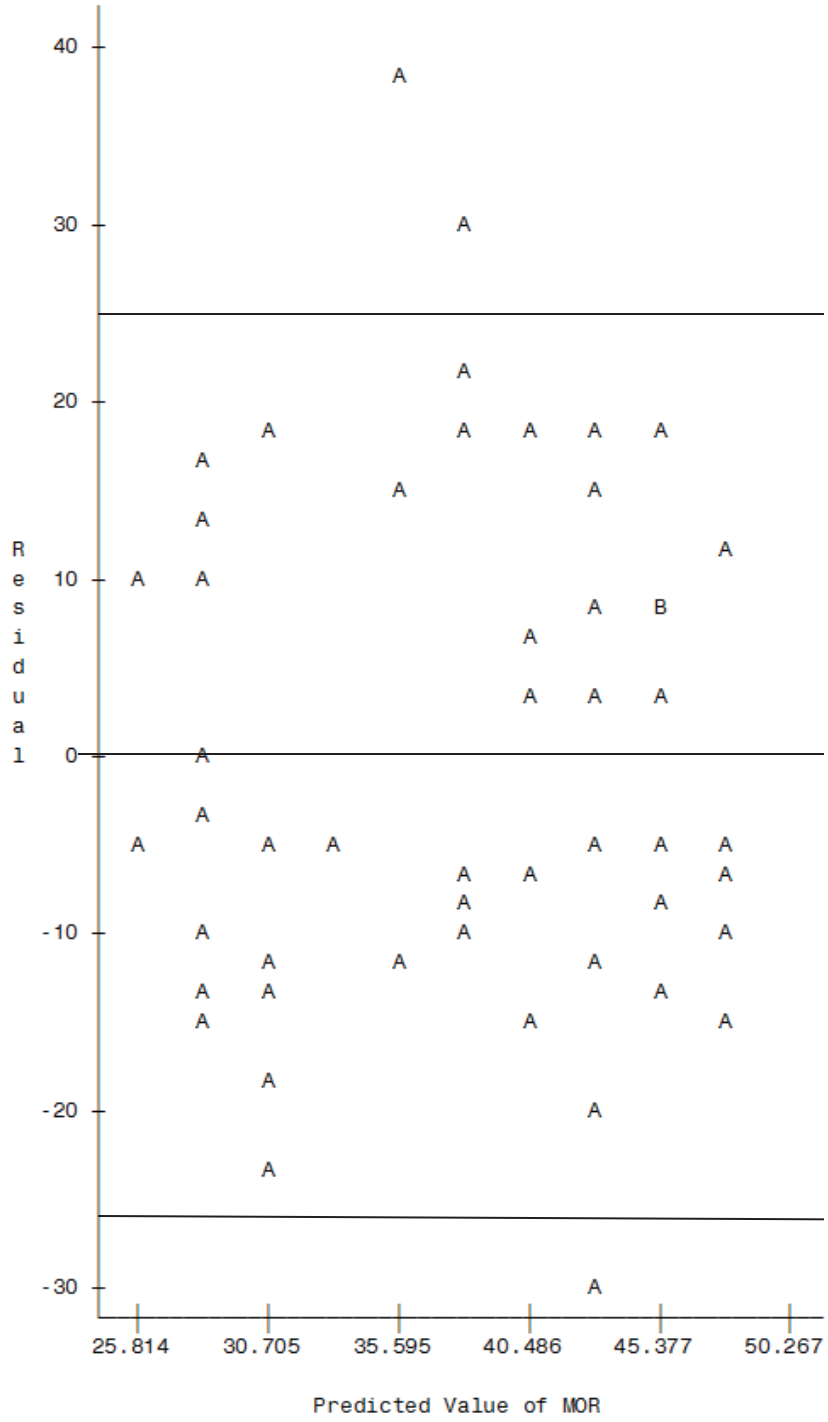

Figure 3.11 Plot of residual* predicted MOR (Tension failure)

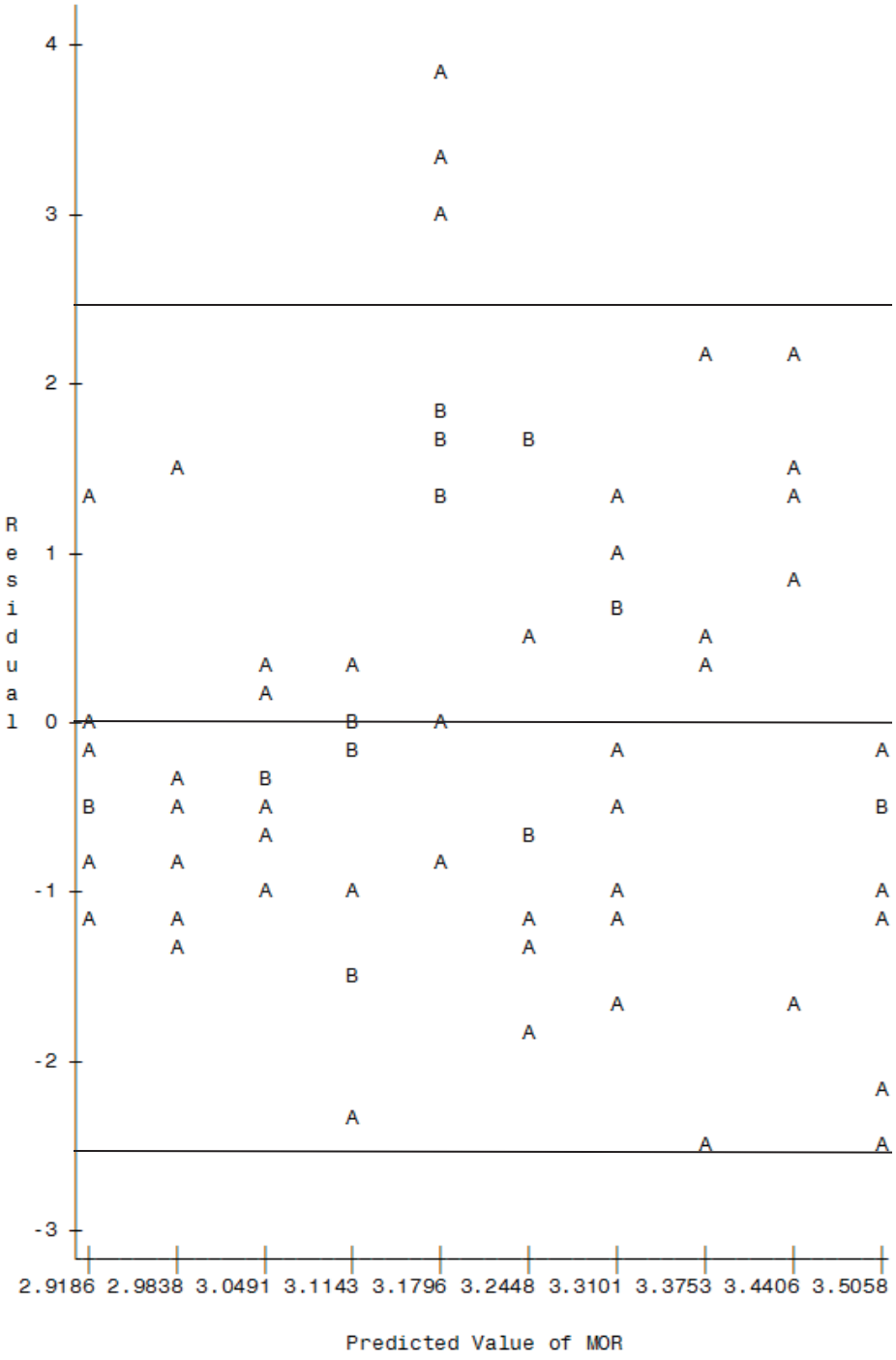

Figure 3.12 Plot of residual* predicted MOR (Shear failure)

Samples treated with 30% FA were taken as an example in this study. According to Table 3.7, shear failure number was 5, and average shear stress and standard deviation are shown in Table 3.9.

Table 3.9 Deduced shear strength of samples treated with 30% FA solution

Sample	Load N	MOR (shear failure) MPa
F30-1	756.67	0.89
F30-2	2316.27	2.82
F30-3	2031.90	2.43
F30-4	1981.53	2.40
F30-5	1802.99	2.11
Mean	1777.87	2.13
Standard deviation	536.54	0.73

New samples for shear strength were prepared from residuals of bending samples with both failure modes, and data are shown in Table 3.10.

Table 3.10 Shear strength of samples treated with 30% FA[1]

Item	load N	Stress MPa	Item	load N	Stress MPa
1-1	5762.75	8.54	2-1	5473.5	8.22
1-2	5922.95	8.50	2-2	5059.65	7.98
1-3	5050.75	7.65	2-3	5954.1	8.95
1-4	1619.8	2.43	2-4	5896.25	8.88
1-5	3973.85	6.00	2-5	5842.85	8.77
1-6	5874	8.69	2-6	5882.9	8.78
1-7	5673.75	8.15	2-7	5340	7.98
1-8	5971.9	8.67	2-8	5081.9	7.57
1-9	5357.8	7.92	2-9	5277.7	7.62
1-10	4765.95	6.85	2-10	5807.25	9.26

[1]Note: 1-1 to 1-10 were for samples with shear failure mode,
2-1 to 2-10 were for those with tension failure mode

Samples were cut in order. According to Table 3.10, there was a much lower stress in Sample 1-4, with a shear strength of only 2.43 MPa, Sample 1-4 was located close to the L/3 point, at which point the mean MOR for shear failure was 2.13 MPa, as shown in Table 3.9. This result confirms a variation of strength within samples, which might be caused by the variation of density (Barnes et al 2010). It is possible that weak points in shear failure region contributed to the shear failure mode in the bending test. The shear strength for samples with tension failure mode was more uniform, with no weak point, thus yielding a tension failure in bending test, which was expected. Further microscopic study should be conducted to explore the causes of these weak points in samples.

