ENVELOPE PROTECTION OF PRESERVATIVE-TREATED PINE DECKING WITH MODIFIED LOW MOLECULAR WEIGHT PHENOL FORMALDEHYDE RESIN

by

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Abstract

Preservative-treated pine is commonly used for outdoor decking in Canada and the United States, but its attractive appearance is lost when it is exposed to the weather. Wood can be protected from ‘weathering’ using low molecular weight phenol formaldehyde (LMW PF) resin. In this thesis, I combine preservative treatments and modification of wood with PF resin to try to develop wood decking with superior resistance to weathering. My hypothesis is that shallow ‘envelope’ modification of treated wood with LMW PF resin containing photostabilizers and wax additives will protect the appearance of preservative-treated pine decking exposed to natural weathering. I first screened different additives for their ability to protect wood from the adverse effects of weathering. The best additives were selected for further testing. Preservative-treated Scots and southern pine boards were modified by dipping or vacuum impregnation with modified PF resins, and modified and treated boards were exposed to the weather. Envelope modification restricted checking of untreated pine boards weathered for two years. Degradation of modified boards was shallow and easily cleaned off. Underneath the weathered grey layer, the colour of PF-modified wood was retained. Envelope modification with different PF resin formulations also protected treated boards weathered for six months. Ferric chloride was a more effective additive than a lignin stabilizer for most substrates (treated or untreated). The dark colour of PF/ferric-modified wood masked mould. The different PF resins I tested improved the performance of treated wood to varying degrees, but their effectiveness depended on the substrate they were applied to. I conclude that: (1) envelope modification with PF and modified PF resins is able to protect treated decking from the adverse effects of weathering; (2) vacuum impregnation with PF resin is a better method than dipping at creating an effective weather-resistant envelope at the surface of treated wood decking; (3) PF and additives need to be tailored to suit different preservative-treated woods; (4) PF modification shows promise as a finishing process to enhance weathering resistance of treated wood.
Lay Summary

Preservative treatment protects wood from decay, but provides little protection against surface degradation caused by the weather. Treated wood exposed outdoors greys and roughens due to erosion and surface cracking. In this thesis, I examined whether wood could be protected from weathering by phenol formaldehyde (PF) resin modification. I screened additives that can improve the ability of PF resin to reduce the discolouration and surface cracking of treated wood exposed outdoors. Ferric chloride was most effective at reducing discolouration; a commercial lignin stabilizer also performed well. I modified the surface of preservative-treated wood decking with PF resin or PF with ferric chloride, lignin stabilizer or ferric chloride/wax. The modified PF-formulations improved the performance of treated wood to varying degrees, although their effectiveness varied with the preservative used to treat the wood. I conclude that modified PF resins show promise as a finish to protect treated and untreated wood from weathering.
Preface

The research in this thesis is the original and unpublished work of Wing Fung George Chan. The experimental work and design, statistical analyses and writing of this thesis were done under the supervision of Professor Philip D. Evans. Some of my experimental work was modified as a result of helpful suggestions made by my committee members, Dr Julie Cool and Dr Simon C. Ellis.
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Chapter 1: General Introduction

1.1 Weathering of wood

Wood is an aesthetically pleasing material that is widely appreciated for its "warmth" and "beauty" (Koch, 1972, pp. 12-18). Every piece of wood has a unique grain orientation that gives it "character" and visual appeal (Koch, 1972, pp. 12-18). Because of its visual appeal, architects like to use wood in places where people can see and touch wood, thereby creating an "organic" and "desirable living environment" (Koch, 1972, p. 12-18).

However, when wood is used outdoors, its ‘beautiful aesthetics’ can be stripped away by the deleterious effects of weathering. Weathering is the synergistic interactions of: (1) solar radiation; (2) oxygen; (3) water; (4) heat; (5) pollutants; and (6) certain microorganisms and insects that causes unwanted chemical and physical changes at exposed wood surfaces (Feist, 1990a; Evans, 2013). ‘Weathering’ commences with the rapid surface photodegradation of wood’s molecular constituents, but several months are needed before the wood turns grey (Evans et al., 1993; Feist 1990a).

Solar irradiation initiates weathering of wood (Kalnins, 1966). Solar radiation chemically degrades all of wood's polymeric components: lignin, hemicellulose and cellulose. Lignin strongly absorbs ultraviolet (UV) light, which is the high energy and low wavelength component of the solar spectrum (Kataoka et al., 2004). UV and violet light have sufficient energy to cleave chemical bonds within lignin and produce aromatic free radicals (Derbyshire & Miller, 1981; Kataoka et al., 2007). These free radicals initiate a chain reaction that accelerates photodegradation by further cleaving chemical bonds and producing yet more free radicals (Kataoka & Kiguchi, 2001; Kataoka et al., 2004).

Photodegradation of wood is faster in the presence of atmospheric oxygen, because oxygen participates in the chemical reactions that create free radicals (Hon & Chang, 1982). These free radicals
continue to attack lignin and result in the accumulation of degraded low molecular weight lignin fragments that result in the yellowing of wood (Kalnins, 1966; Hon et al., 1980; Cui et al., 2004). Hence, colour change at wood surfaces exposed to UV light is rapid. Lighter-coloured woods become yellow or brown, while darker-coloured woods lighten at first, due to degradation of extractives, and then turn yellow or brown (Cui et al., 2004; Kishino & Nakano, 2004; Hon & Minemura, 1991).

Nevertheless, all weathered wood surfaces become grey and increase in roughness, as photodegraded lignin, extractives and fragments of wood are washed away by rain water, resulting in a cellulose-enriched surface (Evans et al., 1993; Liu, 2011). Water absorption at weathered wood surfaces creates moisture gradients, where the wood surface layer is wetter than the core (Evans, 2008). The surface dries faster than the core when it is exposed to sunlight, but shrinkage at the surface is resisted by the wetter core, which creates tensile stresses (McMillen, 1955; Ratu, 2009). When these surface stresses exceed the tensile strength of the weathered wood surface, checks (cracks) form (Schniewind, 1963; Evans, 2008).

Surface degradation of wood exposed outdoors is accelerated by atmospheric pollutants and windblown particulates. For example, atmospheric sulfur dioxide can acidify rain water and accelerate weathering of wood (Raczkowski, 1980). Wind-blown particles of sand, salt, dirt or ice, can erode wood surfaces (Johnson et al., 1992; Feist & Mraz 1978a).

Weathered wood surfaces are susceptible to colonization by certain microorganism including fungi, bacteria and algae (Duncan, 1963; Sailer et al., 2010). Photodegradation of lignin, hemicellulose and cellulose at weathered wood surfaces and the accumulation of low molecular weight phenolic compounds and sugars provide nutrients favourable for colonization of wood by UV tolerant mould fungi that metabolize photodegraded polymers (Schoeman and Dickinson, 1997). For example, the colonization of weathered wood surfaces by the highly melanized mould (yeast), *Aureobasidium pullulans* (de Bary)
Arnaud), is partly responsible for the unwanted surface greying of weathered wood (Duncan, 1963). More information on the weathering of wood is available in comprehensive reviews by Feist (1990a), Williams (2005) and Evans (2013).

Weathering of wood surfaces is inevitable, even when preservatives are used to protect wood from decay. Hence, regular maintenance is required to maintain the appearance of preservative-treated wood used outdoors. This is a big drawback to using wood in many exterior applications, particularly the decking market.

1.2 Surface protection of wood decking

One of the biggest markets for the outdoor application of wood in the United States is for decking. This market is dominated by treated wood and, to a lesser extent, naturally durable tropical hardwoods. Wood’s share of the decking market is 84.2% and annual growth in demand for decking is projected to be 1.1% (Freedonia Group, 2016). However, wood decking faces strong competition from wood plastic composite (WPC). Annual growth for WPC decking is projected to be much higher than that of wood decking at 7.3% (Freedonia Group, 2016). Demand for WPC decking is mainly driven by its high decay resistance and low maintenance requirements (Freedonia Group, 2016; Ganguly et al., 2011). WPC decking is less visually appealing than wood, but it maintains its appearance better when it is used outdoors, especially capstock-coated WPC that has a surface layer made of 100% plastic (Eastin et al., 2005; Freedonia Group, 2014a; Freedonia Group, 2016; Ganguly et al., 2011).

Nevertheless, many people still prefer wood decking because of its natural appearance (Ganguly et al., 2011). Naturally weather resistant tropical hardwoods, such as ipe (Tabebuia spp.) or teak (Tectona grandis L.f.), hold particular appeal as decking timbers because of their aesthetic appeal, high durability and lower maintenance requirements than treated wood (Freedonia Group, 2016; Williams et al., 2001).
However, tropical hardwoods are expensive and many of them are not produced on a sustainable basis (Freedonia Group, 2016). Hence, preservative-treated wood is still a popular choice for decking. Preservative-treated wood decking is inexpensive, readily available and decay resistant (Freedonia Group, 2014b; Freedonia Group, 2016). Preservatives containing copper azole (CA), alkaline copper quat (ACQ) and micronized copper (µC), can provide limited photoprotection through the formation of photo-resistant copper complexes with the lignin in treated wood (Liu et al., 1994; Grelier et al., 2000; Temiz et al., 2005). Preservatives that are free of metals, however, provide little resistance to weathering. Hence, waxes/oils, pigments or UV absorbers are added to them to increase their ability to restrict the weathering of wood (Schauwecker et al., 2009; Zhang & Ziobro, 2013). Nevertheless, preservative-treated wood eventually greys and checks and requires regular maintenance, which explains why their market share is not growing as fast as WPCs’ (Zahora, 2002; Zhang & Ziobro, 2013; Freedonia Group, 2016).

1.3 Penetrating finishes

The weathering resistance of preservative-treated wood decking can be increased with penetrating finishes, which commonly contain resin, water repellant (wax or oil), biocide and cosolvent (Morrell, 2002; Feist and Mraz, 1978b). Figure 1.1 shows the processes involved in finishing preservative-treated pine deck boards. Penetrating finishes are subdivided into two categories: (1) transparent-clear systems; (2) semi-transparent (pigmented) systems (Feist & Mraz, 1980a). Transparent-clear finishes leave the underlying wood visible by allowing passage of UV and visible light, but this exposes the wood substrate to photodegradation (MacLeod et al. 1995). Transparent finishes create a moisture and decay resistant barrier at and under the wood surface and allow the finished wood to weather to a natural gray colour. Hence transparent finishes are also referred to as natural finishes (Knaebe, 2013). Transparent finishes do not delaminate or peel, and they can be employed as a finish or a coating primer (Feist & Mraz, 1980a, Feist, 1990b; Williams and Feist, 1999). Semi-transparent finishes contain solid pigments that can provide
a desired colour and block the transmission of UV radiation to wood surfaces: such finishes resemble stains. The concentration of pigments in the penetrating stain affects the level of UV protection and visibility of the wood surface. Thus, high pigment concentrations provide greater UV protection, but reduce the visibility of the wood (Black et al., 1979; Feist & Mraz, 1980a; Feist, 1983).

Figure 1.1 - Flowchart illustrating processes used to protect the surfaces of pine decking

Penetrating finishes treat 3 to 5 cells from the finished surface of wood. Thus, they act as an envelope treatment and protect the wood surface where weathering takes place (Kataoka & Kiguchi, 2001; Morrell, 2002). Penetrating finishes can be brushed on to the wood or the wood can be more thoroughly treated by dipping or vacuum impregnation (Feist & Mraz, 1978b). However, penetrating finishes are still vulnerable to weathering, because the stain can fail due to cracking of the wood substrate and erosion of pigments from exposed surfaces. Hence, re-finishing of the exposed weathered wood surface is invariably needed (Feist, 1992; Kiguchi et al., 1997; Knaebe, 2013).
1.4 Protection of wood with PF resin

Treatment of wood with phenol formaldehyde (PF) resin is a possible way of protecting wood from weathering. PF resin treatment using low molecular weight (LMW) resin can improve resistance of the treated wood surface to discolouration, cracking, dimensional change and biological decay (Imamura, 2007). LMW PF resin can penetrate into wood cell walls, where the resin molecules can cross-link with hydroxyl groups and bulk the cell wall (Stamm & Seborg, 1936; Stamm & Tarkow, 1947; Smith & Côté, 1971). Cured LMW PF resin molecules can physically block hydroxyl groups that adsorb water and keep the LMW PF treated wood in a swollen state (Stamm & Tarkow, 1947; Stamm & Baechler, 1960), as represented in Figure 1.2. There is even the suggestion that PF resin in wood can act as a massive U.V. absorber (Tarkow et al., 1966).

Figure 1.2 - Wood cell wall bulked by PF resin. PC and CL represent molecular bonding by polycondensation and crosslinking, respectively

LMW PF treated wood is less hygroscopic and more dimensionally stable and decay resistant than untreated wood (Stamm & Seborg, 1939; Stamm & Tarkow, 1947a; Stamm & Baechler, 1960). LMW PF resin can photostabilize wood veneers, and when used as a pretreatment, can restrict failure of clear coatings used on wood laminates (Liu, 2011; Vollmer, 2012; Evans et al., 2013).

Brushing of PF resin onto redwood (Sequoia sp.) and western red cedar (Thuja plicata Donn ex D. Don) has been investigated as a way of protecting from weathering. Two coats of PF resin finish protected
wood surfaces for approximately 2 years according to Black and Mraz (1974). PF resin treatments have not been thoroughly studied as a surface or envelope treatment to protect wood from weathering, but Black and Mraz's (1974) study indicates that a brush-on treatment with PF resin does not provide protection for more than 2 years. A vacuum or vacuum-pressure treatment might be more successful?

Since Black and Mraz (1974) carried out their study, many additives have been developed to protect polymers and wood from photodegradation, for example, UV absorbers, hindered amine light stabilizers (HALS) and pigments (Schauwecker et al., 2009; Robinson et al., 2006). UV absorbers have been used to photostabilize wood or clear coatings. Organic UV absorbers, such as benzophenones and benzotriazoles, photostabilize wood by absorbing and converting UV radiation into heat through cis-trans isomerisation or intramolecular hydrogen transfer (Hayoz et al., 2003). Inorganic UV absorbers, such as titanium dioxide (TiO$_2$) and iron (III) oxide (Fe$_2$O$_3$) nanoparticles, absorb and scatter UV radiation. Photostability of these translucent pigments increases with decreasing particle size (Allen et al., 2002; Yang et al., 2003). Stabilization with HALS involves the Denisov-cycle, where in a cyclic mechanism, the HALS inhibits photooxidation by quenching free radicals generated at the photo-irradiated surface of polymers, and then regenerating itself through conversion reactions (Gijsman et al., 1993; Hodgson & Coote, 2010). The company, BASF, that manufactures many HALS has produced an additive formulated to specifically photostabilize lignin (Schaller & Rogez, 2007). This lignin stabilizer when added to LMW PF resin improved the outdoor performance of PF-treated laminates made from radiata pine (Pinus radiata D. Don) (Evans et al., 2013). Pigments can restrict photodegradation of wood by physically blocking UV irradiation, while providing a desired colour to the wood surface (Black et al., 1979; Feist, 1990a). Waxes can increase dimensional stability of wood by forming a hydrophobic barrier to restrict water uptake at wood surfaces (Feist, 1992; Zahora, 2000).
1.5 Hypothesis and outline of thesis

The aim of this study is to test the hypothesis that envelope treatment using modified low molecular weight phenol formaldehyde resin containing additives, such as photostabilizers, pigments or waxes or combinations of these additives, will improve the weathering resistance of preservative-treated wood decking. Chapter 2 reviews the literature that is directly relevant to an understanding of subsequent experimental chapters (3, 4, 5 and 6), including weathering of chemically modified and preservative-treated woods, and surface protection of modified and treated woods with finishes and envelope treatments. Chapter 3 examines the ability of treatments with different concentrations of PF resin and lignin stabilizer, lignostab, to protect yellow cedar (Chamaecyparis nootkatensis [D.Don] Spach) veneers and kraft paper strips, and compares the photoprotective effects of PF resin treatments on yellow cedar and Scots pine (Pinus sylvestris L.) veneers. Chapter 4 assesses the ability of an envelope treatment using LMW PF resin and a lignin stabilizer to photostabilize untreated Scots pine and southern pine (Pinus sp.) decking. Chapter 5 screens treatments with PF resin containing photostabilizers, pigments or water repellent additives for the best performing additive combination to enhance PF resin treatment of yellow cedar veneers. Chapter 6 assesses the ability of modified envelope treatments (LMW PF resin and additives) to photostabilize untreated or preservative-treated wood. Chapter 7 discusses the results of the experimental chapters, draws conclusions and suggests topics worthy of further research.
Chapter 2: Review of the Literature

2.1 Introduction

Exposure of untreated wood to weathering reduces its visual appeal and numerous studies have examined the weathering of untreated wood (see Feist, 1983; Feist & Hon, 1984; Evans, 2003, 2009; Williams, 2005; Hill, 2006; Rowell, 2006; Freeman & McIntyre, 2008). I begin this review by describing the chemistry of the modification of wood with phenol formaldehyde (PF) resin.

2.2 Phenol formaldehyde resin modified wood

Modification of wood with (PF) resin provides protection against the deleterious effects of weathering (see Sudiyani et al., 1999, Evans et al., 2013, Kielmann and Mai, 2016b), and this section examines the weathering of both chemically modified and preservative-treated wood, particularly PF-modified wood, and treatments that have been commercialized for residential use.

2.2.1 Development of phenol formaldehyde resins

Phenol formaldehyde resin was originally invented as a substitute for natural thermosetting or thermoplastic polymers that became expensive or scarce from commercial overuse (American Chemical Society [ACS], 1993). For example, shellac is a naturally derived thermoplastic that was in high demand in the 19th century and is still used today (Parry, 1935; Hicks, 1961; Dedehayir et al., 2014). Shellac is derived from raw lac, an amber coloured resinous secretion of lac bugs (Tachardia lacca Chamberlin), which feed on the sap of trees growing in Asia (Parry, 1935; Hicks, 1961). Shellac in its refined form is used in a variety of applications including varnish for wooden furniture, insulation for electric wiring and early ‘vinyl’ records (Parry, 1935; Hicks, 1961). As these end uses became more important in the United States and Europe in the 19th century, consumption of shellac increased and its price rose accordingly (Parry, 1935; Hicks, 1961; Dedehayir et al., 2014). High prices for shellac created an incentive to develop a synthetic
substitute (Parry, 1935; Dedehayir et al., 2014). As a result, novolak PF resin was invented by Blumer in 1902 as a substitute for shellac in varnishes. Blumer reacted phenol and formaldehyde (the latter in excess) using an oxy-acid catalyst. Novolak PF resin remained fusible over long storage periods, liquefied when heated, solidified during cooling, and was soluble in solvents, such as acetone or alcohol (Baekeland, 1912a; ACS, 1993). However, the commercial applications of novolak PF resin were limited because it was thermoplastic (Baekeland, 1912a; ACS, 1993).

There were additional incentives to develop an infusible and insoluble synthetic thermosetting polymer substitute in the 19th century. For example, the sport of billiards requires hard balls that rolled true. The balls were originally made from ivory, but only ivory with consistent density found at the center of defect-free elephant tusks was suitable (Callister & Rethwisch, 2012). Demands for high quality billiard balls led to overhunting of elephants, and ivory became increasingly scarce and expensive (ACS, 1993). The billiard industry looked for a substitute material with qualities resembling those of ivory (Callister & Rethwisch, 2012; Khan, 2015). A billiard table manufacturer offered a $10,000 prize in 1863 (approximately $198,865 USD in 2017) to anyone who could find a substitute for ivory for the manufacture of billiard balls (Khan, 2015; Federal Reserve Bank of Minneapolis, n.d.). John Wesley and Isaiah Smith Hyatt developed a celluloid substitute by reacting diluted camphor and nitrocellulose under heat and pressure. Celluloid billiard balls resembled those made from ivory, but when they collided, ‘guncap’-like explosions sometimes occurred and celluloid billiard balls were eventually replaced with balls made from PF resin (Trabish, 2004, pp. 4; Muccio, 1991; Brydson, 1999). Dr. Leo Baekeland created the first completely synthetic resol PF resin, Bakelite, in 1907 (ACS, 1993). Baekeland reacted phenol, formaldehyde at sufficient or equal portions to phenol, and a smaller amount of alkaline catalyst. The resulting ‘resol’ PF resin polymerized under heating into an infusible and insoluble polymer with high strength and hardness, unlike novolak PF resin (Baekeland, 1909a). Bakelite resol PF resin became a commercial success due to its moldability and resistance to heat, electricity and chemicals (Baekeland,
1909a; ACS, 1993; Crespy et al., 2008). Bakelite PF resin was used for billiard balls, jewelry, telephones, knife handles and as insulation in the automotive industry (Baekeland, 1909a; ACS, 1993; Crespy et al., 2008).

2.2.2 Synthesis of phenol formaldehyde resin

Synthesis of phenol formaldehyde resin involves ‘step-growth polymerization in three stages’ (Gardziella et al., 2000; Pizzi & Ibeh, 2014). Stage A is addition of formaldehyde to phenol in a base medium, which deprotonates the phenol, forming a phenoxide ion (Fig. 2.1). The phenolate anion reacts with formaldehyde at the ortho, para, or both para and ortho sites of the phenolic ring and forms ortho- and para-hydroxymethyl phenols (HMP) (Fig. 2.2a, b) (Marra, 1992; Gardziella et al., 2000; Kopf, 2003; Pilato, 2010). Products of initial condensation at this stage consist of mono-, di- and tri- HMPs (Fig. 2.2c, d) (Gardziella et al., 2000). Evans et al. (2013) modified wood with a PF resin that contained 2,4,6-trihydroxymethylphenol and 2,4-dihydroxymethylphenol (41.55%); dimers (16.46%); 2-hydroxymethylphenol (13.39%); 4-hydroxymethylphenol (8.82%); tetra-dimer (7.38%); and 2,6-dihydroxymethylphenol (7.51%). At this initial condensation stage, the resin, referred to as resole, is not viscous and is, “thermoplastic and soluble in inorganic solvents” (Pizzi & Ibeh, 2014, p.16; Kollmann et al., 1975; Marra, 1992).