Mechanical Properties for Southern Pine Solid Wood

WPG was calculated using the same approach as used in PSL. Results are shown in Table 3.11.

Table 3.11 Solution uptake for southern pine solid wood

Chemical	Concentration %	MC %	Solution uptake %	WPG active ingredient oven-dry basis %	Cured WPG active ingredient oven-dry basis %
PF	5	8.66	119	6.45	5.30
PF	15	8.66	124	13.47	19.16
MF	5	8.66	128	6.97	4.43
MF	15	8.66	128	13.87	16.03
FA	20	8.66	119	25.85	20.72

As shown in Table 3.11, the initial moisture content was similar to that of PSL. However, the solution uptake for southern pine solid wood was lower than that for PSL. This result was understandable, since the raw material for PSL was fine scrim, which had much more absorbing surface area and voids than solid wood. Similar WPGs were obtained for PF and MF impregnated southern pine solid wood, while there was a difference for FA treatment. A 21% WPG was obtained for the 20% concentration. Compared to the lower WPG for PSL, there might be a better sealing of aluminum foil for solid wood as its dimension was much smaller than PSL. Another reason might be that solid wood has a much lower surface area per unit volume for evaporation.

Bending strength values of solid wood for each treatment is shown in Table 3.12 and Figure 3.13. It is apparent that MOE values of treated groups are higher than that of controls. MOR values of PF and FA treated groups are higher than that of controls, while those for MF treatment are lower than that of the control group. In addition, WML value of all treated groups was lower than that of controls. The coefficient of variation for WML was all over 30%. Statistically speaking, there was no significant difference for MOE and MOR value between treated and control groups at 95% confidence interval, while solid wood treated with 15% MF, 15% PF, and 20% FA had significantly lower WML values than controls. Results for PF impregnated solid wood agree with previous reports, which revealed a slight increase of MOE and MOR values. However, for MF impregnated wood, there were contradictions. According to Gindl and Gupta (2002), there was a 33% increase of MOE for spruce when the concentration was 24% (v/v).

However, in this research, there was an 11% increase in MOE for the 5% MF impregnated solid wood and a drop in MOE as concentration increased to 15%. Following this trend, there should not be a higher increase as the concentration increased further. Results in this study also contradict Gierlinger's report (2005) which argued that impregnation of solid wood with water-soluble MF resin has led to a significant improvement in MOE. As for furfurylation treatment, results in this study agree with that from Esteves' study (2010). In his study, 70% FA solution was used, and WPG of 38% was obtained, about half of the FA active ingredient evaporated. MOE was little changed. In this study, MOE for 20% furfurylated pine solid wood was 11%, since the concentration was not high. When the concentration went up to 70%, components of wood polymers would hydrolyze severer, consequently, MOE went down.

Results for mechanical properties for southern pine solid wood were different from that for PSL. For PSL, some levels of treated groups had significantly better properties than controls, while for solid wood, there was no significant difference between treated and untreated groups.

Table 3.12 Bending properties of southern pine solid wood

Variable	WPG %	MOE Mean (MPa)	COV %	MOR Mean (MPa)	COV %	Work To Max Load Mean (KJ/m3)	COV %
Control	0	8940.77 A	13.74	89.60 A	14.77	104.51 A	34.98
P5	5.30	9856.21 A	21.61	93.05 A	22.30	88.13 AB	37.86
M5	4.43	9961.67 A	18.04	88.03 A	17..02	71.25 AB	30.11
M15	16.03	9234.69 A	32.10	84.51 A	29.31	69.05 B	41.33
P15	19.16	10399.53 A	14.50	92.84 A	16.31	65.94 B	40.38
F20	20.72	10387.72 A	14.09	90.18 A	20.03	63.41 B	30.08

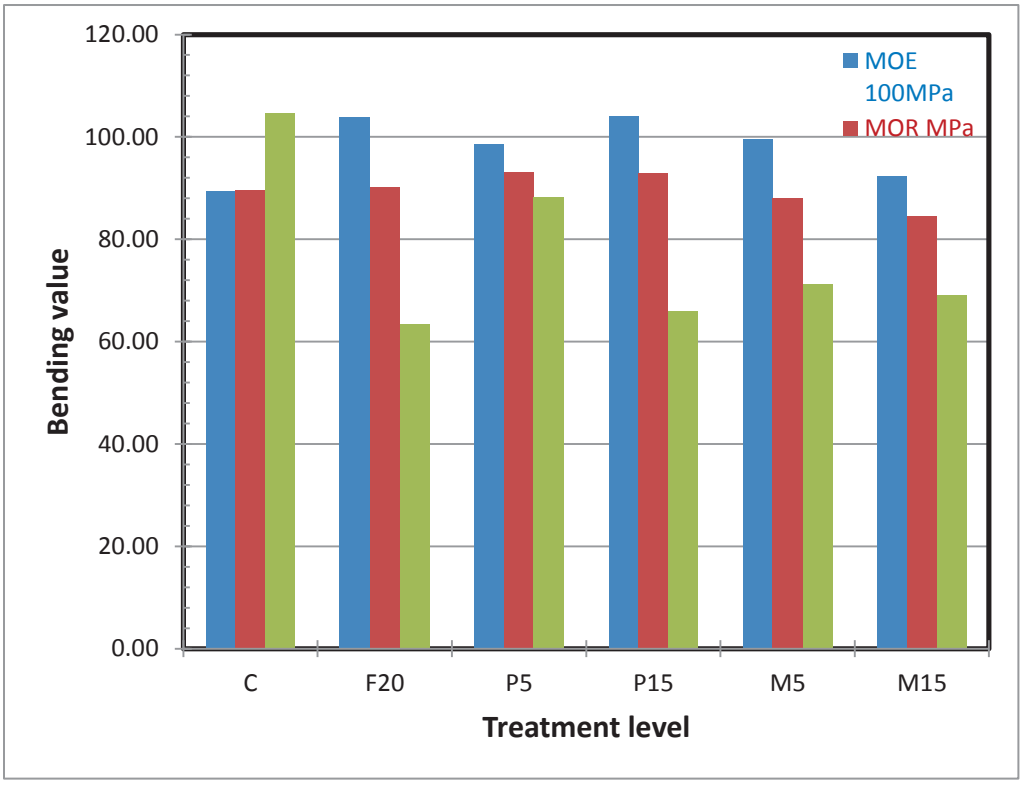

Figure 3.13 Bending properties for southern pine solid wood

Physical Properties

Water Absorption, Tangential Swelling, and Thickness Swelling

Water absorption, tangential swelling (swelling across the long dimension of the scrim perpendicular to the board faces), and thickness swelling were evaluated. Results are illustrated in Table 3.13. None of the treatments included wax to retard water movement.

Table 3.13 Summary statistics for swelling tests of treated and control groups[1]

Variable	WA %	Tangential swelling %	Thickness swelling along the grain %	Thickness swelling perpendicular to the grain %	MC %	Moisture exclusion efficiency (%)
P5	60.40 A	7.49 A	15.40 A	20.07 A	6.91 AB	7.62
P10	53.15 B	5.93 AB	14.62 A	15.33 B	7.76 A	-3.74
P15	51.39 B	6.44 AB	15.13 A	14.76 B	6.48 ABCD	13.37
M5	50.73 B	5.49 BC	14.34 AB	12.66 BC	6.40 ABCD	14.44
Control	48.92 BC	5.49 BC	15.30 A	15.50 B	7.48 A	-
M15	44.64 CD	4.18 CD	7.32 B	8.11 D	7.68 A	-2.67
M10	41.88 D	4.24 CD	9.52 AB	9.47 CD	6.54 ABC	12.57
F20	34.15 E	3.49 D	8.24 AB	8.23 D	5.36 CD	28.34
F40	36.08 E	3.75 D	8.33 AB	6.17 D	5.63 BCD	24.73
F30	27.46 F	3.47 D	9.76 AB	7.15 D	5.00 D	33.16

[1]WA-water absorption
[2]Means not followed by a common letter are significantly different at p = 0.05

As shown in Table 3.13, samples treated with FA solution had a better performance than other groups, and had smaller water absorption, tangential swelling, thickness swelling and lower MC values. For water absorption, samples treated with 5% PF solution performed significantly worse than controls, while those treated with 10 and 15% PF solution and 5 and 15% MF solution had no significant difference from controls. This result means that low molecular weight MF and PF does not prevent samples from absorbing water when submerged under water, while FA solution does.