![Figure 2.1 – Deprotonation of phenol in a base medium. The phenolate anion has negative charge delocalized at the ortho or para sites (reproduced from ©Laborie, 2002)](image-url)
Figure 2.2 – Diagram displaying the formation of HMPs. From the left, (a) addition of formaldehyde to phenol in sodium hydroxide forms (b) ortho- and para- monohydroxymethyl phenols and additional reaction with formaldehyde forms (c) dihydroxymethyl phenols and (d) trihydroxymethy phenols (reproduced from (c) Gardziella et al., 2000)

During stage B of the reaction, additional heat causes the HMPs to condense into higher molecular weight products via two possible linkages. A methylene bridge can be formed at the ortho - para and para - para positions between HMPs, whereas a methylene ether bridge can be formed at the ortho - ortho or para - para positions of HMPs (Fig. 2.3a, b) (Pilato, 2010; Pizzi & Ibeh, 2014). However, “methylene ether bridges [eventually convert] into methylene bridges with the loss of formaldehyde and water” (Poljanšek and Krajnc, 2005, p. 241; Pilato, 2010; Pizzi & Ibeh, 2014). Products of HMP condensation consist of trimers and oligomers of varying degrees of polymerization (Pilato, 2010). At this stage, the resin, known as resitol, has increased molecular weight and viscosity, and decreased solubility according to Pizzi and Ibeh (2014). The resitol resin is “soft and fusible when hot, but hard and brittle when cold” (Pizzi & Ibeh, 2014, p. 16; Kollmann et al., 1975).
Stage C is the final curing of the resin with heat. The resin oligomers polymerize, forming a highly cross-linked polymeric network via the formation of methylene bridges (Christjanson et al., 2010). Methylene ether bridges, formed in the previous stage, convert to more stable methylene bridges, and they release additional formaldehyde and water (Poljanšek & Krajnc, 2005; Christjanson et al., 2010). The resulting resin is referred to as resite; a highly polymerized, “infusible and insoluble” resin (Pizzi & Ibeh, 2014, p. 16; Katović, 1967; Kollmann et al., 1975).

Stage A resole PF resin is ideal for impregnation into wood because of its low molecular weight and low viscosity (Marra, 1992). Stage A resole PF resins are impregnated into wood or paper, and later cured to form stage C resite PF resins (Marra, 1992). Stage B resitol PF resin is suited as a wood adhesive. Resitol PF resin has higher molecular weight and viscosity than those of stage A resole PF resin. Hence, it has reduced penetration into and wetting of wood surfaces, and can form adhesive bond lines (Marra, 1992). Resitol PF resins of desired molecular weight or viscosity are made for specific end uses. They generally have a shelf life of less than 60 days (Marra, 1992; Pizzi & Ibeh, 2014).
2.2.3 Properties of PF resin for wood modification

The ability of PF resin to effectively modify wood is dependent on gross and cell wall penetration of the resin into wood (Stamm & Seborg, 1936; Furuno, et al., 2004; Kamke & Lee, 2007).

2.2.3.1 Effects of PF resin viscosity on gross penetration into wood

Gross penetration of PF resin into wood is determined by the fluid flow and capillary action of the PF resin (Siau & Shaw, 1971; Marra, 1992; Kamke & Lee, 2007). Flow of PF resin into wood is affected by viscosity of the PF resin solution, as described by Equation (1) below (Siau, 1984; Marra, 1992). Reducing the viscosity of the PF resin can improve flow velocity and penetration of PF resin into softwoods, but the resin loading is reduced accordingly. In contrast, a more viscous PF resin solution is less able to penetrate into wood (Siau and Shaw, 1971; Marra, 1992).

\[ Q = \frac{N \pi r^4 \Delta P}{8 \eta L} \]

Where, 
- \( Q \) = volumetric flow rate
- \( N \) = number of uniform capillaries
- \( r \) = radius of capillary
- \( L \) = length of capillary flow
- \( \Delta P \) = pressure differential
- \( \eta \) = coefficient of dynamic viscosity

2.2.3.2 Effects of PF resin molecular weight on wood cell wall penetration

Penetration of PF resin into wood cell walls is essential for effective wood modification (Stamm & Seborg, 1936; Furuno et al., 2004). Penetration of PF resin into yellow-poplar (\textit{Liriodendron tulipifera} L.) cell walls requires PF resin molecules to have an average (low) molecular weight of 270 Mn according to Laborie (2002). Furuno and coworkers (2004) modified Japanese cedar (\textit{Cryptomeria japonica} D. Don) using low (290 Mn), medium (470 Mn) and high (820 Mn) molecular weight PF resins. Electron probe x-ray microanalysis and scanning electron microscopy of bromine-labeled PF (BrPF) resin was used to
observe penetration of PF resin into cell walls of modified cedar. Furuno et al. (2004) observed even penetration of low molecular weight (LMW) PF resin within earlywood and latewood cell walls, and absence of the LMW PF resin deposits on lumen surfaces. In contrast, medium molecular weight (MMW) and high molecular weight (HMW) PF resins were present on lumen surfaces and had reduced cell wall penetration. Jakes et al. (2015) modified loblolly pine (*Pinus taeda* L.) latewood using LMW or HMW bromine-labeled PF resin. They used synchroton-based X-ray fluorescence microscopy to detect Br signal, and found greater cell wall penetration in wood modified with the LMW BrPF resin than that in wood treated with higher MW resins. They also found that LMW BrPF resins were more effective at reducing cell wall hygroscopicity than HMW BrPF resins.

### 2.2.3.3 Effects of PF resin polarity on penetration and affinity to wood cell walls

Penetration of PF resin into wood cell walls can be further improved by using a polar solvent, such as water as the carrier (Stamm & Seborg, 1936; Marra, 1992). Wood cell walls contain microvoids or micropores that swell in presence of polar solvents, improving penetration of PF resin into cell walls (Hill, 2006). Furthermore, PF resin that is polar can bond to cell wall constituents (Stamm & Seborg, 1936; Marra, 1992).

### 2.2.3.4 PF resin catalysts and wood modification

According to Pizzi and Ibeh (2014), alkali hydroxides are used to catalyze the initial polymerization reaction of resole PF resin. Alkaline catalysts are mixed together with phenol and formaldehyde in a reaction vessel for initial polymerization during the bulk production of PF resin. Catalysts have an impact on properties of resole PF resin. For example, alkaline catalysts maintain water solubility of PF resin. The advantages of highly alkaline catalyzed PF resin are their increased reactivity, lower viscosity of the resin and swelling of the wood cell wall, which facilitates resin penetration. However, a disadvantage of such highly alkaline PF resins is loss of wood strength (Kollmann et al., 1975; Marra, 1992; Pizzi & Ibeh, 2014).
The efficiency of alkali catalysts on the initial reaction rate of PF resin can be ranked as follows according to Pilato (2010):

\[ \text{Mg(OH)}_2 > \text{Ca(OH)}_2 > \text{Ba(OH)}_2 > \text{Li(OH)} > \text{Na(OH)} > \text{K(OH)} \]

Sodium hydroxide is the most commonly used catalyst for resole PF resin. Additional catalysts are not needed to cure the PF resin, as the resin is cured by heat (Pizzi & Ibeh, 2014). Alkaline resole PF resin imparts a red-brown colour to PF-modified wood. However, neutral resole PF resin can be used in applications where it is important to maintain woods’ natural colour (Furuno et al., 2004).

2.2.4 Interaction of low molecular weight PF resin with wood cell wall constituents

Chemical interactions occur between PF resin molecules and wood cell wall constituents. Evidence for such interactions is enhanced mechanical properties, dimensional stability and decay resistance of PF resin modified woods (Stamm & Seborg, 1939; Imamura & Kajita, 1990; Takahashi & Imamura, 1990). Interactions between PF resin and wood begin during polymerization of the PF resin within resin impregnated wood (Pizzi et al., 1994).

2.2.4.1 Curing kinetics of wood impregnated with PF resin

Wood impregnated with PF resin must be air dried prior to convective heat curing. Air-drying removes excess free water in the impregnated wood and eliminates steep moisture gradients that can create drying stresses during curing (Stamm & Seborg, 1936; Galperin et al., 1995). Furthermore, excess free water within impregnated wood can affect distribution and penetration of PF resin molecules into wood cell walls. According to Klüppel and Mai (2013), free water in lumens evaporates before bound water in the cell walls during curing under dry conditions. As a result, PF resin in the lumens becomes concentrated and promotes diffusion of PF resin into cell walls. Hence, dry cured PF impregnated wood cell walls are bulked with resin following curing and the wood becomes dimensionally stable (Klüppel &
Mai, 2013). However, a drawback of dry curing is that evaporation of water from the PF-impregnated wood redistributes the resin and concentrates it at the wood surface (Smith & Cockcroft, 1961; Klüppel & Mai, 2013). Such uneven distribution of resin may lead to internal checking of the PF impregnated wood (Nicholas & Williams, 1987; Ashaari et al., 1990). Slow curing or curing under non-drying conditions can overcome this problem (Klüppel & Mai, 2013). However, curing under non-drying conditions can lead to premature polymerization of the resin and lower cell wall bulking and dimensional stability of the PF-modified wood (Klüppel & Mai, 2013).

2.2.4.2 Interaction of PF resin with earlywood and latewood cell walls

Hydroxymethylated phenols in PF resin cured in loblolly pine react with free-phenolic units on lignin in cell walls, according to Yelle and Ralph (2016). Resin in nano-porous cell wall network of wood is sterically hindered from polymerizing, limiting the degree of cross-linking and altering the polymerization mechanism of the PF resin. Evidence for such an effect in loblolly pine latewood was lower levels of methylene bridges and greater levels of HMPs in latewood compared to earlywood cell walls (Yelle & Ralph, 2016).

2.2.4.3 Interaction of PF resin with cell wall polymers

During curing of LMW PF resin in cell walls of loblolly pine, simultaneous degradation of the wood cell wall and bond formation between lignin and PF resin molecules occurred, according to Yelle and Ralph (2016). Such degradation involved alkaline hydrolysis of lignin at β-aryl ether and phenylcoumaran units, producing styryl ethers and stilbenes with a phenolic guaiacyl end-unit, respectively (Fig. 2.4a, b) (Obst et al., 1979; Dimmel & Perry, 1985; Balakshin et al., 2003).
Figure 2.4 – Diagram showing (a) alkaline hydrolysis of β-aryl ether producing styryl ether and formaldehyde; (b) alkaline hydrolysis of phenylcoumaran producing stilbene and formaldehyde. Both styryl ether and stilbene contain guaiacyl end-units (reproduced from Yelle & Ralph, 2016).

The guaiacyl end-unit could form a methylene bridge link at the C5 ortho- position with HMPs (Fig. 2.5). Reactivity of guaiacyl end-unit with PF resin could increase when the PF resin polymerizes to a degree that reaches steric hinderance, because “the surrounding lignin moieties become a more likely point of contact and, thus increase their potential for reaction” (Yelle & Ralph, 2016, p. 33).
According to Yelle and Ralph (2016), alkali degradation and modification of polysaccharides were detected to a greater degree in earlywood than in latewood of loblolly pine during early stages of LMW PF resin curing. Galactoglucomannan and arabinoglucuronoxylan underwent alkaline hydrolysis, resulting in complete loss of 2-O- and 3-O-acetyl groups and partial loss of 4-O-methyl-α-D-glucuronic acid groups, respectively. Levels of cellulose, mannose, xylose, galactose and arabinose in earlywood and latewood decreased during curing of PF resin (Yelle & Ralph, 2016).

2.2.5 Properties of PF resin modified wood

Polymerization of LMW PF resin within cell walls bulk the walls with an insoluble polymer that maintains the wall in a permanently swollen state (Klüppel & Mai, 2013). Such bulking reduces the hygroscopicity of wood by physically blocking water’s access to sorption sites. As a result, woods’ dimensional stability and decay resistance is increased (Stamm & Baechler, 1960). Wan and Kim (2008) studied distribution of cured resole PF resin in southern yellow pine (Pinus sp.). Deposits of LMW PF resin...
were present in ray tracheid cell walls and lumens of longitudinal tracheids. Deposits of HMW PF resin were mainly restricted to ray tracheids. The authors suggested that the PF resin interlocks rays and longitudinal tracheids and this effect restricted dimensional change in the tangential direction.

2.2.5.1 Dimensional stability

Improvements in dimensional stability of woods modified with LMW PF resin have been reported in several studies. Stamm and Baechler (1960) reported increases in the dimensional stability of Sitka spruce (*Picea sitchensis* (Bong.) Carr.) boards vacuum impregnated with LMW resole PF resin. The modified spruce boards had an anti-swelling efficiency (ASE) of 70% at ~40% of treatment weight percentage gain (WPG). Higher WPGs did not significantly increase ASE. Ryu and coworkers (1993) found a maximum ASE of 60% at WPGs of 20% to 30%, when Japanese cedar was treated with a LMW (369 Mn) resole PF resin. Lower ASE values of ~30% were obtained when cedar was impregnated with higher MW resin (383 Mn). Accordingly, ASE values were even lower (20% or 0%) when cedar samples were modified with higher MW (621 or 1143 Mn) resins. Furuno and coworkers (2004) vacuum impregnated Japanese cedar with LMW resole PF resin, LMW novolac PF resin or HMW resole PF resin. The dimensional stability of wood impregnated with LMW resole or novolac PF resin was similar. An ASE of 60% was observed in cedar impregnated with 30% LMW resole or novolac PF resin.

2.2.5.2 Decay resistance

Decay resistance is much improved when wood is modified with LMW resole PF resin. For example, Takahashi and Imamura (1990) exposed Japanese cedar, western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) and Japanese beech (*Fagus crenata* Blume) that had been vacuum treated with LMW resole PF resin to brown rot (*Tyromyces palustris* (Berk. & Curt.) Murr.) and white rot (*Coriolus versicolor* (L. ex Fr.) Quél.) fungi. Decay resistance of modified wood was positively correlated with weight gain of PF resin. Weight gains of > 10% were needed to prevent decay of cedar and hemlock, while weight gains of > 20% were
needed for beech. Furuno and coworkers (2004) also found that weight gains of approximately 10% to 15% were needed to completely stop attack of PF-modified Japanese cedar by brown rot or white rot fungi. Even higher weight gains of 15% were required to prevent brown or white rot attack of PF-modified cedar when it was subjected to a preliminary leaching step. Bosshard and Futo (1963) investigated the decay resistance of wood that had been coated with PF resin. They covered poplar (Populus sp.) plywood with a film of PF resin (Tegofilm), and exposed the resin coated plywood to white rot for four months. The PF resin coating protected the coated plywood from decay, but the protective effects were restricted to the phenolic resin coating.

Decay resistance of PF resin modified wood is positively correlated with its dimensional stability according to Stamm and Baechler (1960). They found a positive correlation between ASE and decay resistance of PF-modified wood Sitka spruce exposed to the brown rot fungus *Lenzites trabea* (Pers.) Fr. Complete resistance to fungal decay was reported at an ASE value of 70%. Ryu et al. (1993) found that modified Japanese cedar with smaller ASE values of 20% to 35% and WPGs of 5% resisted brown and white rot decay. Cedar modified with a highly alkaline PF resin (pH of 12) was less resistant to decay. This was due to alkaline catalyzed deterioration of wood, according to Ryu et al. (1993). Chan et al. (2015) tested termite resistance of Scots pine (*P. sylvestris*) veneers modified with 10%, 20% or 30% LMW PF resin and exposed outdoors in Australia at a site where termites were active. Termite resistance of PF-modified veneers was positively correlated with WPG (Chan et al., 2015).

2.2.5.3 Strength, hardness and abrasion resistance

According to Huang and coworkers (2013), LMW PF resin improves the mechanical properties of wood because the low molecular weight PF molecules penetrate cell walls and crosslink cell wall polymers. They compared the effects of LMW (183-319 Mn) and HMW (2000-3000 Mn) PF modification on mechanical properties of Chinese fir (*Cunninghamia lanceolate* (Lamb.) Hook.). They found that LMW PF
resin modification significantly improved the modulus of elasticity (MOE) and hardness of Chinese fir. However, modification with HMW PF resin decreased MOE due to limited penetration of HMW PF resin molecules into cell walls and alkaline hydrolysis of hemicelluloses (Huang et al., 2013). Hermawan and coworkers (2013) impregnated Japanese cedar lamina with LMW (average 200 Mn) PF resin. The hardness of the PF-modified cedar increased as a result of increase in density of the laminae. Leemon and coworkers (2015) investigated the mechanical properties of sesenduk (*Endospermum diadenum* (Miq.) Airy Shaw) modified with LMW (600 Mn) PF resin. Modulus of rupture and elasticity and hardness of sesenduk increased as a result of treatment. Sesenduk wood samples modified with 20% (w/v) PF resin were stiffer than those modified with 15% (w/v) resin. Wan et al. (2006) modified aspen (*Populus tremuloides* Michx.), yellow birch (*Betula alleghaniensis* Britton) and sugar maple (*Acer saccharum* Marsh.) with LMW (310 Mn) PF resin, and found increases in hardness of all species as a result of PF resin modification. Deka and Saikia (2000) reported improvements in MOR and MOE of bur-flower (*Anthocephalus cadamba* (Roxb.) Miq.) wood modified with PF resin. MOR was positively correlated with treatment weight gain.

2.2.6 Commercial applications of PF resin modified wood products

Phenol formaldehyde resin was used commercially to modify solid wood to improve the wood’s hardness, durability and resistance to wear, moisture and chemicals (Baekeland, 1912b). Wood was impregnated or coated with PF resin and then cured using a hot press. Alternatively, impregnating face veneer hot pressed on to the surface of solid wood (Baekeland, 1909b, 1912b). There was significant commercial, industrial and military interest in chemically modified or ‘improved wood’, particularly PF-modified wood, during the 1940s, specifically to meet material demands during World War II (Champion, 1943; Seborg & Vallier, 1954; Gurvich, 1957; Stamm & Seborg, 1962).
2.2.6.1 Impreg

Wood chemically modified with PF resin by impregnation and curing (without application of pressure) is known as Impreg ("impregnated" wood) (Stamm & Chidester, 1947, pp. 726; Stamm, 1946). Green or kiln-dried sapwood from permeable species, such as ponderosa pine (*Pinus ponderosa* Douglas ex C. Lawson) or basswood (*Tilia americana* L.), was impregnated with PF resin (Stamm & Seborg, 1962; Stamm, 1964a). However, full impregnation of less permeable woods that exceeded 0.3 m in length was difficult and costly, because to obtain adequate resin uptakes, long treatment times and large volumes of resin were needed (Stamm, 1944a; Stamm & Seborg, 1962). Only the “outer zone” of the wood could be impregnated (Stamm, 1946, pp. 154). This was sufficient to impart decay resistance to impregnated wood, but the modified wood lacked sufficient dimensional stability (Stamm & Seborg, 1962). Furthermore, uneven distribution of the resin created stresses between impregnated and unimpregnated parts of the wood, leading to surface and internal checking (Stamm, 1946; Seborg et al., 1962). A practical solution to minimizing treatment difficulties and costs was to impregnate veneers up to 3.18 mm thick with PF resin and press them into a “superior plywood” (Champion, 1943, pp. 4; Stamm & Chidester, 1947; Seborg et al., 1962). Veneers from any species could be used to make Impreg (Stamm, 1944a). Commercial PF resins manufactured by different companies and with different trade names were used to make improved wood, including Bakelite, Amberlite, Compregnite, Durez, Central Process Corporation Resin, General Electric and Monsanto Resinox. However, the most effective and preferred resins had high resin solids content, light colour, low viscosity, high polarity and long shelf life, low molecular weight and were water-soluble, neutral or slightly alkaline (Burr & Stamm, 1945; Seborg et al., 1962). Phenol formaldehyde resin used for Impreg was diluted to solids content of 30% - 35% to impregnate veneers to treatment weight gains of 25% - 32% (Stamm & Seborg, 1939; 1962; Stamm 1944a). According to Stamm and Seborg (1939), there was little additional improvement in ASE of PF resin treated Douglas fir (*Pseudotsuga menziesii* (Mirb.)
Franco) veneers at WPGs that exceeded 30% to 40% because the wood cell walls were fully saturated with resin and excess resin was deposited in the coarse capillary network.

2.2.6.1.1 Manufacture of impregnation

Veneers were impregnated with PF resin using one of three different methods: (1) dip; (2) pressure impregnation; or (3) compression (Stamm & Seborg 1939, 1962; Stamm, 1944b, 1946). The first two methods were also used to treat solid wood, but only thin timber could be treated using compression impregnation (Stamm, 1944b; 1946). Figure 2.6 shows a summary of the steps involved with each impregnation method. Dip impregnation relies on diffusion of PF resin into the coarse capillary network of veneers. Veneers are submerged in PF resin solution without application of pressure until desired resin uptake is achieved (Seborg et al., 1962). Pressure impregnation creates pressure differential in veneers to increase the rate and total uptake of resin. This was done by pulling vacuum, applying pressure, or both (Stamm, 1946). Compression impregnation also creates a pressure differential to improve resin uptake by veneers. Preheated veneers are compressed through compression rollers, which creates a partial vacuum in veneers. The veneers are then submerged in a cooler PF resin solution. Recovery of the compressed thickness and cooling of hot air and water vapor within the veneers create an internal vacuum that draws PF resin solution into wood cells (Stamm, 1944b).
Dip impregnation is a simple process utilizing both diffusion and capillary flow to treat veneers (Stamm & Seborg, 1939, 1962). Green or dry veneers are submerged in PF resin until the veneers attain 25% to 30% resin uptake, which takes 8 – 15 h and 40 – 80 h for submersion for green and dry veneers, respectively (Stamm & Seborg, 1939). Dip impregnation of thin veneers can be rapid, but it is less suitable
for lumber, as the rate of solution uptake is the inverse of the square of wood thickness (Stamm & Seborg, 1939, 1962). Green veneers are more suitable than dry veneers for dip impregnation, because green veneers absorb resin more quickly than dry veneers (Stamm & Seborg, 1939). Freshly peeled green veneers with moisture contents of ~108% were the preferred veneers for dip impregnation according to Stamm and Seborg (1939). The length of dipping depended on veneer thickness, density and wood species. The duration of dipping depends on “square of the thickness” of veneers, so dip impregnation is slow (Stamm & Seborg, 1962, pp. 3; Stamm & Seborg, 1939; Stamm, 1944a). For example, 0.79 mm thick green veneer sheet of sweetgum (Liquidambar styraciflua L.) heartwood needed to be dipped in 30% PF for 1 h at 37.8 °C to attain 35% resin uptake. However, thicker 3.18 mm veneer, required 16 h of dipping to obtain the same resin uptake (Stamm, 1946; Seborg et al., 1962). Hence, dip impregnation is best suited for thin veneers (<1.59 mm) from permeable wood species (Stamm & Seborg, 1939).

Shorter impregnation times or rapid impregnation of thicker or dry veneers can only be achieved using pressure treatments (Stamm & Seborg, 1939; Seborg et al., 1962; Stamm & Seborg, 1962). Dry veneers are impregnated with PF resin in a galvanized iron cylinder, where vacuum, pressure or vacuum and pressure are applied (Stamm, 1946; Stamm & Seborg, 1962). According to Stamm and Seborg (1939), a vacuum only method involved: (1) loading an empty cylinder with veneers; (2) pulling a vacuum (9.14 x 10⁻² MPa); (3) drawing PF resin solution into the cylinder; (4) holding vacuum and submerging veneers for 15 minutes in resin followed by release of vacuum. A pressure only method involved: (1) filling the cylinder with PF resin solution; (2) submerging veneers in resin solution; (3) applying pressure (0.14 – 0.69 MPa) for 15 minutes to 5 hours or overnight, depending on thickness of veneers (Stamm, 1944a; Stamm, 1946; Stamm & Seborg, 1962). A vacuum and pressure method involved a combination of the aforementioned steps (Stamm & Seborg, 1939). Impregnation times for less permeable veneers could be reduced using high pressure (Stamm & Seborg, 1962). Stamm and Seborg (1939) compared treatment uptakes of veneers that were dip, vacuum, or vacuum and pressure impregnated. Treatment uptakes of 57%, 85%
and 152% for the different treatment methods were obtained, respectively. According to Stamm (1946), there was little additional uptake from pulling a vacuum before pressure was applied. Furthermore, vacuum removes volatile formaldehyde from the PF resin solution. Uptakes of 50% for 1.59 mm thick sweetgum heartwood veneer could only be achieved by applying pressure at 414 kPa for 1 h when a 30% - 35% PF resin solution at 29 – 32°C was used to treat veneers (Stamm & Seborg, 1962). Pressure impregnation was most suited for treatment of veneers that were 1.59 – 3.18 mm thick (Stamm & Seborg, 1962).

Another method of impregnating veneers involves the use of compression rollers. This method was suited to continuous operations (Stamm, 1944b). Green or dry veneers can be used, but preliminary compression was needed to remove free water from green veneers (to prevent dilution of the PF resin solution). A set of drying rollers compressed green veneers to half their thickness and removed free water. Hot air was forced across the faces of the veneer to dry the veneer to a moisture content close to fiber saturation point. Dry veneers were also preheated to plasticize the wood to make it easier to compress them. Green or dry veneers preheated to 100 °C passed through a set of compression rollers that were submerged in PF resin solution, which was cooled to room temperature with cooling coils. The compression rollers forced hot air or moisture out of the wood. The veneer exited the rollers, and the release of pressure when veneer was submerged in resin caused compressed wood to springback. This created a vacuum within the wood that draws in the PF resin solution. A vacuum within the wood also results from cooling and condensation of air and moisture in the wood (Stamm, 1944b). PF resin uptakes of more than “the volume of air and water displaced” could be achieved using roller compression treatment according to Stamm (1944b, pp. 2). PF resin concentrations of up to 50% were used. Spruce or cottonwood (Populus spp.) veneers could be compression impregnated with PF resin in approximately 10 seconds, while veneers of harder wood species, such as birch, needed to be submerged in the solution for
up to 10 minutes according to Stamm (1944b). This impregnation method was suitable for the treatment of “more compressible species, such as basswood, cottonwood, and spruce” (Stamm, 1946, pp. 156).

After impregnation, PF resin needs to diffuse under non-drying conditions from the coarse capillary network into wood cell walls or from treated wood to untreated wood. Veneers impregnated with PF resin were stacked and covered with canvas to reduce the rate of air drying (Stamm & Seborg, 1962). The time needed for this diffusion step depended on the distribution of resin within veneer. PF resin was uniformly distributed when veneers were dip impregnated, and as a result a diffusion step could be neglected, according to Seborg and coworkers (1962). PF resin in veneer treated by pressure impregnation can be unevenly distributed. Hence, one to two days of diffusion are needed to achieve more uniform resin distribution (Stamm, 1946).

Drying of treated veneers using a commercial veneer roller dryer or a kiln at temperatures below boiling was used after the diffusion step (Stamm & Seborg, 1962). This dried veneers and prevented the formation of steam that could cause PF resin to accumulate at veneer surfaces during high temperature curing. Furthermore, drying at low and non-polymerizing temperatures assisted in the diffusion of PF resin into wood cell walls, according to Stamm (1946) and Stamm and Seborg (1962). Treated veneers could be dried without humidification using a veneer roller dryer or a kiln, although roller dryers could dry treated veneers quicker than kilns (Stamm, 1946; Stamm & Seborg, 1962). For example, 3 h was needed to dry veneers at 71 °C using a veneer roller, whereas kiln drying at 54 °C required a drying time of 16 h. Furthermore, veneers needed to be horizontally stacked with spacers between each sheet or vertically held at one end to improve air circulation, according to Stamm (1946; 1964a). The drying temperature was raised to 149 - 160 °C to cure the PF resin (Stamm, 1946; Stamm & Seborg, 1962).

Assembly of cured veneers involved applying adhesive to veneer surfaces. Adhesives were hand-spread on the top surface of veneers because cured veneers were too brittle for machine spreading. The
amount of adhesive used for each Impreg panels was approximately 12% by dry weight of untreated veneer (Erickson, 1965). Adhesive amounts of 96.9, 118.4 and 161.5 g/m² were used for Impreg made from sitka spruce, sweetgum or yellow birch, respectively (Erickson, 1965). Additional time was needed during the layup of veneer sheets, because permeability of veneers to adhesive was reduced by the PF treatment (Stamm & Seborg, 1939). For example, according to Stamm and Seborg (1939), an adhesive assembly time of a few minutes produced Impreg with strength properties inferior to those of untreated plywood, but strengths were improved when assembly time was increased to 15 minutes. Assembled veneers were laid up and pressed together (Champion, 1943). Erickson (1965) hot-pressed 17 ply yellow birch Impreg panels at 146.1 °C (platen) and 1.86 MPa for 70 minutes; sweetgum panels at 148.9 °C (platen) and 1.69 MPa for 65 minutes; and sitka spruce panels at 146.1 °C (platen), 1.45 MPa for 65 minutes. However, 11%, 6% and 22% of unintended compression occurred for each of three species, respectively.

2.2.6.1.2 Properties of impreg

In comparison to untreated plywood, Impreg has improved compressive and shear strengths, lower hygroscopicity and electrical conductivity and increased resistance to dimensional change, heat, acids, decay and termite attack (Weatherwax & Stamm, 1945; Erickson & Faulkes, 1949; Stamm & Seborg, 1962; Rowell, 1999). Impreg has increased hardness, reduced grain raising and resistance to face checking (Stamm & Chidester, 1947; Erickson & Faulkes, 1949; Rowell, 1999). Impreg is resistant to grain raising and checking even when it is exposed outdoors without a surface finish (Stamm & Chidester, 1947). Face checking of untreated plywood exposed outdoors is eliminated by using a PF-impregnated face veneer (Stamm, 1945; Stamm & Seborg, 1962). Stamm and Seborg (1939) exposed Douglas fir Impreg (30% WPG) to 6 months of natural weathering, and found that surface plies were free of checks. PF resin treatment also restricted face checking of crotch veneers, which are highly susceptible to checking. Accordingly, it is
worthwhile using PF treatment for crotch or burl veneers employed as decorative face plies for furniture construction (Stamm, 1944a). Browne and Laughnan (1952) applied a coating of paint on a plywood panel made from 3 plies of 3.18 mm thick PF treated Douglas fir veneers, and exposed the panel vertically facing south. The coating on summerwood of Impreg was free of delamination and flaking after 7.5 years of outdoor exposure and surface checking was absent.

2.2.6.1.3 Applications of impreg

Impreg was used as face plies to improve the resistance of plywood to weathering, decay and termite attack (Stamm & Chidester, 1947). Impreg was also used in the automotive industry for die forming. According to Seborg and Vallier (1954), automotive companies in the 40s and 50s faced difficulties in producing metal body parts with consistent dimensions, because untreated wooden models were used for die forming. The wooden models were not dimensionally stable, and changes in their dimensions were transferred to the steel dies and car body component. This production problem was solved by making dies from Impreg (Seborg & Vallier, 1954). “More than a million dollars’ worth” of Impreg die models were produced for the automotive industry according to Stamm (1964a, pp. 329). Impreg pattern and die models made from mahogany (Swietenia spp.) were manufactured by Haskelite Corp., Nickey Bros., Inc., and Koppers Co. for the Ford Motor Company. Furthermore, the Ford Motor Company itself made Impreg crankshaft patterns for experimental crankshaft shell moldings (Seborg & Vallier, 1954; Stamm & Seborg, 1962). The Koppers Co. used Impreg for acid tanks (Stamm & Seborg, 1962).

Impreg was widely used by the military during World War II as housings for electrical control equipment and a substitute for teak decking in aircraft carriers. This application occurred due to the scarcity of teak and other imported tropical hardwoods during the war. Impreg was much lighter than teak, and the tear and splinter resistance of its surfaces were similar to those of teak (Stamm & Chidester, 1947; Stamm & Seborg, 1962). Rifle stocks made from solid Impreg were manufactured by Crane Creek
Company and were evaluated by the U.S. Marine Corps in 1960. Precision rifles require the stock to be highly dimensionally stable to perform well. Rifles with Impreg stocks had “outstanding [...] firing accuracy and consistency” (Dawson & Usher, 1962, pp. 5). However, the Impreg stocks were brittle, which made them susceptible to edge chipping, and unable to withstand impact of repeatedly firing heavier (0.30) caliber rounds according to Dawson and Usher (1962).

![Image of Impreg rifle stock](image)

Figure 2.7 – A small-bore rifle stock made from Impreg core and polyethylene glycol treated walnut faces (Dawson & Usher, 1962)

2.2.6.2 Compreg

Compreg is similar to Impreg in that veneer laminates are impregnated and chemically modified with PF resin. However, unlike impreg, PF resin in treated Compreg laminates are cured and simultaneously pressed into a panel during hot pressing (Champion, 1943). Compreg laminates, plasticized from heating of PF resin, are compressed in the hot press, producing a densified panel. Compreg has increased strength properties proportional to the degree of compression, and has greater toughness than Impreg (Stamm & Chidester, 1947). In comparison to impreg, Compreg is more resistant to decay and attack by termites and marine borers. It has greater moisture, acid, electrical, weather
resistance and dimensional stability and strength properties than Impreg (Weatherwax & Stamm, 1945; Stamm, 1946; Rowell & Youngs, 1981; Rowell, 1999).

2.2.6.2.1 Manufacture of Compreg

Manufacture of Compreg involves drying green veneers (Fig. 2.8). The dried veneers are impregnated with PF resin to obtain the desired weight gain. Impregnated veneers are kiln-dried under non-polymerizing temperatures, and glue is spread on the surfaces of the dried and impregnated veneers and they are left to air dry. Veneers have been dried to low moisture contents (10 – 12%) prior to phenolic resin modification (Anand, 1981). The veneers are then assembled and hot pressed to cure and compress the PF resin impregnated laminates. The resulting Compreg panel is cooled in the press prior to pressure release, according to Erickson and Faulkes (1949), Stamm and Seborg (1960), Anand (1981) and Rowell (1987).

Figure 2.8 – Commercial manufacture of Compreg: (a) green veneers are kiln-dried; (b) veneers are impregnated with PF resin; (c) veneers are kiln-dried at nonpolymerizing temperatures; (d) glue is spread on the surfaces of veneers; (e) veneers are assembled for hot pressing; (f) the assembled veneers are pressed at high temperature and pressure; (g) the Compreg panel is cooled in the hot press under pressure and then the pressure is released (illustration drawn from Stamm & Seborg, 1960)
Veneers used for the manufacture of Compreg were peeled from wood species, such as maple, yellow poplar (*Liriodendron tulipifera* L.), yellow birch (*Betula alleghaniensis* Britt.), American sweetgum and American beech (*Fagus grandifolia* Ehrh.) (Erickson & Faulkes, 1949; Stamm & Seborg, 1960). Veneers of white cedar (*Dysoxylum malabaricum* Bedd. Ex Hiem), Indian copal tree (*Vateria indica* L.) and gurjan (*Dipterocarpus C.F. Gaertn.*) have been used for the manufacture of a Compreg in India (Anand, 1981). European beech (*Fagus sylvatica* L.) veneers were used in Germany to manufacture a compressed PF resin impregnated laminate, known as Panzerholz or Kunstharzschichtholz (Küch & Adlershof, 1939; Thum & Jacobi, 1938). The thickness of veneers used for Compreg was typically between 0.5 mm and 2.0 mm (Stamm & Seborg, 1941; Stamm & Seborg, 1944; Anand, 1981). Veneers up to 2 mm thick were used to manufacture Compreg for structural applications, while thinner veneers up to 1 mm in thickness were used for panels for electrical insulation. Thicker veneers have been used in high strength applications.

According to Anand (1981), the type of phenolic resin used to make Compreg was determined by the end use of the Compreg as follows: (1) water-soluble caustic soda condensed PF resin was used to manufacture Compreg with excellent mechanical properties; (2) water-soluble high caustic soda condensed low molecular weight PF resin was used for moulding applications; (3) water-soluble low condensed PF resin catalyzed with sodium carbonate was used for chemical, or neutron shielding applications. In the latter case, PF-modified veneer was bonded with boron impregnated veneers; and (4) alcohol-soluble ammonia condensed phenol or cresol formaldehyde resin dissolved in industrial methylated spirit was used to manufacture Compreg for electrical insulation applications (Anand, 1981). Resin was applied to veneers using pressure, vacuum or dip impregnation methods. About 30% resin loadings produced Compreg with optimum dimensional stability. A resin loading of 10 – 20% was used where impact strength properties were important (Seborg et al., 1962).
Figure 2.9 has been removed due to copyright restrictions.


Figure 2.9 – Different types of Compreg lamination arrangements. Type 1: completely anisotropic arrangement; Type 2: reduced anisotropic arrangement; Type 3: homogeneous arrangement; Type 4: radial lamination arrangement; Type 5: circular ring arrangement. Arrows show fiber direction of veneer laminates

Compreg used different lamination arrangements, as shown in Figure 2.9. According to Anand (1981), type 1 contains veneers with fibers assembled parallel to the axis of stress. This arrangement was used for the manufacture of threaded and turning components (e.g. rods and sticks). Type 2 has veneers where the fiber orientation of over 70% of veneers is parallel to the axis of substantial stress; the fiber direction of the remaining veneers is perpendicular to the axis of substantial stress. Compreg made with this arrangement was used for tensile link applications (e.g. bolts and rivets). Type 3 contains veneers with the fiber direction perpendicular to the preceding veneer and there are equal numbers of veneers with the fiber direction parallel to the x and y planes. This arrangement was used for sheets and blocks of Compreg. Type 4 is a radial arrangement, where successive veneers are assembled at an angle to the preceding veneer about the center axis. This arrangement was used for Compreg employed in shear stress bearing components (e.g. chucks, gears and wheels). Type 5 contains veneers where fibers in veneers are
oriented at tangents to the ring lamination arrangement, and consecutive layers of veneers staggered in relation to the preceding layer. This arrangement was used in core clamping or pressure rings in electrical applications. Regardless of the lamination arrangement used, the assembled impregnated or coated laminates were hot pressed into Compreg without using additional adhesives. A high pressure hydraulic press was used to press Compreg laminates at 150 °C and 5.88 – 17.65 MPa of pressure for 15 minutes to 8 hours, depending on the thickness of the Compreg panel and the phenolic resin used, according to Anand (1981).

Compreg technology was improved during World War II, when metals, rubber and some tropical woods became scarce. To conserve these scarce materials, research was undertaken by U.S. and British Forest Products Laboratories and the Forest Products Division of the Commonwealth Scientific and Industrial Research Organization in Australia to develop substitutes made from wood (Stamm & Seborg, 1941; CSIRO, 1941b; Stamm & Chidester, 1947). According to Stamm and Seborg (1941), the U.S. Forest Products Lab developed Compreg that was superior to commercially available products. Green or kiln-dried veneers could be dip or pressure impregnated, respectively, in a process similar to that used to make impreg. Pressure at 0.20 – 0.39 MPa was applied in a galvanized iron treating cylinder to impregnate kiln-dried veneers up to 3.2 mm thick with PF resin (Stamm & Seborg, 1941; Erickson & Faulkes, 1949). A water-soluble alkaline PF resin, Bakelite Resinoid XR5995, was used to impregnate veneers to weight gains of 30 - 40%. The phenolic impregnated veneers were dried; and subsequently cured and formed into a panel by hot pressing the dried and impregnated veneers, at temperatures and pressures of 150 - 160 °C and 1.77 – 8.24 MPa, to thicknesses one-third to one-half of the original thickness of veneer lay-ups (Stamm & Seborg, 1941, 1944; 1960). Additional adhesives were not required to bond the phenolic impregnated veneers (Stamm & Seborg, 1941). Different types of Compreg were made, for example, ones with compressed-impregnated face veneers and an uncompressed-unmodified veneer core. This Compreg assembly had improved mechanical properties, moisture resistance, a gloss finish at the surface,
and at lower cost and weight compared to fully compressed and impregnated Compreg (Stamm & Seborg, 1941). However, the uncompressed-unmodified veneer core was still susceptible to moisture absorption and dimensional changes. This problem could be mitigated by using Impreg in the core. Compreg developed by the Forest Products Laboratory was more homogenous and less hygroscopic than commercial Compreg according to Stamm and Seborg, (1941, 1944) and Erickson and Faulkes (1949).

2.2.6.2.2 Properties of Compreg

Compreg had properties superior to those of Impreg (Rowell, 1999). Compreg had greater compression, shear and tensile strengths and toughness, improved dimensional stability and resistance to decay, termite attack and degradation by acids or alkalis (Stamm & Seborg, 1944; Erickson & Faulkes, 1949). Compreg also had greater hardness and resistance to abrasion (Rowell, 1999). Compreg compressed to specific gravities greater than 1 could be sanded and buffed to a high gloss finish without finishing (Stamm, 1946). It could also be molded into desired shapes using compression or expansion molding techniques, because the impregnated veneers were plasticized by the PF resin (Stamm & Seborg, 1941).

2.2.6.2.3 Applications of Compreg

Compreg was used as a high quality modified wood product that was manufactured to levels of accuracy and precision, in accord with customer’s product drawings (Anand, 1981). Consumption of Compreg was greatest during World War II when approximately 0.57 million kilograms was used. Compreg was manufactured in the United States, the Soviet Union and Australia (CSIRO, 1940b; Stamm & Chidester, 1947; Gurvich, 1957; Rowell, 1999). Compreg was used for stress bearing and non-stress bearing military aviation components, including connecting plates, bucket seats, radio antenna masts, fuselage, wing covers, spar plates, landing wheels, test club propellers and most notably, variable pitch propellers (Stamm & Seborg, 1941; 1944; Winslow, 1942; Champion, 1943; Stamm & Chidester, 1947; Rowell, 1999).
Compreg had sufficient shear strength to be used as hubs, airscrews, roots and blades of variable pitch propellers. The moldability of Compreg allowed propeller blades to be fabricated with varying specific gravities within the blades, as shown in Figure 2.11 and Figure 2.12 (Stamm & Seborg, 1941). The advantage of Compreg propellers over their duralumin or magnesium counterparts was their high strength to weight ratio; Compreg propellers for heavy aircraft engines could be 91 kilograms lighter than metal propellers. Such weight savings greatly increased payload and reduced centrifugal load, inertia and gyroscopic forces during the operation of the aircraft. Furthermore, damping of Compreg airscrews could reduce the effects of torque variations generated by engines, and smooth propeller movements (CSIRO, 1940a; 1941a; 1941b). United States Army Air Force produced Compreg propellers for training airplanes in 1942. The Soviet Air Force used Compreg produced from pine (*Pinus spp.*) veneers for the main construction of the LaGG-3 fighter aircraft, and spar flanges of the MiG-3 and YAK-9 fighter aircrafts (Gurvich, 1957; Stamm & Seborg, 1941; Gallay, 1990). Towards the end of the war, an experimental Compreg propeller developed in the US for the P-51 long-range fighter-bomber performed as well as its steel counterpart, while reducing the weight of the aircraft by approximately 45 kilograms. Over the
course of the war, a total of 10,000 - 12,000 Compreg propellers were manufactured in the US. In Australia, experimental Compreg truck wheels were developed using cresol-formaldehyde resin, a less expensive alternative to Bakelite PF resin, to extend the service life of truck wheels used on surfaces containing sharp debris, such as nails and wire cuttings (CSIRO, 1941c).

![Figure 2.11 - Images showing (a) assembly of laminates for a Compreg panel with variable specific gravity at both ends (Stamm & Seborg, 1944); (b) schematic diagrams of construction of a light weight propeller made from a laminated light wood core and Compreg root. Diagram: (top) shows a laminate consisting of a spruce board scarf jointed to a spliced Compreg panel; (middle) shows laminates glued together to form a block; (bottom) shows the block cut into a propeller blade and fitted with propeller components](image)

Figure 2.11b has been removed due to copyright restrictions.

Figure 2.12 – Images showing Compreg propellers made by Engineering and Research Corporation (ERCO). (a) variable pitch hardwood Compreg propeller blades attached to a 2D30 (10˚ and 15˚) hub; (b) Compreg blank blade; (c) threaded root of Compreg blank blade, where a steel ferrule would be attached (©Not Plane Jane, n.d.)

Compreg panels were used as insulators because of their low electrical conductivity, for applications, such as transformer components, switch operating rods and handles, instrument cases, terminal boards, radio housings, battery containers, pressure rings, coil and core clamping rings, lead and axial supports, platforms, lifting rods, bus bar supports and tension plates (CSIRO, 1940b; Anand, 1981). The US Navy used Compreg for electrical control housings of torpedo boats and other components requiring water resistance, low electrical conductivity and high strength (Winslow, 1942). The Australian textile industry began using Compreg in 1941, when the industry was faced with a shortage of imported hickory (Carya spp.) for picking sticks for looms. A Compreg picking stick was developed by CSIRO, and the technology was transferred to the US in 1944, when the US textile industry faced a similar shortage of picking sticks made from solid wood (CSIR, n.d.a). Other applications of Compreg in the textile industry included shuttles, shuttle pegs, broad and narrow loom picker arms, picking sticks, slays, box backs, side lever, race boards and bottom flanges (Anand, 1981).
Compreg was also used during WWII for bearing plates, teeth of mill wheels, gear wheels, pulleys, silent gears, water-lubricated bearings, nuts, bolts, bushes, bearing plates, joint bars used in railway tracks; a flooring substitute for chequered aluminum floor boards used in trains, trams, buses and boats; die forming, molds for light-metal casting, jigs, tool handles and experimental band saw guides developed to replace guides made of hardwood or brass; storage tanks, chemical storage containers, filter plates, filter frames, agitators, tap and neutron shielding material used in nuclear research (CSIRO, 1940b; CSIR, n.d.b; Stamm & Chidester, 1947; Anand, 1981; Rowell, 1999).

Following the war, Compreg continued to be used in some of the previously mentioned applications and it was also used for musical instruments and sporting goods (Seborg & Vallier, 1954; Rowell, 1999). Compreg sports goods included skies, hockey sticks and golf clubs (Anand, 1981). The cutlery industry was the largest consumer of Compreg. For example, approximately 0.45 – 0.68 million kilograms of Compreg handles were manufactured in 1955 alone (Gurvich, 1957).