Anti-swelling efficiency (ASE) results for tangential swelling are illustrated in Figure 3.14.

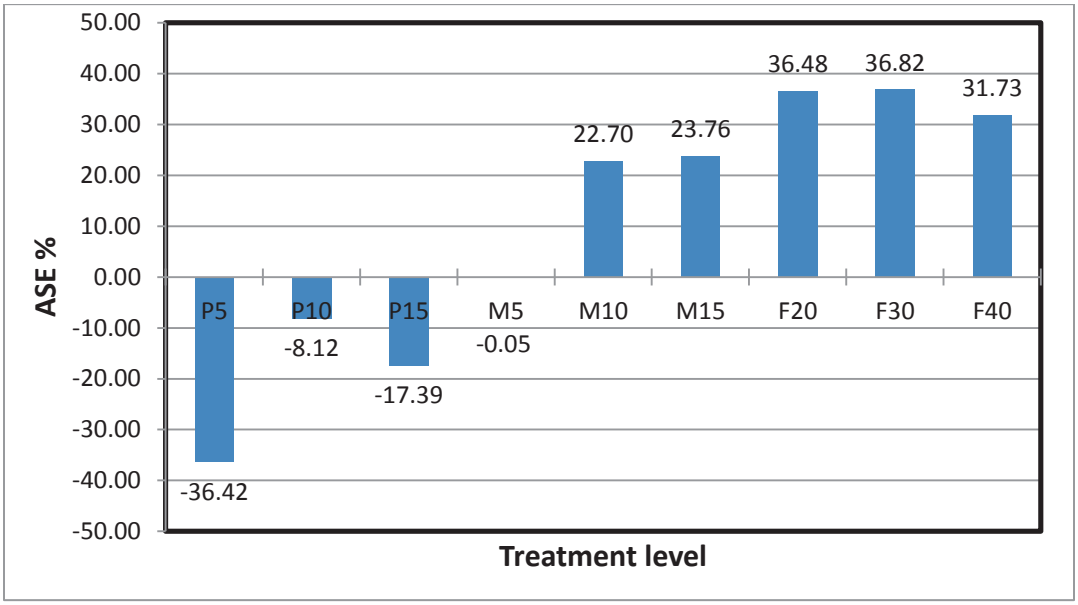

Figure 3.14 ASE for tangential swelling (%)

The highest value was obtained for samples treated with 30% FA solution, which was 36.82%. Statistically speaking, samples treated with all levels of FA solution and 10 and 15% MF solutions showed no significant difference with respect to ASE in tangential swelling. It could be concluded that within each group, there was no significant difference between different concentrations with respect to ASEs for tangential swelling. Thus, when cost was taken into account, the lowest concentration should be utilized in commercial application. It was apparent that samples treated with all three levels of PF solution and 5% MF solution had negative ASEs.

Similar to the results of ASE for tangential swelling, there was no significant difference between samples treated with all levels of FA and all levels of MF solution with respect to the ASE values for thickness swelling along the grain, as illustrated in Figure 3.15. The highest ASE value was 52.17%. The same relationship could be concluded within each group. As for PF impregnated furnish, only small improvement was achieved for thickness swelling along the grain, with a negative value on 5% PF impregnated one.

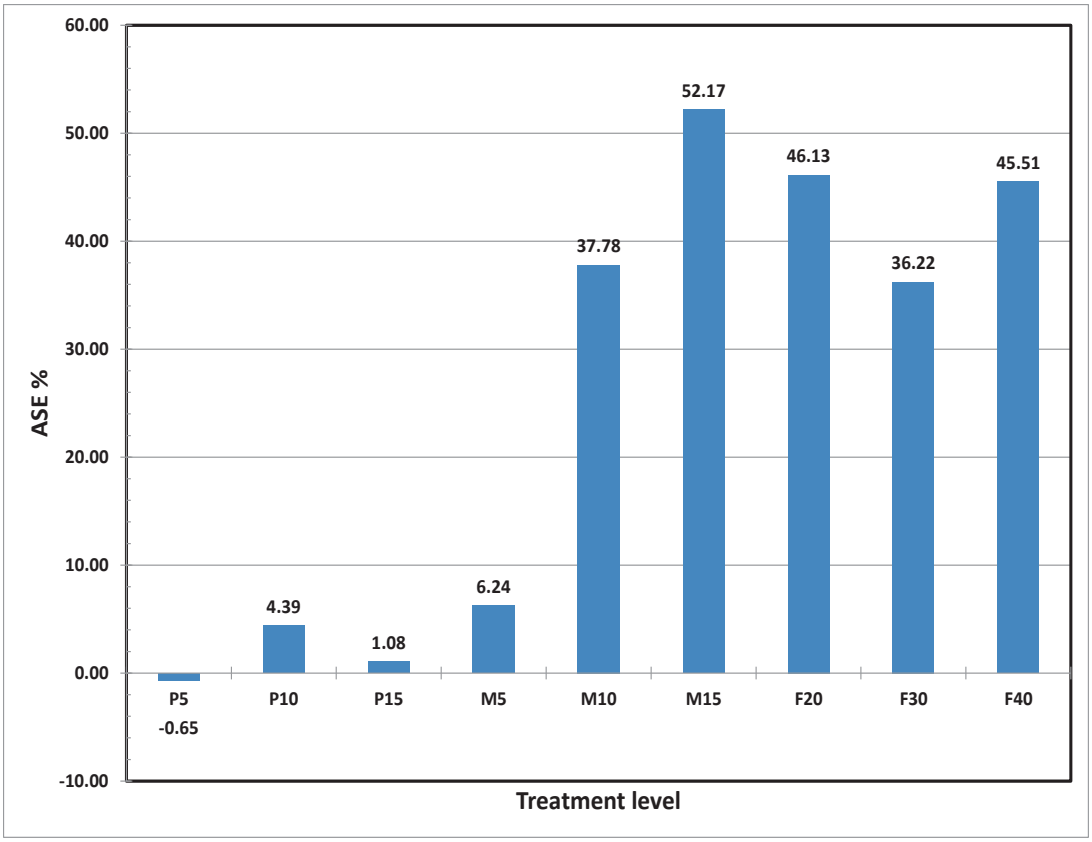

Figure 3.15 ASE for thickness swelling along the grain (%)

As for ASE across the grain, results were similar to the ASE along the grain. However, the highest ASE value was 60.21% for samples treated with 40% FA solution, as shown in Figure 3.16. The ASE values for furfurylated samples agreed with Epmeier's report (Epmeier et al 2004), although their material was pine sapwood, not composite. The relationship within each group was different from the previous one, of which samples treated with 15% MF solution had a significant better performance than that treated with 5% MF solution, and samples treated with 5% PF solution had a significant worse performance than that treated with other two concentrations.

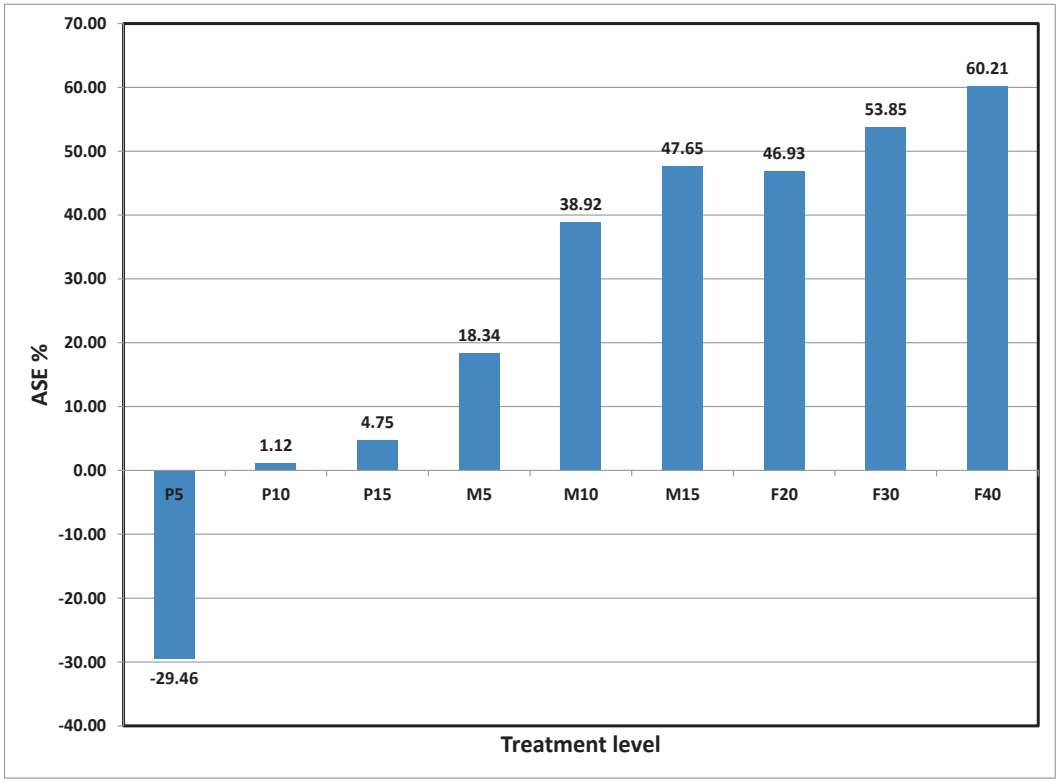

Figure 3.16 ASE for thickness swelling cross the grain (%)

From Figure 3.14 to 3.16, it was obvious that PF impregnation in this study had little positive, sometimes even adverse effect on dimensional stability of PSL. However, according to Wan and Kim's report (2006), ASE values for PF impregnated oriented strandboard (OSB) were up to 26 and 45%, respectively, for 1.0 and 5.0% resin solids content. Probable reasons for the different results were the geometry of raw material, molecular weight of resin. For OSB, there are larger interfaces between each flake, thus yielding stronger internal bond, while for PSL, there were less interfaces between scrim as a result of the geometry of scrim. The molecular weight of PF resin used in OSB

treatment was 310-451, much lower than that used in this study, which was around 1300. Higher molecular weight of PF resin impeded penetration of resin into cell wall, thus could not interlock wood polymers effectively. Larger amount of PF resin deposited in cell lumen could have a negative effect on gluing. All these reasons could render a weak internal bonding strength of samples, which was proved by the fact that the PF impregnated PSL were loose, some of them even fell apart, after submerging under water for 24 h, as shown in Figure 3.17. When samples were loose, more voids were created, thus larger water absorption and less ASE were obtained. Low molecular weight of PF resin should be studied in the future.

Figure 3.17 Shape of samples after 24 h submersion (Treated with 15% of PF solution)

Results for moisture content are shown in Figure 3.18. The moisture exclusion efficiency (MEE) was tabulated in Table 3.13. The definition of MEE is:

$$MEE = (E_C - E_M)/E_C \times 100\ \% \quad (3\text{-}4)$$

Where:

E_C = the EMC of control wood,

E_M = the EMC of the modified wood.

There was no significant difference between groups treated with PF and MF solution, while the furfurylated group had significant lower moisture content and MEE values. Furfuryl alcohol has the smallest molecular weight and can penetrate into wood cell wall easily. It interacts best with hydroxyl group of wood polymers, thus forming a permanently bulked cell wall. This low moisture content phase leads to the high ASE values in tangential swelling and thickness swelling. Furfurylation treatment decreased the anisotropy of wood furnish, since the difference between longitudinal, radial, and tangential swelling was reduced.

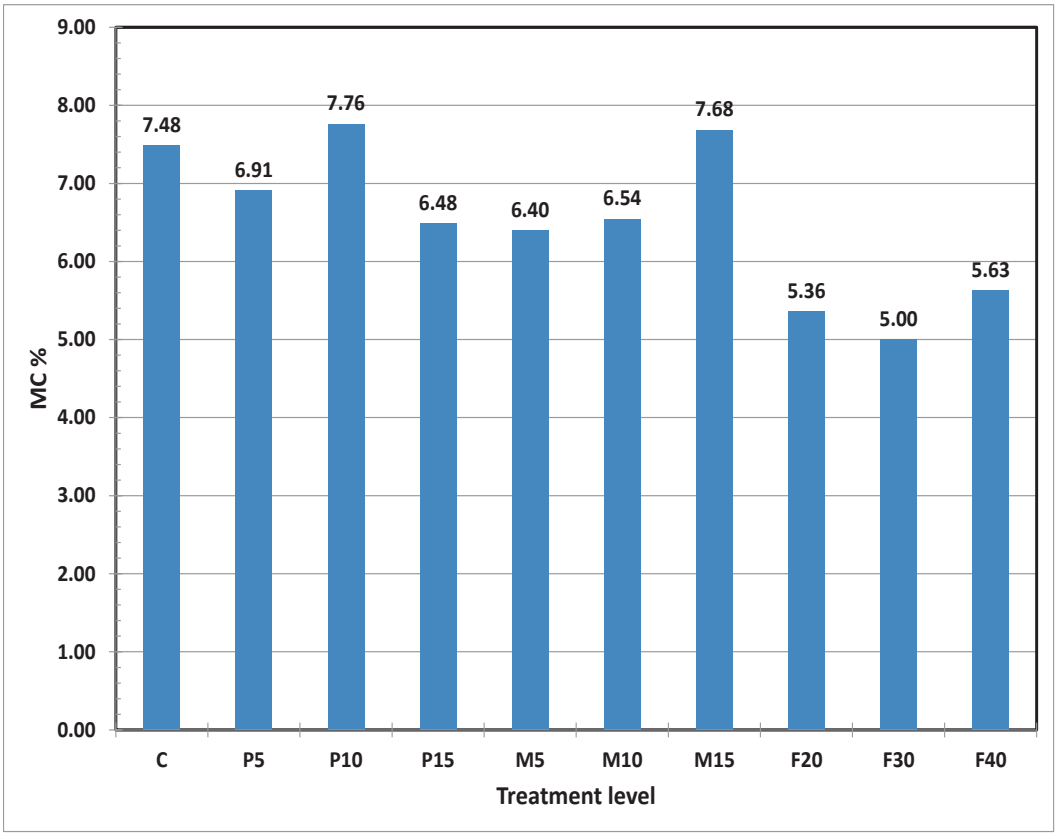

Figure 3.18 Moisture content of both treated and control samples

Dynamic Swelling

Results for dynamic swelling are shown in Figures 3.19 - 3.23. None of the treatments included wax to retard water movement.