2.2.6.3 Resin-modified paper overlays

Resin impregnated paper overlays were developed to improve the aesthetics, strength, and protect plywood or veneer surfaces (Rowell, 1999).

2.2.6.3.1 Structural paper overlays

High density overlays improve the strength, resistance to water absorption, face checking, abrasion, electrical insulation properties of composite panels at a relatively low cost (Higgins, 1948; Rowell 1999). The strength properties of paper overlays are dependent on the inherent strength of the paper (Rowell, 1999). Kraft paper has higher tear strength and dimensional stability than paper produced by acid sulfite pulping (Giertz, 1962; McKenzie & Higgins, 1960; Page & MacLeod, 1992). In comparison to competing materials such as fabric or glass fiber, paper is cheaper. Furthermore, paper impregnated with water-
soluble PF resin has improved compressive strength and resistance to water absorption and dimensional change. It is also cheaper than melamine or urea formaldehyde resin-impregnated paper (Malmstrom, 1951; Rowell, 1999). Water- or alcohol-soluble PF resins have both been used for structural paper overlays, but alcohol-soluble resins are preferred because they impart greater toughness to the overlay (Rowell, 1999). However, paper is less easily penetrated by alcohol-soluble PF resins than water-soluble PF resins, and as a result, overlays impregnated with the former resins have poorer resistance to water than overlays impregnated with water-soluble phenolic resin (Morris & Verdi, 1957; Rowell, 1999). Phenolic resin loadings in high density structural overlays have to be greater than 45% or 52%, for plywood used for industrial or concrete form applications, respectively (APA, 2012). Sheets of phenolic impregnated paper can be orientated across or parallel to plywood sheets. Plywood with parallel lamination of paper overlay was reported to have tensile strengths of 24 – 35 kg/mm² (Stamm and Chidester, 1947). Structural overlays have been extensively used for concrete formwork (Briggs & Tellman, 1999). Other applications of structural overlays include subfloors for buildings and floor assemblies in truck-trailers. Structural overlays on trailer floors provide slip and wear resistance for plywood (Fouquet, 1991; Ou, 2004).

A structural paper resin impregnated product, Papreg, was heavily used by the military during World War II. Papreg had equivalent strength to weight ratios as aluminum (Champion, 1943). Furthermore, Papreg did not tear or splinter during ballistic testing. Papreg, like Impreg and Compreg, was used as a substitute for aluminum and other light metals during WWII (Winslow, 1942; Champion, 1943). It was used for ammunition boxes, catwalks and flooring surfaces of cargo airplanes, and turrets and seats for airplane gunners (Stamm & Chidester, 1947). Attempts were made to produce structural components of aircraft using Papreg. However, Papreg is more brittle than aluminum, and therefore, it was not suitable for use with conventional aircraft fittings. However, an experimental vertical stabilizer for a training airplane was made from Papreg and performed satisfactorily (Stamm & Chidester, 1947). Other
experimental Papreg aircraft components that were tested included flight control surfaces, ribs of the skeletal frame of wings and skins of wing tips (Champion, 1943).

2.2.6.3.2 Masking paper overlay

Paper overlays in masking applications provide plywood, particleboard, waferboard, oriented strand board, solid wood or synthetic foam substrates with improved aesthetics and a better surface for finishing (Eggers & Madsen, 1979; Biblis, 1990; Rowell, 1999; Briggs & Tellman, 1999). They also act as moisture barriers, thus allowing the use of less expensive and lower grade veneers for plywood (Malmstrom, 1951; Briggs & Tellman, 1999; Ou, 2004). The paper used for masking overlays can be of low strength, as the paper has no structural purpose. Masking paper overlays for general or concrete form applications are impregnated with PF resin to minimum treatment weight gains of 27% or 34%, respectively (APA, 2012). Higher phenolic resin loadings provide better properties including a transparent finish, but at increased costs. Lower loadings result in decreased costs, but the overlays have inferior resistance to abrasion and scratching (Rowell, 1999). Masking overlays on plywood conceal physical defects, such as face checks, patches, raised grain; reduce resin and extractive exudation; restrict moisture-induced dimensional changes; resist surface denting, abrasion and chemical degradation; provide a desirable surface texture and a good surface suited for staining and painting (Malmstrom, 1951; Eggers & Madsen, 1979; Feist, 1982; Briggs & Tellman, 1999; Rowell, 1999). Likewise, PF resin impregnated overlays applied on solid wood masks defects, such as knots, coarse grain or surface roughness, provides a flat surface to improve paintability and increases dimensional stability (Fleischer & Heebink, 1964; Heebink, 1954; Heebink et al., 1955). Overlays protect solid wood against weathering and increase outdoor longevity of paint coatings applied on the overlay. Thus, resin-treated paper can upgrade low-grade lumber, according to Heebink (1955) and Fleischer and Heebink (1964).
During World War II, Douglas-fir plywood with masking overlays was used for table tops and storage lockers (Stamm & Chidester, 1947). Following the war, similar products were used for house siding, exterior doors, lining and siding of truck-trailers, cabin linings of airplanes, cabins, hulls and bulkhead of boats; and floors, ramps, containers, refrigerators, concrete forms for building construction and highway marker signs (Stamm & Chidester, 1947; Fleischer & Heebink, 1964; Eggers & Madsen, 1979; Louderback, 1992).

2.2.6.3.3 Decorative paper overlays

Decorative paper overlays are primarily used for indoor furniture or walls. They protect the substrate or provide a permanent finish. Decorative overlays can consist of PF resin impregnated kraft paper and a decorative layer of melamine formaldehyde (MF) resin impregnated paper (Rowell, 1999). Thin translucent sheets of MF resin paper overlay are hot pressed onto the PF impregnated paper and provide the overlay with resistance to chemicals, abrasion and heat. Such overlays are pressed on to plywood, particleboard or hardboard to finish the panel and provide moisture resistance (Morris & Verdi, 1957; Rowell, 1999). However, the decorative overlay and panel cores are still susceptible to moisture-induced dimensional changes. Dimensional changes in the overlay occur at a different rate to that of the wooden core, which results in cupping or bowing of panels. To solve this problem, overlays need to be pressed onto both sides of the panel to balance moisture-induced stresses (Burton & Spear, 1958; Heebink, 1960). Decorative paper overlays are used for tables, desks, vertical faces of walls, doors, cabinet doors and horizontal faces of floors and bowling lanes (Burton & Spear, 1958; Rowell, 1999).

2.2.6.4 Recent commercial applications of PF resin modified wood

Phenolic resin modified wood products are still being manufactured and are marketed as specialty products that take advantage of the properties of the resin and the modified wood substrate.
2.2.6.4.1 Wood panel products modified with PF resin

Impreg and Compreg are still being produced by Permali Deho Ltd in the UK, Dehonit®, Delignit®, Röchling in Germany, AGO Lignostone in The Netherlands and Pyon Sound in South Korea. Their applications are listed in Table 2.1.

Table 2.1 – Current commercial applications of Impreg and Compreg

<table>
<thead>
<tr>
<th>Type</th>
<th>Applications</th>
<th>Products</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impreg</td>
<td>Fire resistant paneling</td>
<td>Fire resistant ceiling, interior walls, panels and flooring</td>
<td>Delignit®, n.d.c, n.d.f</td>
</tr>
<tr>
<td>Compreg</td>
<td>Ballistic</td>
<td>Bullet, blast and fire-proof security panels</td>
<td>Delignit®, n.d.b</td>
</tr>
<tr>
<td>Compreg</td>
<td>Shielding</td>
<td>Neutron shielding in nuclear research, fuel shielding in fuel tanks</td>
<td>Dehonit®, n.d.; Permali Dehol Ltd., n.d.a</td>
</tr>
<tr>
<td>Compreg</td>
<td>Electrical and thermal insulation</td>
<td>Insulating components for transformers, such as pressure rings and fasteners; tank supports in liquefied natural gas (LNG) or liquefied petroleum gas (LPG) transport vessels</td>
<td>Delignit®, n.d.a; Röchling, n.d.a, n.d.b, n.d.d</td>
</tr>
<tr>
<td>Compreg</td>
<td>Engineering and manufacturing</td>
<td>Jigs, molds, fixtures, models and dies; wear strips, industrial flooring, conveyor belts, slider table supporting conveyor belts, skillet decking</td>
<td>Permali Dehol Ltd., n.d.c; Delignit® &amp; obo Automotive, n.d.; Delignit®, n.d.c</td>
</tr>
<tr>
<td>Compreg</td>
<td>Rail</td>
<td>Fishplates, shoe beams</td>
<td>Permali Dehol Ltd., n.d.c</td>
</tr>
<tr>
<td>Compreg</td>
<td>Sports</td>
<td>Gymnastics rings, billiard balls, hockey blades</td>
<td>AGO Lignostone, n.d.b; Delignit® &amp; obo Automotive, n.d.</td>
</tr>
<tr>
<td>Compreg</td>
<td>Audio</td>
<td>Tuning boards and rim panels of piano; arm tubes, headshells and tone-arms for turntables</td>
<td>Delignit® &amp; obo Automotive, n.d.; Delignit®, n.d.d; Mockingbird Distribution, n.d.</td>
</tr>
<tr>
<td>Compreg</td>
<td>Textile</td>
<td>Bobbins, picking sticks, spools</td>
<td>Delignit®, n.d.a</td>
</tr>
</tbody>
</table>

One unusual application of Compreg products (Panzerholz® bulletproof and Panzerholz® Protect 2.0) is as ballistic armor. Both products are resistant to bullets, explosive blast, splintering and fire, and provide “discreet and invisible protection” (Delignit®, n.d.b, p. 7). The Panzerholz® Protect 2.0 was introduced in 2012 and features steel face laminates for added ballistic resistance for military and civil applications (Delignit®, n.d.b; Esler, 2015). European beech veneers are used exclusively by all of the aforementioned companies, with the exception of Pyon Sound, who use 1 mm thick Finnish birch veneers
to produce Picawood® (Mockingbird Distribution, n.d.; Permali Dehol Ltd., n.d.b; Delignit®, n.d.e; Dehonit®, n.d.; Röchling, n.d.c; AGO Lignostone., n.d.a). An oil-based PF resin is applied between the birch veneers while the veneers are stacked with cross-laminate orientations. The veneer lay-ups are compressed to 35% of their original thickness using a hydraulic press and remain under compression for one week, while the PF resin cures. Picawood® has been developed for audio equipment and it is claimed to have resonance damping qualities superior to those of thicker laminates, such as Panzerholz® (Mockingbird Distribution, n.d.).

2.2.6.4.2 Solid wood products modified with PF resin

A PF resin-impregnated solid wood product has been commercialized by Kyushu Wood Industry Co. in Japan (Kyushu Wood Industry Co., n.d.a). The product, known as Eco Accord Wood, is made from Japanese cedar or cypress (*Chamaecyparis obtusa* (Siebold and Zucc.) Endl.) treated with a water-soluble low molecular weight PF resin (Kyushu Wood Industry Co., n.d.b; Uchikura, 2009). The manufacture of Eco Accord Wood takes up to 50 days, with the majority of time devoted to resin impregnation, curing and drying. Impregnation is designed to control the weight gain and penetration of PF resin into the wood (Uchikura, 2009).

Air-dried Japanese cedar or cypress is placed in a pressure cylinder and pressure (200 kPa) is applied for 20 minutes; PF resin refrigerated to 5 °C is then introduced into the cylinder and pressure in the cylinder is subsequently raised and held for 5 minutes at 400, 600 and 800 kPa; and pressure is finally raised to 1000 kPa and maintained for 20 minutes. Cedar posts impregnated with PF resin using this schedule have average treatment loadings of 360 kg/m³ and penetration of approximately 20 mm or more into sapwood. Lumber is air-dried for thirty to forty days and then kiln-dried at less than 100 °C for 2 days. The wood is then cured in a kiln at 130 °C for 1 day. Using this schedule, there is no exudation of PF resin or checking of the modified wood (Uchikura, 2009; Kyushu Wood Industry Co., n.d.c; Liu, 2011). The
modified cedar or cypress is dimensionally stable, and resistant to fungal decay, termite attack, checking and weathering, according to Kyushu Wood Industry Co. (n.d.d, n.d.e).

Unmodified Eco Accord Wood below the PF resin treatment envelope is susceptible to biodeterioration. However, post treatment of any exposed and unmodified wood with preservatives can be carried out (Kyushu Wood Industry Co., n.d.f). Eco Accord Wood is only available in Japan for outdoor recreational and landscaping applications, such as pergolas, gazebo, tables, benches, decking, gates, fences, monuments, wooden bridges, bollards and lanterns; building applications, such as sidings, curtain walls, louvers, porch columns, foundations, fences and guardrails; and cultural building components in shrines, castles and temples (Kyushu Wood Industry Co., n.d.e, n.d.g).

2.3 Furfurylated wood

Furfurylation also impregnates wood with a resin, although for this treatment, a renewable resin, fufuryl alcohol, is used (Lande et al., 2008; Homan & Jorissen, 2004). Furfuryl alcohol is a relatively small molecule, which can penetrate wood cell walls and polymerize by application of heat (Goldstein, 1955).

2.3.1 Polymerization of furfuryl alcohol

Furfuryl alcohol solution containing a cyclic anhydride as a catalyst is stable at room temperature. High temperatures cause polymerization of the furfuryl alcohol solution (Lande et al., 2004c). Two competing reactions occur during the initial polymerization stages of furfuryl alcohol resulting in the formation of linear polymeric products, as shown in Figure 2.13 (Dunlop & Peters, 1953).
A hydroxymethyl group on the furfuryl alcohol monomer condenses with another furfuryl alcohol monomer, forming a methylene bridge. A second condensation reaction results in the formation of an ether bond between two hydroxymethyl groups. The former reaction is favoured (Barr & Wallon, 1971; Maciel & Chuang, 1982; Chuang & Maciel, 1984). The ether bridge is unstable, and the intermediate product converts to a methylene bridge and loses formaldehyde (Chuang & Maciel, 1984). Cross-linking of linear polymeric products formed during initial furfuryl alcohol polymerization occurs between hydroxymethyl group of a furfuyl alcohol and a methylene bridge, as shown in Figure 2.14. Cross-linking is dominant, although formaldehyde formed from initial polymerization also participates as a cross-linking agent (Dunlop & Peters, 1953; Chuang & Maciel, 1984). The products of these cross-linking reactions are a polymeric network within wood cell walls (Venås et al., 2006).
2.3.2 Interaction of furfuryl alcohol with wood cell walls

There has been speculation about the possibility of chemical bonding between furfuryl alcohol and lignin because furfurylated wood is very dimensionally stable. Venås et al. (2006) found that furfuryl alcohol polymerizes within wood cell walls, but they did not find evidence of bonding between furfuryl alcohol and cell wall polymers. Thygesen et al. (2010) found high concentrations of polymerized furfuryl alcohol in middle lamellae and cell wall corners, which are both rich in lignin. Nordstierna et al. (2008) found furfuryl alcohol formed covalent bonds with model lignin compounds.

2.3.3 Properties of furfurylated wood

Furfurylated wood is hydrophobic, and accordingly contact angles of water droplets on furfurylated Scots pine were greater than those on untreated controls and greater on tangential surfaces compared to radial surfaces (Bastani et al., 2015). The lower contact angles on radial surface may have been the result of accumulation of by-products, such as a hygroscopic buffering salt, or unreacted furfuryl alcohol at treated surfaces (Englund et al., 2009; Bryne & Wålinder, 2010). Water uptake in tangential, radial and longitudinal directions is reduced as a result of furfurylation (Bastani et al., 2015). Moghaddam et al.
(2017) noted thickening of earlywood and latewood cell walls in furfurylated longleaf pine (*Pinus palustris* Mill.). Furfurylation also reduced cell wall porosity of southern yellow pine earlywood and Norway maple (*Acer platanoides* L.) latewood. The same authors found that furfurylation reduced water uptake of southern yellow pine and maple. Thygesen and Elder (2008; 2009) suggested that furfurylation of Norway spruce (*Picea abies* (L.) Karst.) caused bulking of cell walls, increased hydrophobicity of cell wall surfaces and sterically hindered water adsorption at available hydroxyl sites, which resulted in decreased relaxation times for bound water and increased relaxation times for free water in lumens. However, the authors found no evidence of cross-linking between furfuryl alcohol and lignin in the modified wood. Bound water relaxation times and the rate at which the relaxation times decreased in furfurylated and unmodified spruce were similar at moisture contents below fiber saturation point (Thygesen and Elder, 2009).

The dimensional stability, stiffness and hardness of furfurylated wood were positively correlated with treatment weight gains (Ryu et al., 1992; Lande et al., 2004b). Density and bending strength also increased with weight gain (Epmeier et al., 2007; Esteves et al., 2011). However, furfurylated wood, is brittle and has reduced impact strength (Westin et al., 2004; Homan & Jorissen, 2004). Furfurylated wood has low ecotoxicity and has less impact on the environment than preservative treated wood, according to De Vetter et al. (2008) and Pilgård et al. (2010). De Vetter et al. (2008) examined the ecotoxicity of furfurylated southern pine and sycamore maple (*Acer pseudoplatanus* L.), and found that leaching of chemical from furfurylated Scots pine was less than that from preservative (CCA, Cu-azole, Cu-amine, Cu-quat) treated pine. Unreacted leachable furfuryl alcohol levels in furfurylated wood are low and the ecotoxicity of furfurylated wood decreases with increases in polymerization of furfuryl alcohol (Lande et al., 2004a; De Vetter et al., 2009). Levels of volatile organic compounds or polyaromatic hydrocarbons released from combustion of furfurylated wood are lower than those released from unmodified wood (Lande et al., 2004a).
2.3.4 Commercialization of furfurylated wood

Furfurylated wood has been commercialized by the Norwegian company, Kebony ASA. Southern yellow pine, radiata pine (*Pinus radiata* D. Don), Scots pine and to a lesser extent, European beech, ash (*Fraxinus* spp.) or maple are impregnated with furfuryl alcohol using a full-cell process, followed by an intermediate drying step (Fig. 2.16) (Homan & Jorissen, 2004; Lande et al., 2008). The impregnated wood is cured using steam injection for 6 to 8 hours at temperatures of 80 °C to 140 °C. The cured furfurylated wood is kiln dried to remove volatile compounds and moisture prior to shipping (Homan & Jorissen, 2004; Lande et al., 2004b; Lande et al., 2008).

![Figure 2.15 – End uses of Kebony® for (a) outdoor decking and (b) outdoor cladding in Norway](image)

Furfurylation is being licensed to other companies and treated products are branded as VisorWood® or Kebony®. VisorWood competes with preservative treated wood (Lande et al., 2008). Scots
pine modified to WPGs of between 20% and 50% is known as VisorWood (Hill, 2006; Brynildsen & Myhre, 2007). VisorWood has a light brown colour and is mainly used for decking, cladding, roof boards, piers, jetties, window joinery, doors, poles, garden furniture and various building materials (Lande et al., 2008; Brynildsen & Myhre, 2007; Hill, 2006). Kebony® products include fully impregnated furfurylated maple, beech, ash, rubber wood (*Hevea brasiliensis* Müll. Arg.), southern pine and radiata pine. Kebony® is separated into two product lines, Kebony® 100 and Kebony® 30. Kebony® 100 is treated to high weight gains of 70 to 100%, and is a dark brown colour. Kebony® 100 competes with tropical hardwoods, such as Merbau (*Intsia spp.*) in flooring applications. Kebony® 30 is modified to lower WPGs of 10 to 30%, and is also marketed as an alternative to tropical hardwoods (Lande et al., 2008). Kebony® products are used in applications requiring dimensional stability, hardness and appearance, similar end uses to those of tropical timber. Applications of Kebony® include interior panels, floor boards, parquet flooring, decking, marine decking, cladding, garden furniture and decorative joinery (Fig. 2.15) (Hill, 2006; Brynildsen & Myhre, 2007; Lande et al., 2008).
Figure 2.16 – Manufacture of Kebony in a factory in Skien, Norway. (a) Kiln-dried radiata pine timber; (b) sorting of radiata pine timber; (c) loading of radiata pine timber in pressure treatment cylinder, which subsequently cures the furfuryl alcohol impregnated pine; (d) sorting of furfurylated radiata pine; (e) quality control of Kebony using an optical scanning; (f) sorting of Kebony; (g) stacking of Kebony for shipping; (h) Kebony packaged for shipment
2.4 Dimethylol dihydroxy ethylene urea (DMDHEU) resin modified wood

Dimethylol dihydroxy ethylene urea (DMDHEU) resin, as shown in Figure 2.17, was first used by the textile industry in the 1960s as a low formaldehyde releasing resin to increase wrinkle resistance of fabrics (Hatch & Maibach, 1995). DMDHEU resin is especially effective on cotton fabrics, which tend to wrinkle after washing. Wrinkling of cotton occurs when adsorbed water in amorphous cellulose causes slippage of hydrogen bonds (Tomasino, 1992; Bajaj, 2002). Hydrogen bonds reform at different locations causing wrinkling. Cellulose cross-linked with DMDHEU is more resistant to intermolecular bond slippage, and thus the treated cotton fabric is wrinkle resistant (Tomasino, 1992; Wei & Yang, 1999; Bajaj, 2002).

![Chemical structure of dimethylol dihydroxy ethylene urea (DMDHEU) monomer](image)

Figure 2.17 – Chemical structure of dimethylol dihydroxy ethylene urea (DMDHEU) monomer

2.4.1 Interaction of DMDHEU resin with wood cell walls

DMDHEU resin can be used to make wood more suitable for outdoor use. Wood modification using DMDHEU resin involves vacuum impregnation of the wood with aqueous DMDHEU and a catalyst; air drying and curing of the impregnated wood at 100 - 150 °C for 16 h (Van der Zee et al., 1998). The reaction mechanism of cell wall polymers with DMDHEU resin is not fully understood, although bulking of cell walls, cross-linking with hydroxyl groups and polymerization of the DMDHEU resin within cell wall voids could all be involved in the reaction of DMDHEU with wood (Yasuda et al., 1994; Van der Zee et al., 1998; Dieste et al., 2008).
2.4.2 Properties of DMDHEU resin modified wood

Wood modified with DMDHEU resin has increased dimensional stability and decay resistance due to its reduced hygroscopicity. However, the level of dimensional stability and decay resistance of DMDHEU modified wood is limited by the hygroscopicity of DMDHEU (Simonsen, 1998; Van der Zee et al., 1998; Dieste et al., 2008).