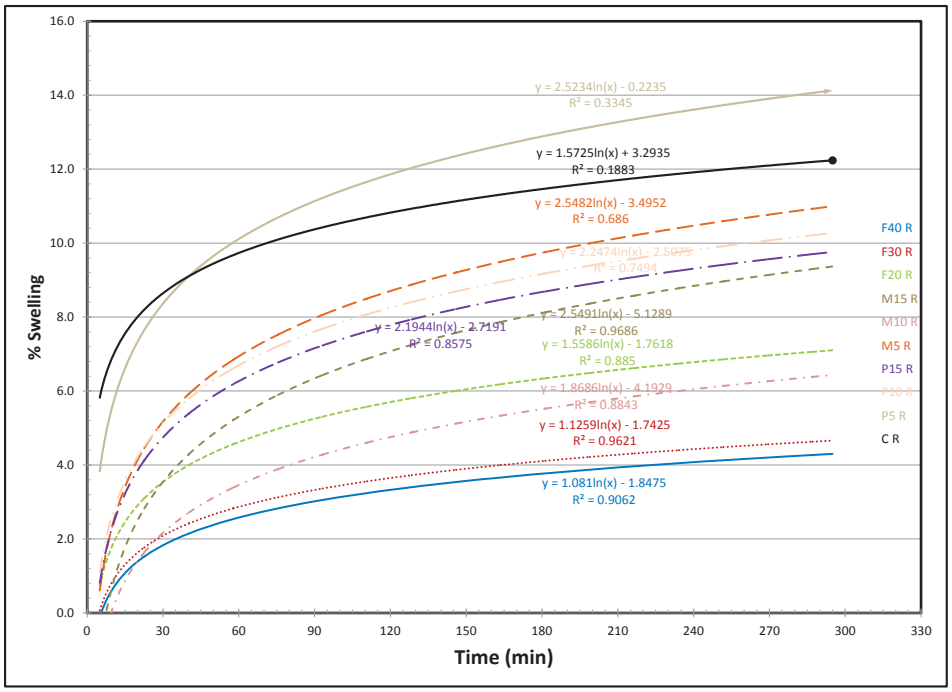

Figure 3.19 Dynamic swelling for PSL in the thickness direction

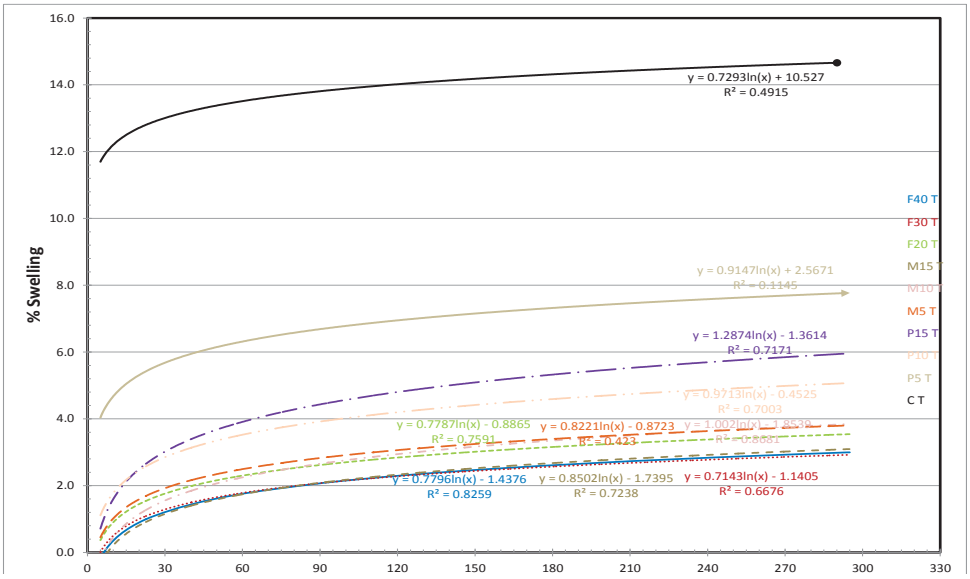

Figure 3.20 Dynamic swelling for PSL in the tangential direction

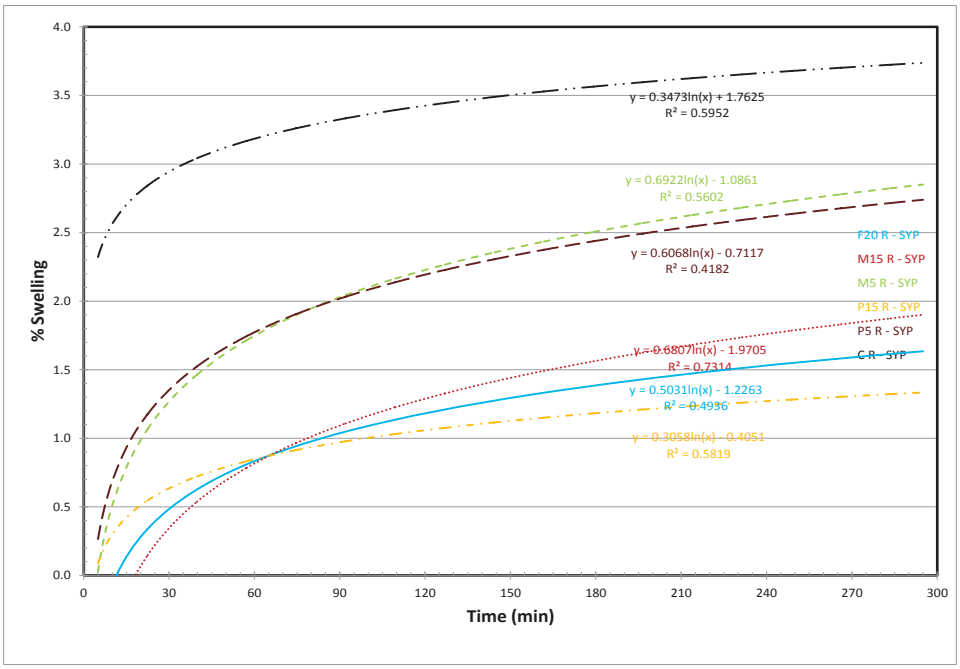

Figure 3.21 Dynamic swelling for SYP in the radial direction

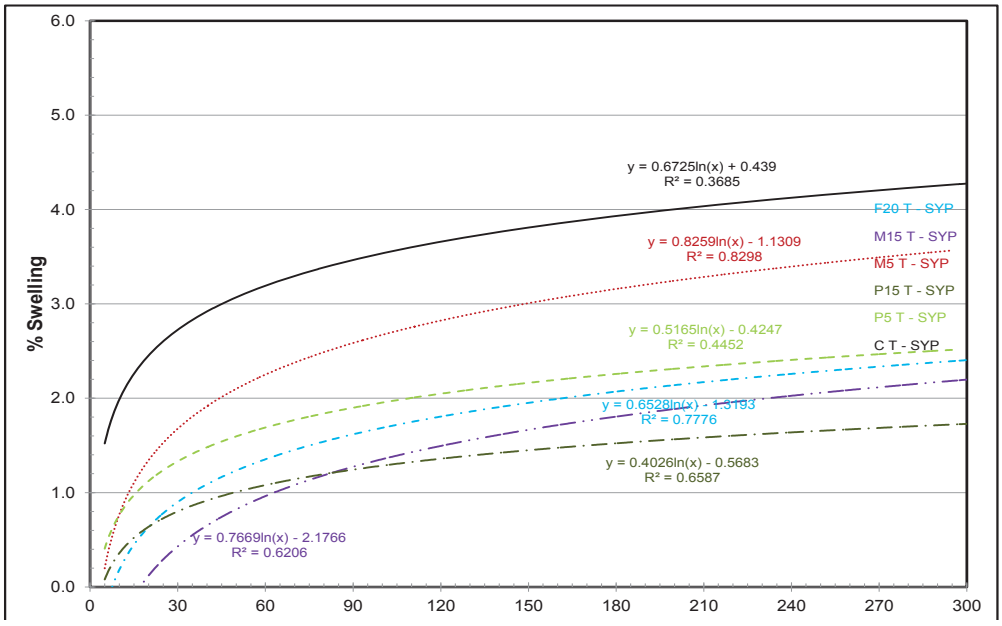

Figure 3.22 Dynamic swelling for SYP in the tangential direction

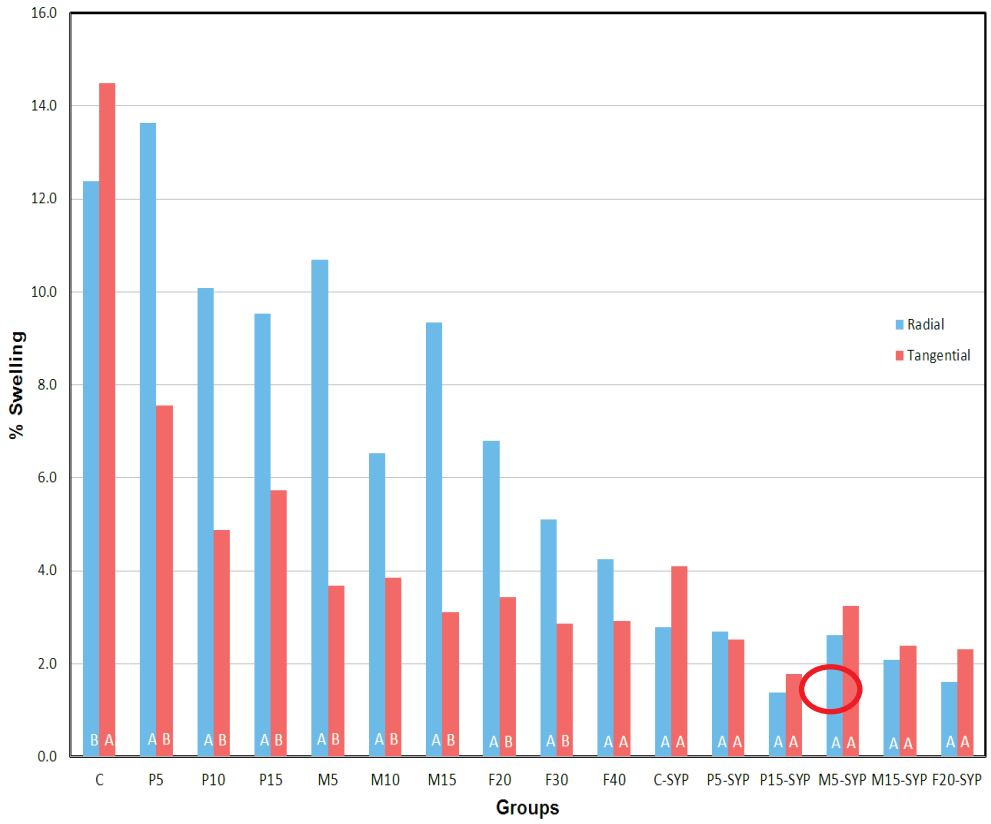

Figure 3.23 Comparison of % swelling between radial and tangential direction

Dynamic swelling for all treatment/substrate combinations was fitted with a logarithmic regression function, with the R^2 illustrated in the Figures 3.19-3.22. As shown in Figure 3.19, there was a decrease in thickness swelling for both PF and FA treated samples, with an increase in WPG. For MF treated samples, there was a decrease in thickness swelling firstly then an increase as the WPG increased. It was unexpected that samples treated with 5% PF had a higher radial swelling than that of untreated one. It was also reported in previous thickness swelling study along with possible reasons.

Compared to the thickness swelling for PSL, performance of tangential swelling for treated samples was far better than untreated one, from half to one fifth of that of untreated one, as shown in Figure 3.20. There was no difference for MF and FA treated samples with respect to tangential swelling. The trend for PF treated samples in tangential direction was the same as in radial direction. However, the performance of tangential swelling for PF treated samples in the 24 h submersion was worse than that in 5 h submersion. Longer submerging time might break the bonds between resin and scrim. Larger specimen dimensions might be another reason.

For all treated southern pine solid wood, there was a decrease in swelling in both radial and tangential directions with the increase in WPG. A 15% PF treated southern pine solid wood performed best in both directions, which was different from that of PSL. The result might confirm previous hypothesis that PF resin used for gluing had a negative effect on PF impregnated PSL. In addition, the panel pressing phase might also affect the physical performance of PF impregnated PSL.

Figure 3.23 demonstrates differences between thickness and tangential swelling for PSL and between radial and tangential swelling for southern pine solid wood. As for PSL, there were significant differences ($\alpha = .05$) between thickness and tangential swelling for both control and treated samples except for the 40% FA treated one. Thickness swelling was always larger than tangential swelling except for the untreated group. This is because that the radial direction was the direction of the pressing load. Dimension recovery mainly occurred in that direction, thus, larger swelling is reported.

On the other hand, there was no significant difference between radial and tangential swelling for southern pine solid wood. It should be noted that the 5% PF treated southern pine solid wood had a larger radial swelling, which was not expected, since ray parenchyma was supposed to constrain radial swelling. A study should be conducted to investigate this case.

Termite Resistance

Evaluation of termite resistance is shown in Tables 3.14 - 3.18. A comparison of weight loss and visual ratings for the various treatments is shown in Figure 3.24. The visual appearance of the blocks after exposure to termites is shown in Figures 3.25 and 3.26. For southern pine positive controls, the average weight loss was 28.4% and the AWPA rating 4 (very severe attack), with no mortality. These results confirmed the validity of the termite test. On the other hand, for both untreated and treated PSL tested, the average weight loss ranged from 1.10% to 1.56%, and the AWPA rating from 8 to 9.3 (moderate to trace attack), with mortality of 100%. This meant both untreated and treated PSL were termite resistant. Figure 3.24 indicates that there was no significant difference between untreated and treated PSL with respect to visual rating and weight loss in this lab scale study. It was noted that for both untreated and treated PSL, termites were all dead after three weeks in the cabinet, which meant that termites did not feed on PSL, whether chemically treated or not. Hence, phenolic resin applied for gluing might prevent the termites from eating the PSL.

Table 3.14 Data summary for southern pine controls samples following 4 weeks of exposure to *Reticulitermes flavipes*[1]

Sample ID	% Wt. loss	Visual Block Rating	Visual Ratings [1]		
			T	P	M
14	28.67	4	+	u/d	s
16	28.53	4	+	u/d	s
17	27.75	4	+	u/d	s
18	28.50	4	+	u/d	s
Avg	28.36	4			
Std dev	0.42	0			

[1]: Visual Ratings: T = Tunneling – "+" = Yes; "-"= No; P = Majority Termite Position – "U" On Surface And "D" Beneath Surface; M = Approximate Termite Mortality – "S" = Slight (0% To 33%); "M" = Moderate (34% To 66%); "H" = Heavy (67% To 99%); "X" = Complete (100%)

Table 3.15 Data summary for Untreated PSL samples following 4 weeks of exposure to *Reticulitermes flavipes*

Sample ID	% Wt. loss	Visual Block Rating [c]	Visual Ratings		
			T	P	M
C-1	1.64	9	+	-	x
C-2	1.41	8	+	-	x
C-3	1.52	8	+	-	x
C-4	1.62	8	+	-	x
C-5	1.30	8	+	-	x
Avg	1.50	8.2			
Std dev	0.14	0.45			

Table 3.16 Data summary for 5% PF-treated PSL samples following 4 weeks of exposure to *Reticulitermes flavipes*

Sample ID	% Wt. loss	Visual Block Rating [c]	Visual Ratings		
			T	P	M
P5-1	1.63	8	+	-	x
P5-2	1.30	8	+	-	x
P5-3	1.27	8	+	-	x
P5-4	1.26	8	+	-	x
P5-5	1.34	8	+	-	x
Avg	1.36	8			
Std dev	0.15	0			

Table 3.17 Data summary for 5% MF-treated PSL samples following 4 weeks of exposure to *Reticulitermes flavipes*

Sample ID	% Wt. loss	Visual Block Rating [c]	Visual Ratings		
			T	P	M
M5-1	1.21	8	+	-	x
M5-2	1.24	9	+	-	x
M5-3	1.42	8	+	-	x
M5-4	1.67	9	+	-	x
M5-5	2.28	8	+	-	x
Avg	1.56	8.40			
Std dev	0.44	0.55			

Table 3.18 Data summary for 30% FA-treated PSL samples following 4 weeks of exposure to *Reticulitermes flavipes*

Sample ID	% Wt. loss	Visual Block Rating [c]	Visual Ratings		
			T	P	M
F30-1	1.24	9.5	+	-	x
F30-2	0.84	9	+	-	x
F30-3	1.30	9.5	+	-	x
F30-4	0.97	9.5	+	-	x
F30-5	1.16	9	+	-	x
Avg	1.10	9.30			
Std dev	0.19	0.27			

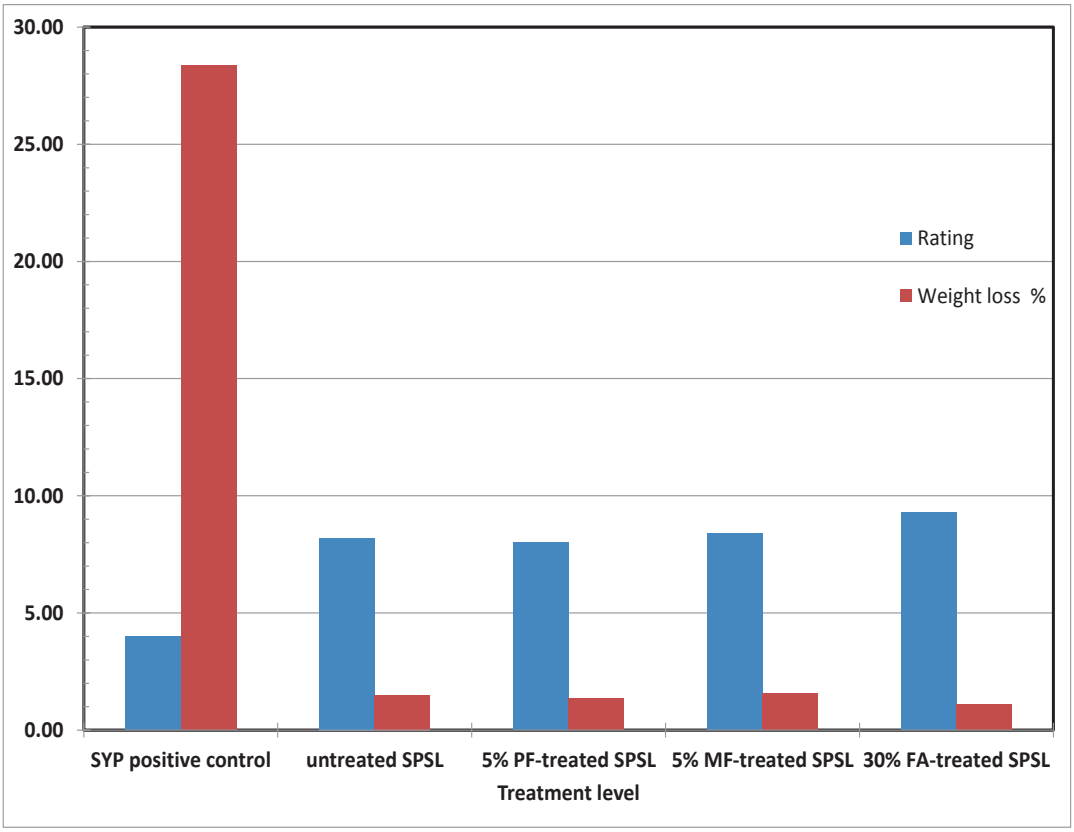

Figure 3.24 Comparison of visual rating and weight loss

Figure 3.25 Block appearance for southern pine positive control after 28-day termite test

Figure 3.26 Block appearance for untreated and treated PSL after 28-day termite test

CHAPTER IV

SUMMARY AND CONCLUSIONS

Data collected from bending test demonstrated that phenol formaldehyde impregnation was not successful in this study, due to the high molecular weight of the PF used for impregnation and the adverse effect of PF resin used for gluing. Melamine formaldehyde impregnation and furfurylation were successful, with the lowest level of MF and medium level of FA performing the best with respect to MOE, MOR, and WML. Data obtained from internal bond test showed that all three treatments improved the internal bond strength. In addition, a low level of chemicals was recommended to modify wood scrim, since low level of PF was better than medium and high levels, and there was no significant difference between levels of MF and FA in internal bond strength, thus low levels were better economically. There was randomness in toughness when comparing both directions but no significant relationship. Samples treated with 10% MF showed better toughness in both directions than untreated one, while furfurylated samples showed equal toughness in both directions in this study. It was unexpected that all three chemical modifications did not significantly improve the bending properties of southern pine solid wood.

Stress and failure analysis showed that failure mode was important in evaluating material strength. Theoretically, the ratio of maximum normal stress to maximum shear stress was 22.6, and it was expected that tension failure would occur for most of samples, but 55.8% shear failure meant that shear strength of some samples was lower than expected. This showed variation of material properties.

Data from 24h thickness swelling test showed that samples treated with FA solution had better performance than other groups in water absorption and EMC. Samples treated at 5% PF had significantly higher WA values than controls while those treated with 10% MF and all FA were significantly lower. The remaining treatments were the same as controls. As for tangential swelling and thickness swelling, PF impregnated samples did not perform better than the controls. Both swelling values for the 5% PF level were higher than the controls. MF and FA impregnated samples were significantly lower in swelling in both directions. Results for dynamic swelling of PSL in radial direction showed that the low level of PF and MF treatment were not significantly different from controls. With increase in weight gain, significantly lower radial swelling was obtained. In the tangential direction, all treatments significantly improved the dimensional stability. PF impregnation was feasible on southern pine solid wood for both radial and tangential directions. This might confirm that it was not the PF solution utilized for impregnation that failed to improve properties of PSL but rather the PF resin used for gluing.