DMDHEU resin introduces additional hydroxyl groups into modified wood, and cured DMDHEU resin swells when these hydroxyl groups adsorb water (Van der Zee et al., 1998; Dieste et al., 2008). Krause et al. (2004) found that DMDHEU modification did not reduce the rate of water uptake of modified Scots pine sapwood, possibly because the resin interacted with water. The authors found the rate of swelling of DMDHEU modified pine was linearly correlated with the moisture content. When the moisture content of the modified wood rose above 15%, the rate of swelling of the modified pine decreased. Van der Zee et al. (1998) reported that DMDHEU treatment up to 20% WPG imparted anti-swelling efficiency (ASE) to Scots pine of up to 50%. Above 20% WPG, the effects of the treatment on dimensional stability were less pronounced. Excess DMDHEU resin in lumens adsorbed water and caused additional swelling. In accord with this finding, Nicholas and Williams (1987) found reductions in ASE in ponderosa pine modified with DMDHEU to weight gains above 20%. A maximum ASE of 50 - 60% for DMDHEU modified wood has been reported in multiple studies (Nicholas & Williams, 1987; Militz et al., 1993; Simonsen, 1998; Van der Zee et al., 1998).

Some drawbacks of DMDHEU resin wood modification include surface hardening, brittleness and tensile strength losses due to cellulose degradation associated with the use of the acidic catalyst, magnesium chloride (Xie et al., 2005; Xie et al., 2007; Brelid, 2013). Leaching of unreacted DMDHEU resin and formaldehyde emissions from DMDHEU modified wood are also of concern (Simonsen, 1998; Brelid, 2013).
2.4.3 Commercialization of DMDHEU resin modified wood

DMDHEU modified wood has been trademarked and marketed in Germany as Belmadur® by the BASF company (Hill, 2006; Militz, 2010; Brelid, 2013). Belmadur® has been used on a pilot scale for windows, decking, garden furniture and weatherproof molded beech wood products, but it is not produced commercially (Becker KG, 2005; Militz, 2010; Münchner Belmadur, n.d.). Currently, there is interest in the treatment in New Zealand, but it is not produced commercially (Derham et al., 2017).

2.5 Acetylated wood

Acetylation modifies wood by substituting hydrophilic hydroxyl groups in wood cell walls with acetyl groups. Commercial acetylation processes use acetic anhydride, as shown in Figure 2.18, to modify wood (Grattan & Matheson, 1922).

Figure 2.18 – Reaction of acetic anhydride with wood (reproduced from Jebrane et al., 2011)

2.5.1 Interaction of acetic anhydride with wood cell walls

Acetylation involves vacuum or pressure impregnation of wood with cold acetic anhydride. The impregnated wood is heated to 100 to 140 °C (Hill, 2006; Rowell, 2013). Acetic anhydride in cell walls reacts with cell wall hydroxyl groups (Fig. 2.18). An ester bond is formed between the less polar acetyl molecule and individual hydroxyl groups and acetic acid is produced as a by-product (Hill, 2006). Acetic acid and any unreacted acetic anhydride in the acetylated wood is removed following acetylation by applying a vacuum within the treatment cylinder (Hill, 2006; Rowell, 2013).
The reactivity of acetic anhydride with different cell wall polymers varies. Lignin is the most reactive polymer, followed by hemicellulose and cellulose, respectively (Rowell et al., 1994). Above weight gains of 15%, holocellulose reacts with acetic anhydride, but there is still incomplete acetylation of hydroxyl groups on lignin (Zhao et al., 1987; Ohkoshi & Kato, 1993, 1997a, b). Acetylation can cause minor depolymerisation of cellulose (Boonstra et al., 1996).

2.5.2 Properties of acetylated wood

Acetylation bulks wood cell walls, keeping them in a swollen state (Thygesen & Elder, 2008; 2009). Cell walls do not swell further, because hydroxyl sites are available for water sorption. Acetylated wood is also less hygroscopic than unmodified wood (Hill & Jones 1996; Hill, 2006). The first report demonstrating that acetylation reduced the swelling of wood is by Stamm and Tarkow (1947a). They acetylated 12.7 mm thick sugar maple, balsa (*Ochroma pyramidale* (Cav. Ex Lam.) Urb.) and Sitka spruce veneers with acetic anhydride and found that acetylation to 19.0, 19.2 and 26.1% weight gain imparted ASE of 70% to the acetylated veneers, respectively. Numerous studies have confirmed this finding. Stamm and Tarkow (1947b) reported that acetylation imparted ASE of 60% to 65% to 1.59 mm thick birch veneers. Tarkow et al. (1953) found that acetylation of 0.318 mm thick sitka spruce veneers to 30% weight gain imparted ASE of 81% to the veneers. Acetylation of solid wood was investigated by Goldstein et al. (1961). They found that ponderosa pine and southern yellow pine timber 2” (50.8 mm) x 6” (152.4 mm) x 48” (1219.2 mm) could be uniformly acetylated by pressure impregnation.

Improvements in dimensional stability of acetylated wood are proportional to weight gains, and bulking of cell walls by acetyl groups (Tarkow et al., 1953). Wood can be acetylated to weight gains of approximately 25% (Hill, 2006). Stamm and Tarkow (1947a) reported that ASE’s of acetylated sugar maple, balsa and Sitka spruce veneers were positively related to their WPG. Similar findings were reported by Rowell et al., (1986) and Tillman et al., (1987).
In addition to dimensional stability, acetylation improves the resistance of wood to biodeterioration. Southern yellow pine acetylated to weight gains of up to 17% was resistant to decay by the fungi, *Coniophora puteana* (Schum. Ex Fries) Karst., *Lentinus lepideus* (Fr.) Fr., *Poria incrassata* (Berk. and M.A. Curtis) Burt, *Lenzites trabea* (Pers.) Fr., *Polyporus versicolor* (L.) Fr. and *Poria monticola* (Murr.) (Goldstein et al., 1961). In ground contact bioassays, Scots pine sapwood acetylated to 20% WPG was resistant to both soft rot attack and brown rot decay (Brelid & Simonson, 1997; Brelid et al., 2000). Decay resistance of rubberwood (*Hevea brasiliensis* Muell. Arg.) flakeboards was increased when boards were made from flakes acetylated to 18% WPG (Hadi et al., 1995).

Acetylation increases the termite resistance of modified wood. However, even though the level of resistance to termite attack increases with weight gain, acetylated wood is still not immune from termite attack, according to Rowell et al. (1988). For example, aspen (*Populus sp.*) flakeboards acetylated to 17.6% WPG were still attacked by the subterranean termite, *Reticulitermes flavipes* Kollar, even though termite mortality was significant (Rowell et al., 1988). Similar findings were reported by Imamura and Nishimoto (1986). They observed weight losses of 6.9%, 6.7% and 4.2% in larch (*Larix leptolepis* Gord.) veneers acetylated to 7%, 12% and 20%, respectively, when veneers were exposed to *Coptotermes formosanus* (Shiraki).

Brelid and coworkers (2000) exposed acetylated Scots pine sapwood samples to two species of molluscan marine borers, *Teredo navalis* (L.) and *Psiloteredo megotara* (Hanley), and a crustacean marine borer, *Limnoria lignorum* (R.). The acetylated pine was attacked by the borers, but the attack was less severe in samples acetylated to higher weight gains.

One of the main disadvantages of acetylation using acetic anhydride is the production of acetic acid as a by-product of the esterification reaction. Acetic acid cannot be fully removed from acetylated wood,
and it imparts an unpleasant vinegar-like odour to wood. In addition, the acetic acid causes acidic hydrolysis of holocellulose and corrosion of metal fasteners (Rowell et al., 1994; Epmeier et al., 2004).

2.5.3 Commercialization of acetylated wood

Acetylation technology has been commercialized by Accsys Technologies PLC in London, U.K.. Two acetylated wood products have been developed, Accoya® and Tricoya®. The former is produced by acetylating plantation grown radiata pine or Scots pine, and is used for decking, cladding, structural components, windows and doors. Tricoya, is a medium density fibreboard made from acetylated solid wood. Tricoya is dimensional stable and resistant to fungal decay (Rowell, 2013; Accsys Group, 2016).

2.6 Thermally modified wood

Thermal modification enhances the properties of wood without the use of preservatives or chemicals. Instead, heat is used to change the chemical composition of wood cell walls (Militz 2002). Different thermal modification processes have been commercialized and these processes are shown in Figure 2.19. Wood can be heated in steam, oil or nitrogen. The use of oil or nitrogen heating media, restricts thermal oxidation of the wood. Depending on the process and heating medium, thermal modification involves first drying wood to low moisture contents, heating it to temperatures of 180 °C to 260 °C, and lastly conditioning the wood to lower its temperature and increase its moisture content to 4% to 7% (Hill, 2006).
In the first phase of the ThermoWood® process, green or kiln-dried wood is dried in a chamber using heat and steam. The temperature in the kiln is quickly ramped up to 100 °C, and from there, the temperature is slowly increased to 130 °C to dry the wood close to 0% moisture content (Fig. 2.20). The second phase is the thermal modification of wood. The temperature is increased to 185 °C or 215 °C for 2 and 3 hours, depending on the product, Thermo-S or Thermo-D. The third phase conditions the thermally modified wood by lowering the temperature in the kiln to 80 °C and 90 °C and the woods’ moisture content is increased to 4% to 7% using water spray, according to ITA (2003).

The Moldrup process differs from the ThermoWood process in that an autoclave is used to apply superheated steam and pressure to thermally modify the wood (Rowell et al., 2013). Steam heating in the
autoclave ramps the temperature up to 80 °C at atmospheric pressure. Vacuum is pulled for 1 h to remove oxygen from the wood, and the wood is then vacuum dried to a low moisture content. The wood is thermally modified by gradually increasing the temperature to between 160 °C and 205 °C. Vapor released from the wood increases pressure in the autoclave, which is regulated to between 800 kPa and 1000 kPa. Moisture content of the wood is reduced to 0 - 2% during modification. The wood is then conditioned, in a similar way to the Thermowood process. A final vacuum is pulled for 30 minutes to remove volatile compounds from the thermally modified wood, according to Rowell and coworkers (2013).

2.6.1 Chemical changes to wood cell walls from thermal modification

Hemicellulose is more susceptible to thermal degradation than cellulose or lignin and it is the most hygroscopic component of wood (Sivonen et al., 2002). When hemicelluloses are degraded, wood becomes less hygroscopic (Sivonen et al., 2002; Weiland & Guyonnet 2003). The amorphous regions of cellulose are also degraded by heat, again reducing the hygroscopicity of wood. However, crystalline cellulose is more resistant to thermal degradation at temperatures below 300 °C. The removal of more amorphous cell wall components during thermal modification results in an apparent increase in the crystallinity of cellulose (Tjeerdsma et al., 1998a; Kim et al., 2001). Thermal treatments also depolymerize lignin and open up reactive sites for cross-linking with other cell wall components, which restricts accessibility of hydroxyl groups to water molecules (Tjeerdsma et al., 1998a; Tjeerdsma & Militz 2005; Boonstra & Tjeerdsma 2006). Extractives in wood are degraded by heat and volatilize during the early stages of thermal modification. Migration of resin acids can create visible resinous spots at the surface of thermally modified wood (Nuopponen et al. 2003; Esteves et al., 2008; Mohareb et al. 2010).

2.6.2 Properties of thermally modified wood

Thermal modification darkens wood throughout its cross-section. Darkening is positively correlated with temperature and duration of thermal modification. Such colour change is attributed to the formation
of quinones and by-products from degradation of hemicellulose and extractives (Tjeerdsma et al., 1998a). The formation of furfural from the degradation of hemicelluloses imparts a distinctive odour to thermally modified wood. However, the odour is slowly lost when thermally modified wood is in service (Militz, 2002; Esteves & Pereira, 2009).

The properties of thermally modified wood depend on a variety of factors including wood species, duration and temperature of heating, moisture level or gas present in the heating atmosphere (Homan et al., 2000). Desirable properties of thermally modified wood include a uniform dark colour; reduced hygroscopicity and lower equilibrium moisture content; and increased durability and dimensional stability (Tjeerdsma et al., 1998a, 1998b; Bekhta & Niemz, 2003). However, thermally modified wood, is weaker than unmodified wood which limits its use in some structural applications (Esteves & Pereira, 2009). For example, thermally modified wood is brittle and has lower modulus of elasticity and modulus of rupture than unmodified wood (Bekhta & Niemz, 2003; Phuong et al., 2007; Shi et al., 2007).

2.6.3 Commercialization of thermally modified wood

There is increasing pressure on the wood protection industry to employ environmentally friendly processes and materials to produce high performance exterior wood products (Mayes, 2015). Of the wood modification processes reviewed here, thermal modification is the most commercially advanced and widespread, with an estimated annual production volume of 300,000 to 400,000 m³ across Europe (Militz, 2015). Processes for the manufacture of thermally modified wood include ThermoWood in Finland, Plato® in the Netherlands, Retification® in France, Le Bois Perdure® in Quebec, Canada, Menz Holz® in Germany and Royale, now Osmose Royale Process® where treatment with a copper-based preservative is combined with heat treatment using oil (Hill, 2006; Koppers Inc., n.d.). Manufacturers of ThermoWood and kilns for the production of ThermoWood are shown in Table 2.2. Sales of ThermoWood alone was 145,000 m³ in 2014, according to Tetri (2015). The market for ThermoWood in 2014 was 7% in Finland, 74% in the rest
of Europe and 19% in other countries worldwide (Tetri, 2015). Pine and spruce are the most common softwood species used for the production of ThermoWood, and in 2014, they each accounted for 46% of production, whereas birch and aspen only accounted for 1% of production (Tetri, 2015).

Table 2.2 – ThermoWood manufacturers and ThermoWood kiln producers. Hill (2006) and Tetri (2015)

<table>
<thead>
<tr>
<th>Thermowood manufacturer</th>
<th>Thermowood kiln producer</th>
<th>Country of origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetsäWood</td>
<td>Jartek Oy</td>
<td>Finland</td>
</tr>
<tr>
<td>Lunawood®</td>
<td>Stella Oy</td>
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<tr>
<td>SWM-Wood Oy</td>
<td>Tekmaheat Oy</td>
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<tr>
<td>HJT-Holz Oy</td>
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<td>SLM Oy</td>
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<td>Heinolan Ruskopuu Oy</td>
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<td>Sahakuutio Oy</td>
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<tr>
<td>Heatwood</td>
<td>Valutec AB</td>
<td>Sweden</td>
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<td>Novawood</td>
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<td>Turkey</td>
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<td>Koshii &amp; Co Ltd.</td>
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<td>Japan</td>
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2.7 Waterborne wood preservatives

Since the voluntary withdrawal of chromated copper arsenate (CCA) from residential use in the U.S. in 2004, CCA has been replaced by water-based preservatives containing copper and an organic co-biocide, for example copper azole (CA), alkaline copper quat (ACQ) and micronized copper (MC) (Freeman et al., 2005; McIntyre et al., 2007; Matsunaga et al., 2009). In CA and ACQ, copper is dissolved in ammonia or another amine, such as an organic amine, monoethanolamine (Freeman & McIntyre, 2008). Ammonia-based systems are used for the treatment of refractory species, such as Douglas fir (Evans, 2003; Groenier & Lebow, 2006; Lebow, 2010).

2.7.1 Copper azole (CA) preservatives

Copper azole consists of a copper compound which provides fungal and insect resistance, and organic or inorganic co-biocides to control copper-tolerant fungi (Freeman et al., 2005; Groenier & Lebow,
Wood treated with CA is brown to green in colour (Groenier & Lebow, 2006; Freeman & McIntyre, 2008; Lebow, 2010). The first CA formulations, CBA-A, contained 49% copper, 49% boric acid and 2% tebuconazole. Boric acid is absent from CA-B, which consists of 96% copper and 4% tebuconazole (Fig. 2.21) (Groenier & Lebow, 2006; Freeman et al., 2005). Another CA formulation contains propiconazole and tebuconazole as organic biocides (Buschhaus & Valcke, 1995). Propiconazole and tebuconazole are part of the triazole group of fungicides (Buchenauer, 1987). Propiconazole protects wood from both stain and decay fungi, and tebuconazole provides additional protection against decay fungi according to Buschhaus and Valcke (1995). The CA-C formulation contains 49% copper, 2% propiconazole and 2% tebuconazole (Freeman & McIntyre, 2008). Copper azole preservatives are produced by Lonza Wood Protection group and are sold using the trade name, Tanalith® E.

![Chemical structures of (a) tebuconazole and (b) propiconazole](image)

Figure 2.21 – Chemical structures of (a) tebuconazole and (b) propiconazole

2.7.2 Alkaline copper quat (ACQ) preservative system

ACQ preservatives contain 67% copper oxide and 33% quaternary ammonium compound (quat) as a co-biocide (Fig. 2.22) (Lebow, 2004; Groenier & Lebow, 2006; Freeman & McIntyre, 2008; Lebow 2010). Three standard ACQ formulations are available, ACQ types B, C and D. The most popular formulations are ACQ-D and ACQ-C, which are typically used to treat pine (McIntyre et al., 2007). ACQ-D can contain ammonia or an amine, or a combination of the two. ACQ-D contains didecyldimethylammoniumchloride...
(DDAC) as a co-biocide (Freeman & McIntyre, 2008; Lebow, 2010). Wood treated with ACQ-D does not smell and is light brown in colour (Lebow, 2004; Groenier & Lebow, 2006; Freeman & McIntyre, 2008). The second most popular formulation, ACQ-C, contains ammonia or an amine but DDAC is replaced by alkylbenzyldimethylammoniumchloride (ADBAC) (Lebow, 2004; Groenier & Lebow, 2006; McIntyre et al., 2007; Lebow, 2010). Wood treated with ACQ-C is a light brown to dark green brown in colour (Freeman & McIntyre, 2008). ACQ-B contains copper, ammonia and DDAC, and is used to treat refractory species like Douglas-fir (McIntyre et al., 2007; Lebow, 2010). Woods treated with ACQ-B are dark green-brown in colour and smell of ammonia (Lebow, 2004; Groenier & Lebow, 2006; Freeman & McIntyre, 2008).

![Chemical structures](image)

Figure 2.22 – Chemical structures of (a) quaternary ammonium compound, where R is an organic radical group, (b) didecyldimethylammoniumchloride and (c) alkylbenzyldimethylammoniumchloride

2.7.3 Micronized copper preservative system

Micronized copper formulations contain particles of copper carbonate and azole or quats (Lebow, 2010; Xue et al., 2013). Copper particulates, 1 nm - 25 µm in size, are milled from copper carbonate and dispersed in water (Evans et al., 2008; Schultz & Nicholas, 2011; Xue et al., 2013). Micronized copper was initially formulated with a quat (MCQ) (Schultz & Nicholas, 2012). However, the use of micronized copper quat is limited to permeable pine species (Lebow, 2010). MCQ has largely been replaced by micronized copper azole (MCA) (Schultz & Nicholas, 2012). Woods treated with MCA or MCQ are light green in colour.
Micronized copper is less evenly distributed in treated wood, than ionic systems according to Zahora (2010). For example, copper particles accumulate within the surface layer of treated wood and there is little penetration of particles into wood cell walls (Evans et al., 2008; Matsunaga et al., 2009). However, elemental copper can be detected in cell walls of wood treated with a micronized wood preservative (Matsunaga et al., 2009).

2.7.4 Metal-free preservative systems

Environmental concerns about the leaching of metals from treated wood and the disposal of metal-treated wood have encouraged the development of water-based metal-free preservative systems containing organic fungicides (Evans, 2003; Schultz et al., 2007; Wong & Chin, 2016; Reinprecht, 2016).

A water-based metal-free preservative formulation, known as Wolman® AG, which only contains organic compounds was developed in 2006 (Arch Wood Protection Inc., 2016a). The Wolman® AG formulation in the U.S. consists of 5% tebuconazole and 5% propiconazole, 0.5% imidacloprid (insecticide) and other non-biocidal components (U.S. EPA, 2011). Imidacloprid is not registered in Canada, and a quaternary amine compound is used instead (Lonza Wood Protection, 2017). Wood treated with Wolman® AG is branded as Wolmanized® EraWood® lumber (Lonza Wood Protection Inc., 2017). Wolmanized woods are resistant to decay and termite attack (Fox, 2007). Additionally, stabilizers, coloured pigments or water repellants can be incorporated into the preservative to enhance the weathering resistance of the treated wood (Fox, 2007; Arch Wood Protection Inc., 2016b). Wolmanized wood has better gluing and machining properties, and is less corrosive than wood treated with copper preservatives according to Fox (2007). The treated wood can be finished with paint or stain, like wood treated with copper-based preservatives (Arch Wood Protection Inc., 2016b). Wolmanized woods are restricted to above ground uses including millwork, fencing, decking and furniture (Fox, 2007). Another metal-free preservative formulation, Tanalith M, was also developed by Arch Wood Protection. It consists
of <0.4% tebuconazole, <1.2% propiconazole and <0.13% permethrin (Arch Timber Protection, 2010). Timber treated with Tanalith M is branded as Tanalised Clear (Arch Timber Protection, 2011).

A water-repellant and organic only preservative, Ecolife™, has been developed and commercialized by Viance LLC. Woods impregnated with Ecolife™ have improved dimensional stability and resistance to weathering and attack by fungi and termites. The preservative is resistant to leaching and the treatment imparts water repellency to the treated wood for up to 3 years of weathering (Viance LLC, 2016). Wood treated with Ecolife™ is restricted to above ground applications. The treated wood may be used outdoors without a finish for uses such as decking, fencing, gazebos and structural framing, or with a finish for siding, trim and millwork. Ecolife™ treated woods can also be used in damp or dry interior end-uses, according to Viance LLC (2016).

2.8 Weathering of chemically modified wood

The weathering of chemically modified wood has been reviewed by Evans (2009; 2013), Williams (2005) and Rowell (2014). This section updates these reviews and focuses on new publications on the weathering of modified woods. I focus in particular on the deleterious effects of weathering on the aesthetics of modified woods.

2.8.1 Weathering of PF resin modified wood

Modification with LMW PF resin reduces the permeability of wood and increases its dimensional stability, as mentioned above. As a result, the susceptibility of wood to cupping and surface checking is reduced (Cheng & Evans, 2012; Sudiyani et al., 1996; 1999; Kielmann & Mai, 2016b). For example, Cheng and Evans (2012) found that modification of white spruce (Picea glauca (Moench) Voss) deck boards with PF resin to a WPG of 15.5% reduced the number, length and width of surface checks and also the cupping of boards exposed outdoors for 24 weeks (Fig. 2.23). Kielmann and Mai (2016b) found that PF-modified
beech samples developed fewer checks after 32 months of natural weathering than untreated controls. However, according Sudiyani et al. (1996), PF resin modification of Japanese cedar to WPG of 10% to 20% did not reduce the checking of samples exposed outdoors to 1 year of natural weathering.