Evaluation of termite resistance for showed that for southern pine positive controls, the average weight loss was 28.36% with an AWPA rating of 4 (very severe attack) and no mortality. However, for both untreated and treated PSL tested, the average weight loss ranged from 1.10% to 1.56%, and the AWPA rating from 8 to 9.3 (moderate to trace attack), with 100% mortality. Thus it was concluded that phenolic resin applied for gluing was capable of preventing termites from eating wood. For PSL, chemical modification treatments were effective in preventing termite attack.

REFERENCES

ASTM (2005) D 4761-05. Standard Test Methods for Mechanical Properties of Lumber and Wood-Base Structural Material. American Society for Testing and Materials, West Conshohocken, PA.

ASTM (2006) D 1037-06a. Standard Test Methods for Evaluating Properties of Wood-Base Scrim and Particle Panel Materials. American Society for Testing and Materials, West Conshohocken, PA.

ASTM (2007) D 143-94. Standard Methods for Testing Small Clear Specimens of Timber. American Society for Testing and Materials, West Conshohocken, PA.

AWPA (2010) E1-09. Standard Method for Laboratory Evaluation to Determine Resistance to Subterranean Termites. American Wood Protection Association. Woodstock, MD.

Barnes HM, Choong ET, Mcllhenny RC (1969) An evaluation of several vapor phase chemical treatements for dimensional stabilization of wood. Forest Prod J 19(3):35-39.

Barnes HM, Seale RD, Linton JM (2010) Steam-pressed scrim lumber (SPSL). Pages 1-8 in International Convention of Society of Wood Science and Technology and United Nations Economic Commission for Europe-Timber Committee, 11-14 October 2010, Geneva, Switzerland.

Baysal E, Osaki SK (2004) Dimensional stability of wood treated with furfuryl alcohol catalysed by borates. Wood Sci Technol 38:405-415.

Bourgois J, Guyonnet R (1988) Characterization and analysis of torrified wood. Wood Sci Technol 22:143-155.

Burmester VA (1973) Effect of heat-pressure treatments of semi-dry wood on its dimensional stability. Holz Roh Werkst 31:237-243.

Burmester VA (1975) Zur Dimensionsstabilisierung von Holz. Holz als Roh- und Werkstoff 33:333-335.

Chang ST, Chang HT (2001) Comparisons of the photostability of esterified wood. Polym Degrad Stabil 71:261-266.

Choong ET, Barnes HM (1969) Effect of several wood factors on dimensional stabilization of southern pines. Forest Prod J 19(6):55-60.

Choura M, Belgacem N M, Gandini A (1996) Acid-catalyzed polycondensation of furfuryl alcohol: mechanisms of chromophore formation and cross-linking. Macromolecules 29(11):3839-3850.

Codd P, Banks WB, Cornfield JA, Williams GR (1992) The biological effectiveness of wood modified with heptadecenylsuccinic anhydride against two brown rot fungi: *Coniofora puteana* and *Gloephyllum trabeum.* Intl. Res. Group on Wood Preservation Doc. No. IRG/WP 3705.

Dai CP, Yu CM, Zhou C (2007) Theoretical modeling of bonding characteristics and performance of wood composite. Wood Fiber Sci 39(1):48-55.

Dunlop AP, Peters FN (1953) The Furans. Reinhold Publishing Corp, New York. 867pp.

Epmeier H, Westin M, Rapp A (2004) Differently modified wood: comparison of some selected properties. Scand J For Res 19(5):31-37.

Esteves B, Nunes L, Pereira H (2010) Properties of furfurylated wood (*Pinus pinaster*). Eur J Wood Prod 10.1007/s00107-010-0480-4.

Evans P, Wallis FA, Owen NL (2000) Weathering of chemically modified wood surfaces: Natural weathering of Scots pine acetylated to different weight gains. Wood Sci Technol 34:151-165.

Fagan GB, Mclain TE (1983) The influence of small grain angle variation on toughness. Wood Fiber Sci 15(2):94-101.

Foo LY, Hemingway RW (1985) Condensed tanning: reactions of model compounds with furfuryl alcohol and furfuraldehyde. J Wood Chem Technol 5(1):135–158.

Forster SC (1998) Decay resistance of modified softwood. PhD thesis, University of Wales, Bangor, UK.

Forster SC, Hale MD, Williams G (1997) Efficacy of anhydride as a wood protection chemical. Intl. Res. Group on Wood Preservation doc. IRG/WP/97-30162.

FPL (2010) Wood Handbook - Wood as an engineering material. Gen Tech Rep FPL-GTR-190. USDA For Serv Forest Products Laboratory, Madison, WI. 509 pp.

Fuchs W (1928) Genuine lignin. 1. Acetylation of pine wood. Ber 61B:948-51.

Furuno T, Imamura Y, Kajita H (2004) The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenol-resin and resin penetration into wood cell walls. Wood Sci Technol 37:349-361.

Furuno T, Ueharaa T, Jodai S (1992) The role of wall polymer in decay durability of wood-polymer composites. Mokuzai Gakkaishi 38(3):285-293.

Gehards CC (1968) Effects of type of testing equipment and specimen size on toughness of wood. USDA For Serv Research Paper. FPL 97.

Giebeler E (1983) Dimensionsstabilisierung von Holz durch eine Feuchte/Warme/Druck-Behandlung. Holz Roh Werkst 41:87-94.

Gierlinger N, Hansmann C, Roder T, Sixta H, Gindl W, Wimmer, Rupert (2005) Comparison of UV and Raman microscopy to measure the melamine-formaldehyde resin content within cell walls of impregnated spruce wood. Holzforschung 59:210-213.

Gindl W, Dessipri E, Wimmer R (2002a) Using UV microscopy to study diffusion of melamine-urea-formaldehyde resin in cell walls of spruce wood. Holzforschung 56:103–107.

Gindl W, Gupta HS (2002b) Cell-wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation. Composites, Part:A 33:1141-1145.

Gindl W, Miller U, Teischinger A (2003a) Transverse compression strength and fracture of spruce wood modified by melamine-formaldehyde impregnation of cell walls. Wood Fiber Sci 35(2):239-246.

Gindl W, Zargar-Yaghubi F, Wimmer R (2003b) Impregnation of softwood cell walls with melamine-formaldehyde resin. Bioresource Technol 87:325-330.

Goldstein IS, Dreher WA (1960) Stable furfuryl alcohol impregnating solutions. Ind Eng Chem 52(1):57-58.

Hadi YS, Westin M, Rasyid E (2005) Resistance of furfurylated wood to termite attack. Forest Prod J 55(11):85-88.

Hill CAS (2002) How does the chemical modification of wood provide protection against decay fungi? COST E22 Meeting, Finland, 3-4 June.

Hill CAS (2009) Why does acetylation protect wood from microbiological attack? Wood Material Sci Eng 1(2):37-45.

Hill CAS, Forster SC, Farahani MRM, Hale MDC, Ormondroyd GA, Williams GR (2005) An investigation of cell wall micropore blocking as a possible mechanism for the decay resistance of anhydride modified wood. Int Biodeter Biodegr 55:69-76.

Hill, CAS (2006) Wood modification: Chemical, thermal and other processes. John Wiley and Sons. West Sussex. 239 pp.

Hillis WE (1984) High temperature and chemical effects on wood stability. Part 1. General considerations. Wood Sci Technol 18:281-293.

Hon DNS (1996) Chemical modification of lignocellulosic materials. Marcel-Dekker Inc. New York. 370 pp.

Hua L, Flodin P, Ronnhult T (1987b) Cellulose scrim-polyester composites with reduced water sensitivity (2)-Surface analysis. Polym. Comp 8:203–207.

Hua L, Zadorecki P, Flodin P (1987a) Cellulose scrim-polyester composites with reduced water sensitivity (1)-Chemical treatment and mechanical properties. Polym. Comp 8:199–202.

Imamura Y, Nishimoto K (1986) Resistance of acetylated wood to attack by subterranean termites. Wood Res 72:37-44.

Imamura Y, Nishimoto K (1987) Some aspects on the resistance of acetylated wood against biodeterioration. Wood Res 74:33-44.

Inoue M, Ogata S, Kawai S, Rowell RM, Norimoto M (1993a) Fixation of compressed wood using melamine-formaldehyde resin. Wood Fiber Sci 25(4):404-410.

Inoue M, Ogata S, Nishikawa M, Otsuka Y, Kawai S, Norimoto M (1993b) Dimensional stability, mechanical properties, and color changes of a low molecular weight melamine-formaldehyde resin impregnated wood. Mokuzai Gakkaishi 39:181-189.

Jebrane M, Sebe G (2007) A novel simple route to wood acetylation by transesterification with vinyl acetate. Holzforschung 61(2):143-147.

Kollmann FFP, Fengel D (1965) Changes in the chemical composition of wood by thermal treatment. Holz Roh Werkst 12:461-468.

Kollmann FFP, Kuenzi EW, Stamm AJ (1975) Principles of Wood Science and Technology. II.Wood Based Materials. Springer -Verlag. Berlin. 703 pp.

Kollmann FFP, Schneider A (1963) On the sorption-behaviour of heat stabilized wod. Holz Roh Werkst 21(3):77-85.

Kumar S (1994) Chemical modification of wood. Wood Fiber Sci 26(2):270-280.
Kumar S, Agrawal SC (1982) Chemical modification of wood with thioacetic acid. In David N. S.Hon, ed. Graft copolymerization of lignocellulosic scrim. ACS Symp Series 187, Am Chem Soc. Washington, DC.

Kumar S, Indradev, Singh SP (1991) Hygroscopicity and dimensional stability of wood acetylated with thioacetic acid and acetyl chloride. J Timb Dev Assoc (India) 37(1):25-32.

Kumar S, Kohli K (1986) Chemical modification of wood: Reaction with thioacetic acid and its effect on physical and mechanical properties and biological resistance. In E. E. Carraher and L. H. Sperling, eds. Renewable resource materials-New polymer sources. Polymer Sci Tech Plenum Press. New York.

Lande S, Eikenes M, Westin M (2004a) Chemistry and ecotoxicology of furfurylated wood. Scandi J For Res 19(suppl.5):14-21.

Lande S, Westin M, Schneider M (2004b) Properties of furfurylated wood. Scandi J For Res 19(Suppl.5):22-30.

Lande S, Westin M, Schneider M (2008) Development of modified wood products based on furan chemistry. Mol Cryst Liq Cryst 484:367-378.
Larsson, Brelid P (2002) The influence of post-treatments on acetyl content for removal of chemicals after acetylation. Holz Roh Werkst 60:92-95.

Militz H (1991) Improvement of shrinking and swelling behavior and durability of wood by treatment with noncatalyzed acetic anhydride. Holz Roh Werkst 49(4):147-152.

Minato K, Yusuf S, Imamura Y, Takahashi M (1993) Hygroscopic, vibrational, and biodeterioration characteristics of medium-density scrimboard treated with formaldehyde. Mokuzai Gakkaishi 39(2):190-197.

Mohebby B, Mai C, Militz H (2003) Soft rot decay in acetylated wood: microcalorimetry and ergosterol assay in decayed wood. Pages 197-202 in Proceedings of the First European Conference on Wood Modification, Ghent, Belgium.

Morozovs A, Buksans E (2009) Fire performance characteristics of acetylated ash (*Fraxinus excelsior L.*) wood. Wood Material Sci Eng 1(2):76-79.

Nordstierna L, Lande S, Westin M, Karlsson O, Furo I (2008) Towards novel wood-based materials: Chemical bonds between lignin-like model molecules and poly (furfuryl alcohol) studied by NMR. Holzforschung, 62:709-713.

Oshima M (1965) Wood chemistry process engineering aspects. Noyes Development Corporation. Park Ridge, New Jersey. 157pp.

Papadopoulos AN, Hill CAS (2002) The biological effectiveness of wood modification with linear chain carboxylic acid anhydrides against Coniophora puteana. Holz Roh Werkst 60:329-332.

Pilgard A, Alfredsen G, Hietala A (2010a) Quantification of fungal colonization in modified wood: Quantitative real-time PCR as a tool for studies on trametes versicolor. Holzforschung 64:645-651.

Pilgard A, Vetter LD, Acker JV, Westin M (2010b) Toxic hazard of leachates from furfurylated wood: Comparison between two different aquatic organisms. Environ Toxicol Chem 29(5):1067-1071.

Ramsden MJ, Blake FSR (1997) A kinetic study of the acetylation of cellulose, hemicellulose and lignin components of wood. Wood Sci Technol 3(1):45-50.

Rapp AO, Bestgen H, Adams W, Peek RD (1999) Electron loss spectroscopy (EELS) for quantification of cell-wall penetration of a melamine resin. Holzforschung 53:111-117.
Rowell RM (1983) Chemical modification of wood. Forest Products Abstracts 6:363-382.

Rowell RM, Ibach RE, Mcsweeny T, Nilsson T (2009) Understanding decay resistance, dimensional stability and strength changes in heat treated and acetylated wood. Wood Material Sci Eng 1(2):14-22.

Ryu JY, Imamura Y, Takahashi M, Kajita H (1993) Effects of molecular weight and some other properties of resins on the biological resistance of phenolic resin treated wood. Mokuzai Gakkaishi 39(4):486-492.

SAS Institute. 2009. Version 9.2. SAS Institute, Cary, NC.

Scheurch C (1968) Treatment of wood with gaseous reagents. Forest Prod J 18(3):47-53.

Schneider MH (1995) New cell wall and cell lumen wood polymer composites. Wood Sci Technol 29:135-158.

Scott JAN, Procter AR, Fergus BJ, Goring DAI (1969) The application of ultraviolet microscopy to the distribution of lignin in wood. description and validity of the technique. Wood Sci Technol 3:73-92.

Seborg RM, Tarkow H, Stamm AJ (1953) Effect of heat upon the dimensional stabilization of wood. J For Prod Research Society 3(3):59-67.

Shafizadeh F, Chin PPS (1976) Thermal deterioration of wood. In: Goldstein wood technology chemical aspects. ACS Symp Series 181, Am Chem Soc. Washington, DC.

Shams MI, Kagemori N, Yano H (2006a) Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin : species dependency. J Wood Sci 52:179-183.

Shams MI, Morooka T, Yano H (2006b) Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin : effects of steam pretreatment. J Wood Sci 52:389-394.

Shams MI, Yana H (2009) A new method for obtaining high strength phenol formaldehyde resin-impregnated wood composites at low pressing pressure. J Trop For Sci 21(2):175-180.

Shams MI. Yano H, Endou K (2005) Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin : effects of sodium chlorite treatment. J Wood Sci 51:234-238.

Shams MI., Yano H (2004) Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin :effects of processing parameters. J Wood Sci 50:343-350.

Simonson R, Rowell R (2000) A new process for the continuous acetylation of lignocellulosic scrim. Pages 190-196 in Proceedings of the 5th Pacific Rim Bio-based Composites Symposium, 10-13 December 2000, Canberra, Australia. Department of Forestry, The Australian National University.

Stamm AJ (1964) Wood and Cellulose Science. Ronald Press. New York. 549 pp.

Stamm AJ, Baechler RH (1960) Decay resistance and dimensional stability of five modified woods. Forest Prod J 10:22-26.

Stamm AJ, Seborg RM (1936) Minimizing wood shrinkage and swelling. Treatment with synthetic resin forming materials. Ind Eng Chem 28(10):1164-1169.

Stamm AJ, Seborg RM (1939) Resin-treated plywood. Ind Eng Chem 31(7):897–902.

Tarkow H (1945) Decay resistance of acetylated balsa. Madison, WI: Forest Products Laboratory, USDA For Serv.

Tarkow H (1946) A new approach to the acetylation of wood. USDA For Serv Forest Prod Lab, Madison, WI.

Thygesen LG, Barsberg S, Venas TM (2009a) The fluorescence characteristics of furfurylated wood studied by fluorescence spectroscopy and confocal laser scanning microscopy. Wood Sci Technol 44:51-65.

Thygesen LG, Elder T (2009b) Moisture in untreated, acetylated, and furfurylated Norway Spruce monitored during drying below scrim saturation using time domain NMR. Wood Fiber Sci 41(2):194-200.

Thygesen LG, Engelund ET, Hoffmeyer P (2010) Water sorption in wood and modified wood at high values of relative humidity. Part 1: Results for untreated, acetylated, and furfurylated Norway Spruce. Holzforschung 64:315-323.

Tjeerdsma BF, Boonstra M, Pizzi A, Tekely P, Militz H (1998) Characterization of thermally treated wood: molecular reasons for wood performance improvement. Holz Roh Werkst 56(5):94-96, 98-99.

Troughton GE (1969) Accelerated aging of glue-wood bonds. Wood Sci 1:172-176.
Troughton GE, Chow SZ (1968) Evidence for covalent bonding between melamine formaldehyde glue and wood. Part I-Bond degradation. J. Inst. Wood Sci 21:29–33.

Ugural AC (1991) Mechanics of materials. McGraw-Hill, New York. 441 pp.

Venas TM, Rinnan A (2008) Determination of weight percent gain in solid wood modified with in situ cured furfuryl alcohol by near-infrared reflectance spectroscopy. Chemometr Intell Lab 92:125-130.

Verma P, Dyckmans J, Militz H, Mai C (2008) Determination of fungal activity in modified wood by means of micro-calorimetry and determination of total esterase activity. Appl Microbiol Biotechnol 80:125-133.

Vetter LD, Pilgard A, Treu A, Westin M. Acker JV (2009) Combined evaluation of durability and ecotoxicity: A case study on furfurylated wood. Wood Material Sci Eng 1(2):30-36.

Videlov KH (1986) The resistance of acetylated Scots pine wood to fungus pests. Nauch Trud Mekh Tekh Drves 30:177-182.

Wan H, Kim MG (2008) Distribution of phenol-formaldehyde resin in impregnated southern pine and effects on stabilization. Wood Fiber Sci 40(2):181-189.

Westin M (1995) Development and evaluation of new alternative wood preservation treatments. Mid-term status report to the Swedish Council for Forestry and Agricultural Research (SJFR). In Swedish with English summary.

Westin M, Ohlsson B, Simonson R, Nllsson T (1996) New chemicals for wood preservation and new ways of chemical modification. Pages 25-29 in Proceedings of the 212th ACS National Meeting, Part I, Cell: 006, August 1996, Orlando. Florida.