PF modification reduces the photodegradation of wood according to Sudiyani et al. (1999) and Evans et al. (2013). For example, Evans et al. (2013), found that PF resin treatment restricted the distortions of tracheids in yellow cedar (C. nootkatensis) samples exposed to 1070 hours of artificial weathering. However, separation of secondary cell wall from the middle lamella, and formation of cell wall micro-cracks at the corners of wood cells occurred (Evans et al., 2013). Degradation of thin walled earlywood tracheids was greater than that of latewood. The corners of PF-modified earlywood cell walls developed micro-checks, which were absent from latewood cell walls. Some photostabilization of lignin as a result of PF resin modification of wood has been reported. Such effect is more pronounced in samples treated with higher concentrations of PF resin (Evans et al., 2013; Kielmann & Mai, 2016a). Improved photoprotection of cellulose is also evident when wood is treated with higher concentrations (20% or

Figure 2.23 – Images of white spruce deck boards (a) untreated and (b) treated with 10% low molecular weight PF resin exposed to 24 weeks of natural weathering. Scale bar is 60 mm ((c)Cheng and Evans, 2012)
30% of PF resin. However, the photoprotective effects of PF resin on lignin are only temporary, according to Evans et al. (2013).

Modification with PF resin restricts discolouration of wood during weathering, possibly because phenol formaldehyde resin absorbs UV radiation (Tarkow et al., 1966; Sudiyani et al., 1999). However, according to Kol’tsov et al. (1985) the photostabilizing effects of PF resin modification are not long-lasting, because of the susceptibility of PF resin to photodegradation by UV light. Photodegradation of PF resin results in colour changes at modified wood surfaces and colonization of the surface by dark coloured staining fungi (Kielmann & Mai, 2016a, 2016b). Evans and coworkers (2013) also found that PF resin modified wood changed colour and became darker, redder and yellower. This darkening and increase in redness of the weathered surfaces was more pronounced when wood was treated with higher concentrations of PF resin (20% or 30%). However, the addition of the lignin stabilizer, Lignostab, to PF resin reduced the discolouration of PF resin treated wood (Evans et al., 2013). Kielmann et al. (2017) found that beech treated with PF resin containing 0.15% ferric salt or 1.5% tannin was a dark brown colour. These additives enhanced the colour stability of treated wood when it was exposed to 672 hours of artificial weathering in a QUV weatherometer.

PF resin modification enhances the outdoor performance of clear coatings on wood. For example, Tarkow and coworkers (1966) reported that polyurethane and polyacrylate (latex) clear coatings performed well on PF-modified pine boards exposed to accelerated weathering. The boards were envelope treated to 6% weight gain, clear coated and exposed to 8 weeks of artificial accelerated weathering in an Atlas weatherometer. The PF treatment restricted checking and bleaching of the clear coatings. The PF treatment was unable to prevent the polyurethane coatings from becoming brittle, but it reduced loss of gloss of the polyacrylate (latex) coatings. Black and Mraz (1974) found that surface pretreatment of redwood and western red cedar (T. plicata) panels with two coats of PF resin (28.5%
solids) helped to prevent degradation of a long oil-aromatic polyurethane varnish and silicone resin clear coating on panels when they were exposed to 3 years of natural weathering. Evans et al. (2016) observed that acrylic, alkyd and spar varnishes were still performing well on PF-modified radiata pine panels after 4 years of outdoor exposure. Clear coatings were performing particularly well on panels that had been modified with 30% PF resin to high weight gains of 52.9%.

2.8.2 Weathering of furfurylated wood

Furfurylation imparts some photostability to modified wood according to Temiz and coworkers (2007) and Rüther and Jelle (2013). Mantanis and Lykidis (2015) exposed furfurylated maple and pine decking exposed for 3 years and observed that modified decking only developed mild cupping. Mild surface checking occurred at the surface of furfurylated maple. Furfurylated radiata pine had numerous small checks that were distributed across the decking, but a longer and wider check developed near the centre of deck boards. In comparison, surface checking of furfurylated southern yellow pine was more severe, but the width of the checks was less than 1 mm. Fungal staining was absent from the surface of furfurylated decking. Photo-induced discolouration of furfurylated decking was initially rapid, but rate of discolouration decreased with increasing exposure. Discolouration was less than that of similarly exposed Ipê (Handroanthus spp.) deck, according to Mantanis and Lykidis (2015). In contrast, rapid discolouration of furfurylated wood during weathering was noted by Temiz et al. (2007), Lahtela and Kärki (2015), and Rüther and Jelle (2013). According to Temiz and coworkers (2007), the poor colour stability of furfurylated wood is related to its inability to protect lignin and hemicellulose from photodegradation, and restrict leaching of degradation products from exposed wood surfaces. Figure 2.24 shows the discolouration of furfurylated decking exposed to natural weathering. The colour of the weathered modified wood surface turned to an even grey.
Figure 2.24 – Images showing (a) greying of weathered walkway made from Kebony® decking and (b) greying and surface checking of weathered Kebony® deckboards

2.8.3 Weathering of DMDHEU resin modified wood

Modification of wood with DMDHEU resin provides limited photoprotection to wood, but it increases the resistance of wood to surface checking (Sudiyani et al., 1999; Xie et al., 2008). However, resistance to checking is not positively correlated with WPG due to modification. For example, Sudiyani and coworkers (1996) found the checking resistance of Japanese cedar samples modified with DMDHEU and exposed to natural or artificial weathering was not increased when the WPG of samples was increased from 12.5% to 22.6%. Furthermore, weight losses of samples were positively correlated with WPG,
possibly due to leaching of chemical from modified wood surfaces. DMDHEU only provided short-term photostability to lignin, hemicellulose and cellulose according to Xie et al. (2005). Photodegradation of lignin, resulting in increased formation of carbonyl groups was more pronounced in wood modified with DMDHEU, according to Pfeffer et al. (2012). Wood modified with DMDHEU resin weathers to a light brown colour, and then to a uniform dark grey colour due to colonization of wood surfaces by staining fungi. However, the DMDHEU resin reduced the penetration of hyphae from sapstain fungi into wood via pits according to Pfeffer et al. (2012). Adamopoulos et al. (2011) found that DMDHEU modification restricted growth of blue stain fungi hyphae in samples that were stained or painted with water-borne finishes.

2.8.4 Weathering of acetylated wood

Acetylation reduces checking at modified wood surfaces during weathering (Sudiyani et al., 1999). Checks formed at the surface of acetylated wood during weathering are small and dispersed across the surface, in contrast to the large checks that develop at unmodified wood surfaces (Akhtari, 2011). Chan and Evans (2016) found that acetylation restricted widths of checks that developed at the surface of Scots pine deck boards exposed to accelerated check testing. Acetylation also reduced the variation in check widths. Acetylation restrict photoyellowing of wood during weathering (Sudiyani et al., 1999; Mitsui & Tolvaj, 2005). Surface photodiscolouration of acetylated wood is initially rapid, but thereafter the colour is more stable (Hung et al., 2012; Lahtela & Kärki, 2015). According to Mitsui (2010) and Hung et al. (2012), acetylation does not prevent photodegradation of lignin, a conclusion that accords with findings of Evans et al. (2000). Acetylation provides some resistance against surface staining fungi, and this beneficial effect of acetylation increases with the level of acetylation (Gobakken et al., 2011; Hung et al., 2012).

2.8.5 Weathering of thermally modified wood

Thermal modification does not photostabilize wood, although its effects on the weathering resistance of wood varies with wood species (Huang et al., 2012a, b; Tomak et al., 2014; Altgen & Militz,
2016). For example, Tomak et al. (2014) exposed thermally modified iroko (*Chlorophora excels* (Welw.) Benth.), European ash (*Fraxinus excelsior* L.), Oriental spruce (*Picea orientalis* L.) and Scots pine to two years of natural weathering. They found that thermally modified softwoods developed larger checks than hardwoods. Thermally modified iroko, oriental spruce and Scots pine became rougher after weathering, whereas this effect was not observed in modified ash. Thermally modified wood is hydrophobic, but this effect of thermal modification is soon lost when wood is exposed to natural weathering. For example, Huang et al. (2012b) found that contact angles of water droplets on thermally modified jack pine was similar to that of unmodified controls after samples were exposed 1500 hours of artificial weathering.

Thermal modification does not reduce photodiscolouration of wood surfaces or prevent colonization of wood surfaces by staining fungi (Jämsä et al., 2000; Huang et al., 2012b). During outdoor exposure, thermal modified woods darken initially. Leaching of photodegraded fragments occurs and wood surfaces become grey after 6 months exposure to natural weathering (Jämsä et al., 2000; Tomak et al., 2014). According to Huang et al. (2012b), thermally modified wood lightened and became less red and yellow during artificial weathering. The lightness, redness and yellowness of thermally modified woods were similar to those of unmodified woods after 1500 hours of artificial weathering (Huang et al., 2012b). Thermally modified woods are initially darker than unmodified wood and they weather to the same extent as unmodified wood. Therefore, the overall colour change of thermally modified wood during weathering is greater than that of unmodified woods (Huang et al., 2012b; Srinivas & Pandey, 2012).

The inability of thermal treatments to reduce colour changes in modified wood exposed to weathering is clearly related to its inability to photostabilize lignin (Srinivas & Pandey, 2012; Huang et al., 2012a; Yildiz et al., 2013). Thermal modification does not prevent lignin in hardwoods or softwoods from photodegradation (Yildiz et al., 2013; Altgen & Militz, 2016). Yildiz et al. (2013) noted significant loss of lignin at the surface of thermally modified Scots pine, Oriental spruce, iroko and ash subjected to 400
hours of artificial weathering. Furthermore, lignin was photodegraded more rapidly in thermally modified jack pine than lignin in unmodified controls (Huang et al., 2012b). Photodegradation of lignin results in the formation of yellow compounds, such as quinones, which discolor modified and unmodified wood (Deka et al., 2008; Srinivas & Pandey, 2012; Tomak et al., 2014). However, according to Huang et al. (2012b), the formation of these compounds varies with wood species. Loss of extractives during thermal modification may also contribute to the poor color stability of the wood, because extractives in wood can act as antioxidants (Huang et al., 2012b).

Photodegradation of middle lamellae and micro-checking of cell walls and bordered pits occurs when thermally modified wood is exposed to artificial weathering (Huang et al., 2012b). Cells delaminated as a result of degradation of middle lamellae and transverse micro-cracks (perpendicular to fibre axis) developed at pit apertures. Photodegradation of secondary cell walls in thermally modified wood was more severe than that in unmodified cell walls. Ray cells were also completely degraded after 336 hours of artificial weathering. Huang et al. (2012b) observed large numbers of small longitudinal (parallel to fibre axis) and transverse micro-cracks in cell walls at tangential surfaces. Earlywood and latewood cell walls photodegraded differently at radial surfaces. Large longitudinal micro-cracks separated earlywood and latewood. Many earlywood cells delaminated, and numerous diagonal micro-checks developed. However, transverse micro-cracks were absent. In contrast, diagonal micro-checks were absent in photodegraded latewood cells, but large transverse micro-cracks formed as a result of photodegradation of ray cells, according to Huang et al. (2012b).

2.9 Weathering of preservative-treated wood

The weathering of preservative-treated woods has been described by Evans (2003) and Freeman and McIntyre (2008), although, as mentioned in the introduction to this chapter, far less has been written
about the weathering of preservative-treated wood than untreated wood. The following section focuses on recent findings on the effects of weathering on preservative treated woods.

2.9.1 Weathering of copper containing preservative-treated wood

As mentioned in the review by Evans (2013), treatment of wood with CA or ACQ increases photostability of treated wood (Liu et al., 1994; Cornfield et al., 1994). Copper in CA and ACQ forms complexes with woods’ chemical components and these complexes increase the photostability of the treated wood (Grelier et al., 2000; Temiz et al., 2005).

Cornfield and coworkers (1994) assessed the outdoor performance of CA-treated Scots pine. The treatment protected lignin from photodegradation in samples exposed outdoors for 1 month. After 6 months of exposure, checking of cell walls, damage to crossfield and bordered pits and fine checking at lumen surface were observed. Some fungal staining was evident in wood treated to a low retention with CA. Fungi were observed along longitudinal tracheids and in ray parenchyma at and below exposed surfaces. Colour of the CA-treated pine changed from its initial green colour to brown after 15 months of outdoor exposure (Cornfield et al., 1994).

Ammoniacal copper quat can also photostabilize treated wood according to Liu and coworkers (1994). They found that a 2% ACQ treatment reduced delignification of southern pine exposed to 35 days of natural weathering. Both Liu et al. (1994) and Temiz et al. (2005) found that ACQ restricted discolouration of wood exposed to natural or artificial weathering, respectively.

The weathering performance of CCA, ACQ-C and CA-B treated wood was compared by Nejad and Cooper (2011). Treated wood was more photostable and resistant to fungal decay than untreated wood. ACQ-C and CA-B were more effective than CCA at restricting photodiscolouration, although CA-B was less effective than CCA at inhibiting fungal staining. None of the treatments reduced checking at wood surfaces.
Morris et al. (2017) compared weathering resistance of CA-B and ACQ-D treated jack pine, Pacific silver fir (Abies amabilis (Dougl.) Forb.) and white spruce deck boards exposed to ten years of natural weathering. The performance of decking treated with CA-B or ACQ-D was not significantly different. Temiz et al. (2005) compared the performance of Scots pine treated with CCA, ACQ or CA and exposed to 600 hours of artificial weathering. Copper azole reduced photodiscolouration of treated Scots pine, but it was less effective than CCA and ACQ.

Ozgenc and Yildiz (2016) recently examined outdoor performance of Oriental spruce sapwood treated with micronized copper quat (MCQ). The MCQ treatment only provided slight colour stability and resistance to erosion when samples were exposed to 15 months of natural weathering. In accord with these findings, Zhang and Ziobro (2013) noted that woods treated with copper-based preservatives all eventually discoloured from green to dark grey when they were exposed to the weather.

Copper-based preservatives can enhance outdoor performance of wood coatings in addition to their ability to restrict surface photodegradation of wood. For example, Baysal et al. (2013) found that a CA-treatment improved colour and gloss retention of a polyurethane varnish on Scots pine exposed to 500 hours of accelerated weathering. Similar improvements in the performance of a polyurethane coating on CA-treated wood were observed by Turkoglu et al. (2015) when coated samples were exposed to 6 months of natural weathering.

2.9.2 Weathering of wood treated with metal-free preservatives

Metal-free organic preservatives are less effective at photostabilizing wood compared to metal-based preservatives (Schauwecker et al., 2009; Zhang & Ziobro, 2013). Wood treated with metal-free preservatives rapidly greys like untreated wood when it is exposed outdoors (Zhang & Ziobro, 2013). However, the weathering resistance of wood treated with metal-free preservatives can be improved by
using additives, such as pigments, UV absorbers and hydrophobes (Shauwecker et al., 2009; Zhang & Ziobro, 2013).

2.10 Surface protection of modified and treated wood

As I have pointed out in this review, the surface of chemically modified or preservative treated woods is still susceptible to the damaging effects of weathering. The following section reviews envelope treatments that can enhance the weathering resistance of modified or treated woods.

2.10.1 Film-forming finishes

Film-forming finishes form a physical barrier at wood surfaces and restrict the ingress of moisture into wood (Feist, 1983). Various types of film-forming finishes are available, including clear or semi-transparent coating, high build stains and opaque paints. Clear coatings are transparent and allow transmission of light through the coating (Feist, 1983). The other finishes contain pigments that block UV light from reaching the wood substrate. However, they mask the natural appearance of the wood substrate depending on their degree of pigmentation (Feist, 1983; Feist & Mraz, 1980a). However, all coatings are susceptible to the deleterious effects of weathering. Moisture ingress through paint films or via joints and end grain causes shrinkage and swelling of the wood substrate, which can result in cracking of paint especially when it loses flexibility, as shown in Figure 2.25 (Williams et al., 1997; Forest Products Laboratory [FPL] 1966b, 1966c). When coatings lack pigments or UV absorbers, UV light degrades the underlying wood substrate, and the coating fails by delamination at the wood-clear coat interface (Cassens & Feist, 1991).
2.10.2 Penetrating finishes

Penetrating stains allow wood's attractive appearance to be seen, while providing protection to finished wood surfaces (Feist and Mraz, 1980a). Penetrating finishes can be an effective alternative to film-forming finishes, according to Feist and Mraz (1980a). Because they lack a physical film, penetrating finishes do not flake, crack or delaminate, which all compromise the performance of paints and clear coatings (Black et al., 1979). Ideally, penetrating finishes should erode during weathering, reducing their maintenance requirements when the finished wood needs to be refinished (Hill, 1973; Feist & Mraz, 1978, 1980a, 1980b). Penetrating finishes that contain water repellants slow the deleterious effects of weathering by controlling the rate of moisture gain and loss from finished wood. As a result, dimensional changes at wood surfaces are reduced when wood is finished with water repellants, (Banks, 1973). Most importantly, the water absorbed within the finished wood is free to evaporate, lowering the moisture...
content of the wood and reducing its susceptibility to decay (Hill, 1973; Feist & Mraz, 1980a; Feist 1992; Williams & Feist, 1999). Application of penetrating finishes is simple and inexpensive (Feist & Mraz, 1980a), and their maintenance is simpler than that of film-forming finishes, because the finish can be applied directly to new or weathered wood surfaces (Black et al., 1979; Feist, 1992). Penetrating finishes perform particularly well at protecting rough and horizontal wood surfaces, such as decks, railings and stairs. There are two main categories of penetrating finishes: 1) transparent clear systems and 2) semi-transparent (pigmented) systems (Feist & Mraz, 1980a).

2.10.2.1 Transparent water-repellent penetrating finishes

Transparent clear finishes are the most translucent of penetrating finishes, and the natural attractive appearance of wood is retained when they are used to finish wood (Feist and Mraz, 1980a).

2.10.2.1.1 Water repellants

Water repellants (WR) are a type of transparent clear finish. They are composed of paraffin wax (hydrophobe), resin or drying oil (binder), and mineral spirit or turpentine (solvent). Water repellants make wood hydrophobic, increasing dimensional stability of wood and reducing its susceptibility to checking during natural weathering (FPL 1966a, 1966d, 1966e; Banks, 1973; Feist & Mraz, 1978; Morrell, 2002). However, health and environmental concerns around the use of organic solvents have led to the development of water- or oil-based formulations that have lower levels of volatile organic compounds (VOC) (Williams & Feist, 1999; Morrell et al., 2001; Morrell, 2002). Rainguard® Plugger 25™ is an example of a water-based WR formulation that contains modified silicone acrylic to provide water repellency (Rainguard International, 2015). Thompsons’s® Water-Seal® Advanced Clear Multi-Surface Waterproofer is a low VOC oil-based WR, consisting of paraffin wax (1 - 3%, w/w) and coconut oil diethanolamide (0.1 - 0.3%, w/w) dissolved in a medium aliphatic hydrocarbon solvent (The Thompson’s Company, 2015).
Regular resealing of a finished deck with WR is important to protect wooden decks from weathering and fungal colonization (Morrell, 2002).

2.10.2.1.2 Water repellant preservatives

Water repellant preservatives (WRP) are another type of transparent clear finish. The composition of WRP is similar to that of WR, except WRP's contain a preservative that provides fungal resistance to the finished wood. Pentachlorophenol (PCP) or copper naphthenate have been added to WR to create WRP (Feist, 1984). They impart a golden tan or brown and green colour, respectively, to wood, but they reduce the transparency of the finish (Feist & Mraz, 1980a; Williams & Feist, 1999). Less toxic WRP formulations have also been developed due to health and environmental concerns around the use of PCP (FPL, 1987; Williams & Feist, 1999). Newer biocides used in transparent and semi-transparent penetrating finishes are azoles, copper or zinc naphthenate, 4,5-dichloro-2-octyl-4-isothiazolin-3-one (DCOIT), dichlofluanid or tolylfluanid, N-(trichloromethyl) thiophalimide and iodopropynyl butylcarbamate (IPBC). The main insecticides used in WRP are bifenthrin, cyfluthrin, cypermethrin and permethrin (pyrethroid class), fipronil (phenyl pyrazole family), imidacloprid (neonicotinoid class) or boron (Biocide Information Limited, 2017; Freeman, 2008; Williams & Feist, 1999; Schultz & Nicholas, 2004). Biocide combinations of IPBC and propiconazole or IPBC, propiconazole and thiabendazole are effective at restricting the growth of surface staining fungi, such as A. pullulans and E. nigrum (Link) (Stirling et al., 2011). WoodRx® Clear Water-repellent is an example of a contemporary water based-WRP finish. A proprietary silicone technology and IPBC (1 – 5%, w/w) are used to provide the finished wood with resistance to water and mildew (Inseco Inc., 2009; Inseco Inc., 2016). An example of an oil-based WRP is Olympic WaterGuard® for Wood Waterproofing Sealant Clear, which consists of a proprietary alkyd resin (1 – 5%, w/w) and chlorothalonil (<1%, w/w) (PPG Industries Inc., 2018a).
WRs or WRPs can enhance the performance of wood coatings used outdoors, because they increase the dimensional stability and fungal resistance of wood (FPL, 1966a, 1966d, 1966e, 1972; Feist & Mraz, 1978). As a result, moisture induced stresses are restricted, and coatings show improved adhesion and resistance to cracking or delamination (FPL, 1966e; Black & Mraz, 1974; Feist & Mraz, 1978; Williams & Feist, 1999). WRPs used as primers for paints have lower concentrations of wax than WRP used as a stand-alone finish (Williams & Feist, 1999). Paints on siding pretreated with WRP weather uniformly and there is little delamination of the coating after 5 years of outdoor exposure, according to Feist and Mraz (1978). Coatings on window frame and sashes that were pretreated with WRP did not peel after 5 years of weathering, even at joints between rails and stiles (Feist & Mraz, 1978). White cypress pine \((\text{Callitris sp.})\) and brush box \((\text{Lophostemon confertus} \ (\text{R.BR.})\) Peter G. Wilson and J.T. Waterh.\) decking finished with a WRP containing zinc naphthenate and two subsequent coats of oil-base stain performed well after 5.5 years of natural weathering in Brisbane, Australia, and almost no decay or significant change in the appearance of the decks were observed (Cause & Stringer, 1993). The WRP and stain finish, however, was less effective than an oil-based primer and two top coats of acrylic decking paint at restricting surface checking of white cypress pine decking. However, white cypress pine decking finished with WRP and stain was still more decay resistant than decking coated with acrylic paint. The preservative in the WRP provided decay resistance, even though checks in the decks had exposed untreated sapwood to water (Cause & Stringer, 1993). Not all commercial WR and WRP products can be used as primer due to their formulations. Differentiating between a transparent primer and a stand-alone finish can be difficult because these products are often vaguely labeled by the manufacturer. Generally, those that are labeled as a “sealer” or “sealant” are formulated for use as a primer.
Alternatively, WRP can be used as a stand-alone clear exterior finish that does not alter the natural and attractive appearance of wood. Water-repellants, as their name suggests, repel water at the finished wood surfaces (Feist & Mraz, 1978). As a result, WRs increase the dimensional stability of wood (as mentioned above), and reduce extractive and iron staining (Feist & Mraz, 1978; Williams & Feist, 1999). However, water-repellants are not recommended as a stand-alone finish, unless they contain a preservative. WRP products can contain copper- or zinc- naphthenate preservatives at concentrations of up to up to 15% (w/w). In comparison, products marketed as WR contain 0.5 – 2% (w/w) preservatives and mildewcides (Biocide Information Limited, 2017). Transparent penetrating finishes can also contain photoprotective additives, such as UV absorbers, hindered amine light stabilizers (HALS) or pigments (Morrell et al., 2001; Feist & Mraz, 1980a). WRP containing pigments are sold as toners, as mentioned above, and their colours can resemble those of western red cedar or redwood. An example of a toner is Waterguard® Wood Tinted Waterproofing Sealant Toner from Olympic®, which contains a proprietary alkyd resin (1% - 5%, w/w) and chlorothalonil (<1%, w/w) (PPG Industries Inc., 2018b). The companies that dominate the market for transparent, semi-transparent and water-repellent preservative finishes include Behr®, Flood®, Olympic® and Thompson’s®, followed by Cabot®, Cuprinol® and Wolman® according to Biocide Information Limited (2017) and Freedonia Group (2017). A window unit dipped in a WRP containing high water repellent concentrations lasted more than 30 years when used outdoors (Williams & Feist, 1999). In contrast, water-based WR or water- or oil-based WRP applied on western red cedar and Douglas-fir decks required refinishing after 12 months of natural weathering. Water repellency of most oil-based WRP coatings was lost within 12 months, and was inferior to that of water-based formulations. However, the mildew resistance of oil-based WRPs (21 months) was superior to that of water-based WRPs (Morrell et al., 2001).
2.10.2.2 Semi-transparent (pigmented) finishes

Semi-transparent finishes contain more pigment than toners and as a result, they obscure wood
surfaces to a greater extent than toners or fully transparent finishes. However, the higher concentrations
of pigments in semi-transparent finishes provide better weather resistance to finished surfaces (Black et
al., 1979; Feist & Mraz, 1980a).

2.10.2.2.1 Semi-transparent stains

Semi-transparent penetrating stains contain pigments suspended in an organic solvent. Water-
repellents and preservatives are included in such stains (Black et al., 1979; Knaebe, 2013). They are longer
lasting than WRP and provide greater weather resistance to finished wood than WRP (Feist & Mraz,
1980a). DIY semi-transparent stains can have preservative and mildewcide concentrations of 0.5 – 2%
(w/w) according to Biocide Information Limited (2017). ‘Major suppliers’ of wood stains to the North
American market are Akzo, Behr, Benjamin Moore, PPG, Samuel Cabot and Sherwin-Williams-Valspar
(Biocide Information Limited, 2017, pp. 22). The ‘second-tier suppliers’ include Flood, Thompson and
Wolman according to Biocide Information Limited (2017, pp. 22).

Semi-transparent penetrating stains can impart a uniform colour to the finished wood and reduce
photodegradation, because the pigments block UV radiation from reaching wood surfaces (Feist, 1983;
Feist, 1992). The U.S. Forest Products Laboratory developed an oil-based penetrating stain that consisted
of boiled linseed oil, paint thinner, paraffin wax, pentachlorophenol, zinc stearate and pigments, including
burnt sienna, raw umber or red iron oxide (Black et al., 1979). The composition of the penetrating stain
could be adjusted to suit particular end uses. For example, increased preservative concentrations
enhanced the outdoor performance of the finish; or increased concentrations of hydrophobes improved
water-repellency and durability of the stain (Black et al., 1979). The colour of the stain could be varied
from charcoal black, smoky gray, chocolate brown, fruitwood brown, tan, green gold through to forest green by changing the type and ratio of pigments in the stain (Black et al., 1979). Some of the colours matched those of common deck woods, such as Philippine mahogany (Shorea spp.), western red cedar and redwood (Black et al., 1979; Feist, 1992). Greater colour saturation and improved outdoor performance could be achieved by increasing the concentration of pigment in the stain, at the expense of reduced transparency of the finish (Sell & Leukens, 1971; Black et al., 1979). Traditional pigments used in stains are obtained from minerals. Smaller, nano-sized pigments can be manufactured by grinding iron oxides or titanium dioxide. These pigments are more expensive than traditional pigments but they can remain suspended in a stain for longer than traditional pigments (Knaebe, 2013). Trans- or iron-oxide and titanium dioxide pigments, along with long-oil alkyds, tung oil and natural linseed oil, IPBC and aliphatic petroleum distallate, are used in Australian Timber Oil produced by Cabot® (The Valspar Corporation, 2015; Cabot, 2015).

Penetrating stains can be applied to smooth or rough wood surfaces, but stains perform better when applied to rough surfaces, either weathered surfaces or unweathered coarsely sanded or rough sawn wood (Arnold et al., 1992; Feist 1992; Williams et al., 2005; Knaebe, 2013). The performance of penetrating finishes depends on solids content of the finish and presence of UV stabilizers in the finish (Morrell et al., 2001; Williams et al., 2005). During weathering of stained wood surfaces, the stain is slowly eroded from the wood. Discolouration of the finish by extractives or mould indicates that refinishing should occur (Black et al., 1979). Oil-based semi-transparent stains with solids contents ranging from 36.4 – 67.1% lasted 1 – 2 years on western red cedar and Douglas fir before refinishing was needed (Morrell et al., 2001). An oil-based semi-transparent stain containing 77.7% solids on smooth-planed and rough-sawn western juniper (Juniperus occidentalis Hook.) timber exposed outdoors lasted 1 and 5 years, respectively (Williams, et al., 2005). Oil-based semi-transparent (76% solids) or solid-colour (60% solids) stains (2 coats) lasted approximately 5 - 6 years outdoors when applied to sweetgum and yellow-poplar plywood.
(Williams & Feist, 2004). Both semi-transparent and solid-colour stains perform better on saw-textured surfaces than on smooth-sanded ones. Checking of finished smooth-sanded plywood exposed to the weather for 1 year was much more severe than on similarly exposed and finished saw-textured surfaces. The semi-transparent stain still remained on rough-sawn surfaces after 12 years of weathering, whereas the stains’ life on smooth sanded plywood was only 5 – 6 years (Williams & Feist, 2004).

2.10.2.2.2 Latex-base stains

Latex-base stains are water-based semi-transparent finishes. They do not penetrate the wood substrate, unlike oil-base stains, and as a result they are susceptible to flaking or peeling (Knaebe, 2013; U.S. General Services Administration, 2016). An example of a latex-base stain is Semi-Transparent 100% Acrylic Stain WeatherOne® from Cloverdale Paint Inc. It contains 0.4% IPBC as a biocide (Cloverdale Paint Inc., 2017). Reductions in the amount of latex resin and addition of raw linseed oil to latex-base stains increase penetration of the stain into wood surfaces, according to Williams et al. (1999). An example of a hybrid stain is Wolman™ DuraStain® One Coat Semi-Transparent Stain. It contains alkyd and acrylic resins, ethylene glycol, 2,2,4-trimethyl-1,3-pentanediol isobutyrate and quartz and titanium dioxide pigments (Rust-Oleum Corp., 2016; 2017). Two coats of latex-base semi-transparent (25% solids) stain or solid-colour (45% solids) stain lasted 5 – 6 years outdoors on sweetgum and yellow poplar plywood. Thereafter, the stain flaked and required refinishing. A latex-base semi-transparent stain was less effective than an oil-base stain at restricting checking of face ply when finished plywood was exposed to natural weathering (Williams & Feist, 2004). Rough-sawn western juniper timber finished with two coats of a latex-base solid-colour stain with 46.6% solids performed well after 6 years of natural weathering, whereas the same finish on smooth-planed juniper timber failed after 5 years of exposure (Williams et al., 2005).
2.10.2.2.3 Waterborne inorganic salts

Waterborne inorganic salts have been tested as a semi-transparent finishes in the laboratory and in the field. The treated surfaces are coloured by the particular inorganic salt in the formulation (Feist & Mraz, 1980a). Inorganic compounds containing chromium and copper ions, such as copper chromate or chromated copper arsenate, provide wood with resistance to decay and photodegradation. Chromium VI compounds in particular confer UV resistance to treated wood surfaces (Black & Mraz, 1974; Feist, 1980a; Hon & Chang, 1985; Evans et al., 1992). Hence, they can be used as photoprotective primers beneath clear coatings. For example, white pine (*Pinus strobus* L.) became brown when treated with ammoniacal copper chromate. This colour was unchanged when the pretreated wood was coated with a silicone clear coat and exposed outdoors for 5 years (Black & Mraz, 1974). The outdoor performance of other coatings was also enhanced when inorganic salts were used as primers (Black & Mraz, 1974). For example, latex- and oil-base stains lasted almost twice as long on wood exposed outdoors when it was pretreated with acid copper chromate. Extractive staining of latex paints on western red cedar and redwood was restricted by priming the wood using copper and chromate salt solutions. Growth of surface staining fungi on a linseed oil-base paint on wood exposed outdoors for 7.5 years was also inhibited by a primer containing chromium and copper.

There has been limited commercial exploitation of inorganic salts for exterior wood finishing, with two exceptions: (1) use of iron sulphate as a stain to give wood a weathered grey appearance (European Wood, n.d.); (2) commercial use in Japan of chromic acid as a photoprotective primer for clear coatings (Ohtani, 1987). Iron III compounds provide partial photoprotection to treated wood surfaces, and they have been used commercially. Pandey and Pitman (2002) found that treatment of rubberwood with 5% ferric chloride increased its resistance to mould when the wood was exposed outdoors for 1 year. Hon and Chang (1985) found that ferric chloride could complex with lignin and cellulose, but Evans and
Schmalzl (1989) found that the treatment accelerated photodegradation of lignin and cellulose at treated wood surfaces exposed to natural weathering. Marian and Wissing (1960a, 1960b) found that ferric ions on their own oxidize cellulose, causing tensile strength losses in wood veneers. However, oxidizing reactions initiated by ferric ions can be stopped by antioxidants, such as phenols (Marian & Wissing, 1960c).

2.11 Envelope treatment of wood

Water repellants, water repellant preservatives and penetrating stains can be applied to wood surfaces using dipping or brushing. Dipping is preferred to brushing as the wood is more thoroughly coated with finish (Feist & Mraz, 1978). Uniform staining and penetration of wood by semi-transparent stains, however, can be achieved with brushing. Spraying is not recommended, because over-spray can contaminate the environment (Black et al., 1979). Brushing or dipping are both used to finish wood with water-borne solutions of inorganic compounds (Black & Mraz, 1974; Feist, 1979). Finishing with chromium III compounds requires additional heating of the finished wood at 135 °C for 10 minutes to fix chromium ions (Feist, 1979). Such heating is not required with chromium VI compounds, such as chromic acid (Schmalzl et al., 1995). The initial colouration of wood finished with inorganic solutions may be uneven, but the colour becomes more even when the wood is exposed to weathering or is refinished (Feist & Mraz, 1980a).

Penetrating finishes protect wood from weathering, until the finish erodes and the protective effects wears off, as mentioned above (Hill, 1973; Black et al., 1979). Feist and Mraz (1980a) observed that WR and WRP finishes on smooth Douglas-fir, redwood and western red cedar siding lasted 2 to 3 years outdoors, but similar finishes on Douglas-fir and western red cedar decking lasted only approximately 1 year (Morrell et al., 2001). The first coating of pigmented penetrating stains on wood and hardboard siding can last about 2 to 3 years according to Black and coworkers (1979), and Feist and Mraz
(1980b). Pigmented stains, however, have a shorter (2 year) life on Douglas fir and western red cedar decking (Morrell et al., 2001).

Penetrating finishes on rough and weathered wood surfaces perform better with increased finish loading according to Feist and Mraz (1978), Black et al. (1979) and Feist and Mraz (1980a). However, Arnold and coworkers (1992) found little effect of higher finish loadings on the service life of semi-transparent oil-base stains. Furthermore, they did not recommend finishing weathered wood with semi-transparent stains because of increased costs resulting from the high absorption of stain by weathered wood. Similarly, Morrell et al. (2001) found that the longevity of commercial WR, WRP and penetrating stains was not affected by the volume of finish applied to the wood, but depended on the level of solids and pigments retained at the finished surface following evaporation of solvent. However, application of higher levels of WRP on wood can have negative effects, such as greater susceptibility of the finish to delaminate, collect dirt and become slippery (Morrell, 2002).

2.11.1 Envelope treatment of thermally modified wood with water-repellants

Preservative and wood modification treatments are designed to improve the dimensional stability and resistance of wood to decay and insect attack. The treated or modified wood is still susceptible to photodegradation, although some treatments can reduce the rate of photodegradation (Zahora, 1992; Freeman & McIntyre, 2008; Evans, 2009). Therefore, modified or preservative-treated wood is sometimes given an envelope treatment to improve its resistance to weathering.

Elustondo et al. (2017) treated thermally modified Scots pine sapwood with water, rapeseed oil or rapeseed oil methyl esters. Boards were pre-heated at 20 °C, 90 °C, 120 °C or 150 °C for 4 hours and submerged in the oil at 20 °C. Alternatively, boards were submerged in oil at room temperature, compressed by 6 mm in thickness for 10 seconds, and the compressed board was submerged in oil for an
additional 3 minutes. The uptake of oil or water increased with increasing impregnation temperature, as expected. Pine boards impregnated with water developed internal checking, which increased their internal volume, leading to greater water uptakes (x1.8) compared to boards treated with oils. Boards treated with the heating-and-cooling and compression-and-expansion impregnation techniques absorbed similar levels of oil or water. However, one drawback of the compression-and-expansion technique was that impregnated boards only recovered half of their compressed thickness during impregnation, and it was suggested that undesirable spring back could occur during service, according to Elustondo et al. (2017).

Ahmed and Morén (2012) and Ahmed et al. (2013a) examined surface treatment of thermally modified Scots pine and Norway spruce with water-repellents. Samples were treated at 170 °C for 1 hour, and submerged in either a modified water-based preservative containing tert-butylhydroquinone and modified linseed oil, or a solution of linseed oil turpentine and commercial pine tar (Ahmed and Morén, 2012; Ahmed et al., 2013a). Heated samples absorbed more preservative as expected (Ahmed & Morén, 2012). Scots pine was more susceptible to thermal degradation than spruce. Collapse of cell walls in rays, complete or partial opening of bordered pits both created additional voids that increased preservative absorption by pine (Ahmed et al., 2013a). Collapse in spruce may have accounted for its lower preservative uptake compared to pine (in addition to its lower permeability) (Ahmed et al., 2013a). Preservative uptake was higher in latewood than in earlywood, but the preservatives gradually diffused from latewood into earlywood (Ahmed et al., 2013a).

Ahmed et al. (2013b) used the same treatments to treat larger thermally modified aspen and white birch (*Betula pubescens* Ehrh.) samples. Contrary to their earlier findings, thermally modified aspen and birch absorbed less preservative than the untreated controls. Ahmed et al. (2013b) suggested that anatomical changes resulting from thermal modification such as shrinkage-induced cell wall fractures, or
collapse of ray parenchyma from thinning of cell walls and buckling of vessels reduced preservative uptake. They also suggested that chemical changes to cell wall constituents may have contributed to reduced uptake of preservative.

2.11.2 Impregnation of wood with wood preservatives containing water-repellant additives

Wood can be treated with preservatives that contain wax and/or oil. The treatment is not an envelope treatment, but the wax or oil forms a protective envelope at the surface of the wood. This envelope increases the hydrophobicity of wood, reduces the rate of absorption of water and increases the dimensional stability of treated woods (Banks, 1973; Zahora, 1992; Evans et al., 2009). Wood samples treated with preservatives containing wax or oil emulsion additives also check less when they are exposed outdoors (Borgin & Corbett, 1970; Zahora, 1992; Evans et al., 2009). However, waxes and oils can be leached from treated wood, as they are not chemically bonded to wood cell walls (Banks, 1973). Leaching of water-repellants from wood has adverse effects on the performance of wood. For example, Zahora (2000) reported that approximately 50% of the hydrophobicity at the surface of CCA-wax treated southern yellow pine was lost after 3 years of natural weathering. After 9 years of weathering, about 80-90% of the hydrophobicity was lost. Loss of hydrophobicity occurred within the upper 6 mm of the treated pine boards. However, CCA wax treated boards still checked less after 9 years of weathering than the untreated controls (CCA, or untreated boards).

In comparison to wax emulsion additives, oil emulsions are more mobile. The oil in the treated wood may migrate to the surface of the treated wood and maintain the surface hydrophobicity during weathering (Evans et al., 2009). Evans et al. (2009), came to this conclusion after observing that swelling and water absorption of CCA and oil treated radiata pine boards decreased after a year of outdoor exposure, while those of CCA and wax treated pine boards increased. Additional applications of brush-on
water-repellent treatments can help protect surfaces of treated woods from the adverse effects of weathering (Zahora, 2000, 2002).

2.11.3 Chemical modification of wood surfaces

The following section reviews surface chemical modifications designed to enhance the surface qualities of modified woods.

2.11.3.1 Envelope modification of thermally modified wood with thermosetting resin

Militz and coworkers (2013) patented a method of producing a substitute for teak used for marine decking. Their method combined thermal modification with an impregnation treatment containing aqueous melamine formaldehyde (MF) resin. Thermal modification reduces the hygroscopicity and increases dimensional stability and durability of wood and made it browner. MF resin impregnation improved the resistance of the wood to checking and increased the hardness and dimensional stability of the treated wood. Permeable softwood or hardwood species such as pine (Pinus spp.), alder (Alnus spp.), birch, beech (Fagus spp.) and maple were modified using one of three methods: (1) wood was impregnated with an aqueous MF resin without catalyst, cured using steam, and then thermally modified; (2) MF resin modification and subsequent thermal modification was done continuously without a cooling step; (3) thermally modified wood was impregnated with MF resin and cured using steam (Militz et al., 2013). According to Militz et al. (2013), the MF resin solution did not contain catalyst or other additives. Concentrations of the MF resin solution were 5, 10, 15, 20, 25, 30, 35 or 40%, and the resin was partially or fully impregnated into wood using vacuum alone or vacuum and pressure at 800 to 1400 kPa. Steam curing of the resin impregnated wood occurred at temperatures of 90 °C to 120 °C. Volatile organic compounds such as formaldehyde that were released during curing of MF resin were removed during the steaming process. Thermal modification of the wood used the hydrothermal (Plato) or retification processes. The former involved heating wood to temperatures of 180 °C to 240 °C in water vapor for 24
to 48 hours, 4 to 24 hours or 6 hours. Retification involved heating wood to temperatures or 160 °C to 250 °C in a nitrogen atmosphere for 0.5 to 4 hours (Militz et al., 2013).

Giebeler and Willhem (1987) combined wood impregnation with thermosetting monomeric chemicals, thermal pressure and a vibration treatment to improve dimensional stability and acoustic properties of inexpensive woods to the level of woods used for musical instruments. Woods, such as poplar, pine or spruce, at 2% to 5% moisture content were impregnated with aldehydes, such as formaldehyde, acetaldehyde or ketones, reactive compounds, including phenol, urea, melamine or furfuryl, or combinations of both types of chemicals. Wood was soaked in an aqueous solution or treated in the gaseous phase. The impregnated wood was thermally modified at temperatures of 140 °C to 200 °C under 300 to 1500 kPa of pressure and 16 to 4 000 Hz of vibration for 0.5 to 8 h. Giebeler and Willhelm (1987) claimed that the hygroscopic hemicelluloses were hydrolyzed during thermal modification, and the resulting acidic by-products catalyzed condensation of the thermosetting resin in wood cell walls. The modified wood was claimed to have increased dimensional stability, enhanced clarity and reduced dampening of sound. Furthermore, the acoustic properties of the modified wood was unaffected by changes in humidity or weather, according to Giebeler and Willhelm (1987).

2.11.3.2 Envelope treatment of modified wood

Fadl and Basta (2005) examined the effect of an envelope treatment with PF resin or linseed oil on the moisture resistance of acetylated spruce and okoume (Aucoumea klaineana Pierre). Acetylated wood was vacuum impregnated with 5%, 10% or 15% alcoholic solutions of novolac PF resin or boiled linseed oil, and cured at 100 °C for 1 h. The PF resin or linseed oil treatment improved the ASE of the acetylated wood, but the dual-treated wood had a lower ASE than wood simply impregnated with PF resin or linseed oil. The uptake of linseed oil and PF resin was greater for acetylated wood, with the exception of
acetylated spruce impregnated with 15% PF resin. Fadl and Basta (2005) reported that increases in curing
temperature and time further improved the ASE of the acetylated or impregnated wood.

Balfas and Evans (1994) combined chemical modification and sanding to improve dimensional
stability and glue-bond strength of karri (*Eucalyptus diversicolor* F. Muell.) and jarrah (*Eucalyptus
marginata* ex Sm.) laminates exposed to artificial weathering. Surface modification of modified laminates
involved sanding wood with an 80 grit sand paper and using sodium hydroxide to improve adhesive
wettability and adhesive-wood bond strengths, respectively (Balfas & Evans, 1994). Laminates were
acetylated using 25% acetic anhydride in xylene or furfurylated using a furfuryl alcohol (98%) and zinc
chloride (1%) as a catalyst. Surface modification on its own reduced delamination of jarrah laminates
during accelerated weathering. The combination of surface modification and chemical modification
significantly reduced the delamination of laminates and improved their dry and wet bond strengths.

2.11.4 Mechanical modification of surfaces

Alexander (1958) developed a physical treatment, known as "Microseal", which enhanced wood
surface properties using high speed pressure rubbing. A cork belt made contact with a wood surface, and
the heat generated from rubbing plasticized the surface. The duration of contact and pressure between
the wood and belt controlled the level of gloss and surface densification of the wood. The duration of
treatment was less than 56 millisecond and a contact pressure of 241 kPa was preferred. Temperatures
of at least 204 °C to 274 °C were generated and wood surfaces were compressed by 63.5 and 127 μm. The
treatment increased the gloss and hardness of the wood and reduced its roughness and porosity. It was
claimed that the "Microseal" process increased the quality and consistency of wood surfaces and reduced
production costs associated with finish sanding.
2.11.5 Treatments combining chemical modification and mechanical treatments

Wood surface densification using heat and pressure has been used to improve the appearance and longevity of wood used outdoor. Carl (1949) developed a process to densify wood surfaces for furniture components (legs, tabletops, chair arms) that are susceptible to wear during service. The edges or corners of furniture were densified using a combination of heat and pressure. The densified outer shell was able to resist surface splintering, rupturing, wear or impact. Carl’s (1949) process densified wood surfaces using a die and press. The wood could also be impregnated with a thermosetting resin to help plasticize the wood during hot pressing. A resin impregnated or unimpregnated veneer could be applied to the wood surface, and the wood substrate and veneer could be densified together. The surface of the densified wood could be subsequently stained or varnished.

Smedberg (1985) patented a wood surface finishing and treatment procedure that reduced finishing costs by replacing puttying and priming steps. Solid wood or panels were coated with a layer of heat curable paint or lacquer. The coated wood was then subjected to two thermal modification steps. The first step dried and cured the wood coating. The temperature and duration of the first thermal modification step was dependent on the wood coating used. The second step involved thermal compression modification at temperatures and pressures of 150 °C to 350 °C and 1.49 to 68.64 MPa for a maximum of 60 seconds, respectively. This step allowed the coating to flow and seal pores at the wood surface, producing a smooth surface finish.

Van Hartesvedt and Wahl (1966) developed a method of hardening wood surfaces to increase their wear and impact resistance. The wood was preheated at temperatures up to 191 °C using heating blocks positioned on mandrels that compressed the wood surface. Preheating plasticized fibers at the wood surface to minimize damage from compression and reduce the force needed to compress the wood surface. Preheating also removed moisture and air from the wood to prevent buildup of steam during
compression. The heated and compressed wood was subjected to a secondary heating stage and cooled to 98 °C using cooling blocks positioned after the mandrels. This cooling step inhibited flash evaporation of moisture from the compressed layer and prevented drying and blistering of the compressed surface. This wood surface hardening process could include wood surface impregnation with resin and application of paper overlays (Van Hartesveldt & Wahl, 1966). For example, prior to surface compression, the wood surface could be impregnated with a thermosetting resin, such as a stage B resitol PF resin, or resins or waxes. Resin impregnated wood surfaces were dried in an oven at 43 °C overnight or using infra-red lamps at 121 °C to 182 °C.

Dimond (1965) developed a surface modification process for finishing of solid wood or panel products. An aqueous low viscosity and partially polymerized thermosetting resin, such as phenol formaldehyde, was applied to a wood surface as a coating by spraying, brushing or roller coating. Alcohol or organic solvent-based thermosetting resin were preferred to water-based resins, because fast evaporating solvents reduced production times and grain raising. Resin concentrations varied between 15% and 50%. Solutions containing 15% resin solids were preferred for commercial applications, but the optimum concentration of resin depended on the porosity of the wood substrate (Dimond, 1965). High resin concentrations were better for finishing highly porous woods and low resin concentrations were preferred for porous woods. Low viscosity resin was preferred as it produced a thin coating at wood surfaces (Dimond, 1965). The resin coated wood was fed on a conveyor belt through a rubbing machine, where a roller in the machine buffed the coated wood surface at high speed and at pressures of 0.36 Pa to 47.88 Pa. The resinous coating polymerized as a result of heat generated by friction during the rubbing process. The buffed resin created a glossy coating that was resistant to grain raising, reduced over-penetration of subsequent coatings, and produced a good substrate for subsequent staining, top or base coatings (Dimond, 1965).
2.12 Literature overview

The natural appearance of wood is appealing and much appreciated by consumers, but without an effective surface treatment, the attractive appearance of wood products, such as decking, is short-lived when they are used outdoors (Feist, 1990a; Ganguly et al., 2011). Stains are effective wood surface treatments, but they mask the attractive features of wood. Furthermore, erosion of stains during weathering reduces their protective effects and has adverse effects on the appearance of the finished wood (Black et al., 1979; Morrell et al., 2001). A few studies have investigated envelope treatments of wood with water-repellants and water-repellant preservatives (Fadl & Basta, 2005; Ahmed & Morén, 2012; Ahmed et al., 2013a, b; Elustondo et al., 2017). However, very few studies have examined the use of resins as envelope treatments for preservative-treated wood (Giebeler & Willhem, 1987; Fadl & Basta, 2005; Militz et al., 2013). This thesis will examine the ability of envelope treatments with low molecular weight PF resin to protect preservative-treated wood from natural weathering. Additives that can enhance the photoprotective effects of PF resin treatment will also be explored.
3.1 Introduction

Weathering causes chemical and physical changes to wood surfaces, most noticeably surface greying, roughening and checking, as mentioned in Chapter 2. Modification of wood with low molecular weight phenol formaldehyde resin imparts photostability to wood, and the level of photostability increases when higher concentrations of PF resin are used to treat wood (Stamm & Seborg, 1939; Sudiyani et al., 1996; Evans et al., 2013). Alternatively, wood can be protected from weathering by overlaying the wood surface with PF resin impregnated paper (Fleischer & Heebink, 1964). However, PF resin absorbs UV light and photodegrades, becoming redder and yellower on exposure to light (Evans et al., 2013; Kielmann & Mai, 2016a, 2016b). As a result, wood modified with high concentrations of PF resin (24 – 48%) discolours more during outdoor exposure than wood modified at lower concentrations (12%) (Tarkow et al., 1966; Evans et al., 2013). Polymers, as described in Chapter 2, can be photostabilized with the addition of the lignin stabilizer, Lignostab. Accordingly, Evans et al. (2013) found that addition of 2% lignin stabilizer to 10% PF resin reduced the photodiscolouration of radiata pine laminates treated with modified resin to a greater extent than those treated with only 10% PF resin. They tested the weather resistance of radiata pine laminates treated with higher concentrations of PF resin (20 and 30%), but did not examine if the addition of Lignostab reduced the discolouration of the composite. However, photostabilizers are added to polymers in bulk (100%) and are effective at photostabilizing polymers at low concentrations (Gilg et al., 1978). Hence, I hypothesize that lignin stabilizer will enhance the photostability of wood and paper treated with higher concentrations of PF resin. To test this hypothesis, I carried out two experiments. The first experiment examined the photostability of yellow cedar veneers and kraft paper strips treated with solutions of 10, 20, 30% PF resin and 30% PF resin and 2% Lignostab.
The second experiment tested the photostability of yellow cedar and Scots pine veneers treated with PF resin (20%) or PF resin (20%) and Lignostab (2%). My experiments on the effects of PF resin treatments on the photostability of wood veneer or paper strips were complemented by scanning electron microscopy (SEM) of the microstructure of PF resin-treated wood blocks exposed to natural weathering.

3.2 Materials and methods

3.2.1 Experimental design and statistical analyses

My first experiment examined the effects of different PF resin solutions (10% PF, 20% PF, 30% PF, 30% PF and 2% Lignostab) on the photostability of two types of samples (yellow cedar veneers, kraft paper strips) exposed to 50 days of natural weathering. My second experiment examined the effects of two different treatments (20% PF, 20% PF and 2% Lignostab), on the photostability of yellow cedar and Scots pine veneers exposed to 50 days of natural weathering. Veneer and paper strips for the first experiment were cut from four different yellow cedar blocks and four different sheets of kraft paper, respectively. Veneers for the second experiment were each cut from four different yellow cedar and Scots pine blocks. This approach provided replication at the higher (block) level, and statistical analyses accounted for random variation between wood blocks or paper sheets and batches of veneers or strips. In both experiments, ten veneer or paper strips from each block were batched together and randomly assigned to a treatment or untreated control.

Analysis of variance (ANOVA) examined the effects of treatment on the following measures of the resistance of wood veneers or paper strips to natural weathering: (1) colour change; (2) weight loss; (3) tensile strength loss. Statistical analyses for both experiments used Genstat Version 17.1, 18.1 or 18.2 (VSN International, 2014, 2015, 2016). Transformation of some data and diagnostic checks were carried out to ensure that the assumptions of ANOVA (normality of residuals, homogeneity of variance,
independence of sampling, independent observations) were met. Statistically significant \((p<0.05)\) results are graphed, and individual means can be compared using error bars (± standard error of difference) derived from ANOVA or least significant difference (LSD) bars derived from Fisher’s least significant difference test (Williams & Abdi, 2010).

3.2.2 Preparation and characterization of wood veneers, paper strips and SEM samples

Yellow cedar heartwood and Scots pine sapwood blocks \((80 \text{ mm [longitudinal]} \times 40 \text{ mm [tangential]} \times 19 \text{ mm [radial]})\) were cut from four different parent boards using a sliding table saw (Martin T75 PreX, Otto Martin Maschinenbau GmbH & Co. KG, Otteobeuren, Germany) and a chop saw (Omga® T55-300, OMGA, Inc., South Bend, I. N. U.S.A.). Blocks were submerged in distilled water for 10 days until they were saturated with water. Veneers, \(100 \pm 7 \mu\text{m} \) thick, were cut from the saturated (softened) blocks using a sledge microtome (Spencer Lens Co. Buffalo, N.Y. U.S.A.) fitted with a blade holder (Feather® No. 160, Feather Safety Razor Co. Ltd, Osaka, Japan) and a disposable microtome blade (Feather® Type S35, Feather Safety Razor Co. Ltd, Osaka, Japan) (Fig. 3.1). A new microtome blade was used to cut veneers from each block. Veneers were clamped on glass backing plates, air dried in a fume hood for 12 hours, and conditioned in a constant climate control room at \(20 \pm 1^\circ\text{C} \) and \(65 \pm 5\% \) relative humidity (r.h.) for 5 days.

Kraft paper strips, \(80 \text{ mm [length]} \times 19 \text{ mm [width]} \times 151.5 \pm 3.5 \mu\text{m} \) (thick), were cut using scissors from four different sheets measuring \(309 \text{ mm [length]} \times 308 \text{ mm [width]} \). The length of the strips was parallel to the fibre direction. The paper strips were conditioned in a constant climate control room for 5 days, as above.
Small samples for scanning electron microscopy (SEM) measuring 3 mm (tangential) x 2 mm (radial) x 20 mm (longitudinal) were cut from parent yellow cedar, Scots pine (as above) and southern pine boards using a band saw (Ryobi® BS902, Ryobi Limited, Hiroshima-ken, Japan). Southern pine samples were prepared because subsequent experiments described in Chapter 4 and 6 examined the effects of PF resin treatments on the weathering of southern pine panels. Samples were trimmed to their final dimensions using a hand-held chisel (Irwin Tools, Martinsville, O.H. U.S.A.). Samples were submerged in distilled water for 10 days until they were saturated. They were then clamped in a vice on the stage of a binocular microscope (Nikon Instruments Inc., Melville, N.Y., U.S.A.) and viewed at a magnification of 4x. A microtome blade, as above, was used to prepare clean transverse surfaces, while samples were viewed using a stereo microscope. Samples were conditioned in a constant climate control room for 5 days prior to PF resin modification and natural weathering.

3.2.3 Synthesis and preparation of modified PF resin

Phenol formaldehyde resin solutions were synthesized by Arclin USA Inc. (Springfield, O.R. U.S.A.). They supplied me with three batches of aqueous water soluble low molecular weight PF resin containing
45.89%, 46.69% or 45.89% of solids. Low molecular weight PF resin was synthesized with technical grade, 90% aqueous phenol, or industrial grade 99.7% aqueous phenol, industrial grade 52% aqueous formaldehyde, industrial grade 50% aqueous NaOH and tap water. The properties of a typical batch of resin are shown in Table 3.1.

Table 3.1 – Properties of low molecular weight PF resin used to prepare treatment solutions for modification of wood veneers and kraft paper strips (Evans et al., 2013)

<table>
<thead>
<tr>
<th>Phenolic resin property</th>
<th>Specific ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted phenol (%)(^a)</td>
<td>7.5 - 8.5</td>
</tr>
<tr>
<td>Unreacted formaldehyde (%)(^b)</td>
<td>0.7 - 0.9</td>
</tr>
<tr>
<td>Formaldehyde/phenol molar ratio</td>
<td>1.5 – 2.0</td>
</tr>
<tr>
<td>NaOH to phenol molar ratio</td>
<td>0.10 – 0.15</td>
</tr>
<tr>
<td>Total water</td>
<td>40 – 45%</td>
</tr>
<tr>
<td>Non-volatile solids (%)</td>
<td>46 - 48</td>
</tr>
<tr>
<td>Gel time @100 °C (min.)</td>
<td>70 - 80</td>
</tr>
<tr>
<td>pH @ 25 °C</td>
<td>9 - 10</td>
</tr>
<tr>
<td>Viscosity @ 25 °C (Centistokes)(^c)</td>
<td>10 - 30</td>
</tr>
</tbody>
</table>

\(^{a}\)Gas chromatography  
\(^{b}\)(Hydroxylamine HCl method)  
\(^{c}\)Converted from G-H viscosity

A water-soluble lignin stabilizer, Lignostab® 1198, supplied by CIBA Specialty Chemicals Corp (Tarrytown, N.Y. U.S.A.) was used as a photoprotective additive in the two experiments, and SEM studies. Phenol formaldehyde resin was diluted to the desired concentrations using tap water. Lignostab was dissolved in tap water and added to diluted PF resin solutions.

3.2.4 Treatment of wood veneers, paper strips and SEM samples

Batches of veneers and paper strips and SEM samples were submerged in a 150 mL beaker containing PF resin at room temperature for 10 minutes. Treated samples were held against the wall of a 400 mL beaker for 5 minutes to drain off excess solution. Samples were then fixed at one end to a wire rack and air dried in a fume hood for 30 minutes. The air-dried samples were cured in a convection oven (G01305A, Lindberg/Blue M™, Riverside, M.I., U.S.A.) at 130 ± 5 °C for 120 minutes. Treatments for both veneer experiments are summarized in Table 3.2.
Treated veneers and paper strips and untreated controls were oven dried at 105 ± 5 °C for 3 hours in a convection oven and cooled to room temperature in a vacuum desiccator for 20 minutes. Three samples were removed at a time from the desiccator, and weighed using a digital analytical balance (GR-200, A&D Company, Limited., Japan).

Table 3.2 – Impregnation method, concentrations of PF resin and additive and abbreviated treatment names for the two veneer trials

<table>
<thead>
<tr>
<th>No.</th>
<th>Impregnation</th>
<th>PF resin concentration (% w/w)</th>
<th>Lignostab concentration (% w/w)</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Dip</td>
<td>0</td>
<td>0</td>
<td>Water</td>
</tr>
<tr>
<td>2.</td>
<td>Dip</td>
<td>10</td>
<td>0</td>
<td>10% PF</td>
</tr>
<tr>
<td>3.</td>
<td>Dip</td>
<td>20</td>
<td>0</td>
<td>20% PF</td>
</tr>
<tr>
<td>4.</td>
<td>Dip</td>
<td>30</td>
<td>0</td>
<td>30% PF</td>
</tr>
<tr>
<td>5.</td>
<td>Dip</td>
<td>30</td>
<td>2</td>
<td>30% PF+Lstab</td>
</tr>
</tbody>
</table>

Experiment 1: Yellow cedar veneers and kraft paper strips

|     |              |                                |                                 |              |
| 1.  | Dip          | 0                              | 0                               | Water        |
| 2.  | Dip          | 20                             | 0                               | 20% PF       |
| 3.  | Dip          | 20                             | 2                               | 20% PF+Lstab |

Experiment 2: Yellow cedar and Scots pine veneers

Weight gains of yellow cedar veneers and kraft paper strips as a result of treatment are shown in Table 3.3. There is a positive correlation between weight gain of veneers and paper strips and concentration of PF resin solution used to treat veneers and strips. Addition of Lignostab to PF resin treatment significantly ($p<0.001$) reduced weight gain of treated veneers. In the second experiment, treated yellow cedar veneers were significantly ($p=0.002$) heavier than Scots pine veneers.
Table 3.3 – Average weight gains of wood veneers and paper strips treated with modified and unmodified PF resin

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Percentage (%) (SD)</th>
<th>Percentage (%) (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yellow cedar</td>
<td>Kraft paper</td>
</tr>
<tr>
<td>Experiment 1: Yellow cedar veneers and kraft paper strips</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% PF</td>
<td>16.2 (2.3)</td>
<td>16.3 (4.1)</td>
</tr>
<tr>
<td>20% PF</td>
<td>34.4 (5.2)</td>
<td>32.7 (2.2)</td>
</tr>
<tr>
<td>30% PF</td>
<td>56.9 (7.5)</td>
<td>51.3 (2.9)</td>
</tr>
<tr>
<td>30% PF+Lstab</td>
<td>52.3 (8.4)</td>
<td>51.1 (2.8)</td>
</tr>
<tr>
<td>Experiment 2: Yellow cedar and Scots pine veneers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow cedar</td>
<td>24.2 (2.6)</td>
<td>23.0 (5.4)</td>
</tr>
<tr>
<td>20% PF+Lstab</td>
<td>25.1 (3.4)</td>
<td>23.0 (5.0)</td>
</tr>
</tbody>
</table>

3.2.5 Weathering trials

Five treated veneers or paper strips from each batch were laid on 750 mm x 120 mm glass backing plates and secured at both ends using two 750 mm x 20 mm glass strips. Different glass backing plates were used for samples from the four blocks. The positions of batches of 5 veneer or paper strips on the plates were randomized. The glass strips were covered and fixed to each backing plate using black polyethylene adhesive tape. The tape protected the ends of the veneer and paper strips from solar radiation. The glass strips were clamped at regular intervals using butterfly clips. Plates containing veneers or paper strips were exposed horizontally to the weather on the campus of the University of British Columbia for 50 days from August 29th to October 18th, 2012, (Experiment 1) and June 3rd to July 23rd, 2016, (Experiment 2) (Fig. 3.2). Meteorological data during the exposure trials are shown in Table 3.4. The remaining five veneer or paper strips from each batch in both experiments acted as unweathered controls. These were stored in a constant climate control room for the duration of the weathering trials.
### Table 3.4 – Weather conditions in Vancouver, British Columbia, Canada during the two 50-day exposure trials (Experiment 1, wood veneer v. kraft paper, and 2, yellow cedar v. Scots pine veneer)

<table>
<thead>
<tr>
<th>Date</th>
<th>Temperature (°C)</th>
<th>Total Precipitation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum¹</td>
<td>Mean</td>
</tr>
<tr>
<td>August 2012</td>
<td>23.5</td>
<td>19.0</td>
</tr>
<tr>
<td>September 2012</td>
<td>19.6</td>
<td>15.4</td>
</tr>
<tr>
<td>October 2012</td>
<td>13.4</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Experiment 1: Yellow cedar veneers and kraft paper strips

Experiment 2: Yellow cedar and Scots pine veneers

<table>
<thead>
<tr>
<th>Date</th>
<th>Temperature (°C)</th>
<th>Total Precipitation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum¹</td>
<td>Mean</td>
</tr>
<tr>
<td>June 2016</td>
<td>20.2</td>
<td>16.1</td>
</tr>
<tr>
<td>July 2016</td>
<td>22.0</td>
<td>18.3</td>
</tr>
</tbody>
</table>

¹Average maximum and minimum daily temperatures

Data collected for Vancouver International Airport, [http://climate.weather.gc.ca/historical_data/search_historic_data_e.html](http://climate.weather.gc.ca/historical_data/search_historic_data_e.html)

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Figure 3.2 – Veneers exposed to the weather for 50 days on the campus of UBC: (a) modified and unmodified yellow cedar veneers and kraft paper strips on the 27th day of exposure; (b) modified and unmodified yellow cedar and Scots pine veneers on the 1st day of exposure

Yellow cedar, Scots and southern pine SEM samples were clamped at one end with alligator clips. The circular end of each alligator clip was inserted vertically into a 4.3 mm hole drilled into a strip of wood measuring 505 mm (length) x 60 mm (width) x 25 mm (thickness). The wooden strip containing SEM samples was fastened horizontally to a rack with sub-frame and legs made from pressure-treated 2’ x 4’ lumber. Yellow cedar, Scots pine and southern pine SEM samples were exposed outdoors on UBC’s campus for various lengths of time, as shown in Table 3.5 (Fig. 3.3).
Table 3.5 – Outdoor exposure times for scanning electron microscopy (SEM) samples

<table>
<thead>
<tr>
<th>Species</th>
<th>Start date</th>
<th>End date</th>
<th>Duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow cedar</td>
<td>June 3, 2016</td>
<td>September 11, 2016</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>June 3, 2016</td>
<td>August 1, 2017</td>
<td>424</td>
</tr>
<tr>
<td>Scots pine</td>
<td>August 17, 2015</td>
<td>November 4, 2015</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>September 8, 2016</td>
<td>December 17, 2016</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>December 4, 2015</td>
<td>September 9, 2016</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>December 4, 2015</td>
<td>August 1, 2017</td>
<td>606</td>
</tr>
<tr>
<td>Southern pine</td>
<td>June 3, 2016</td>
<td>September 11, 2016</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>June 3, 2016</td>
<td>August 1, 2017</td>
<td>424</td>
</tr>
</tbody>
</table>

Figure 3.3 – Outdoor exposure of treated and untreated scanning electron microscopy (SEM) samples

3.2.7 Assessment of the effects of PF resin treatments on the properties of veneers and paper strips

Weathered wood veneers and paper strips were removed from glass backing plates and conditioned in a constant climate control room (as above) for a minimum of seven days, and measurement of the properties of samples commenced. Wood veneer and paper samples were scanned at a resolution of 1200 dpi resolution, 256 colours and 100% scale using a flatbed scanner (Microtek® Scanmaker® i800, Microtek International Inc., Hsinchu, Taiwan). Samples were scanned before and after treatment, and rescanned after 50 days of weathering.
3.2.4.1 Measurement of colour

Colour of wood veneer and paper strips was measured using a spectrophotometer (Minolta CM-2600D, Konica Minolta, Tokyo, Japan). Surfaces of samples were not reflective, therefore colour was measured in ‘specular component included’ (SCI) mode, which is a colour parameter obtained by measuring specular reflection and diffuse reflection at a sample’s surface (Konica Minolta, 2007). Colour measurement in SCI mode has been used in previous studies by Cheng (2015) and Kilian et al. (2010) to assess the colour of wood exposed to weathering. Colour is expressed using the CIE 1976 L*a*b* Space System, in which the L* parameter represents lightness on a scale from 0 to 100, where 0 = black and 100 = white; the a* parameter represents redness on a scale from -100 to +100, where negative a* is green and positive a* is red; the b* parameter represents yellowness on a scale from -100 to +100, where negative b* is blue and positive b* is yellow (McGuire, 1992). Colour of weathered and unweathered wood veneers and paper strips was measured at three locations after treatment and again after weathering. Change in colour of samples as a result of weathering is expressed as a ratio of a colour parameter after weathering divided by the same colour parameter before weathering. A ratio above or below 1 indicates increase or decrease in colour parameter after weathering, respectively.

3.2.4.2 Measurement of weight and tensile strength losses of veneers and paper strips

Veneer and paper strips were weighed before and after oven drying and after treatment using a digital analytical balance (GR-200, A&D Company Limited, Japan). Weight gains from treatment were calculated. Veneers and paper strips were reweighed after outdoor exposure and weight losses as a result of weathering were calculated.
The thicknesses of conditioned wood veneers and paper strips were measured using a digital micrometer (HWS 5781, AB Lorentzen & Wettre, Sweden) located in a constant climate control room (Fig. 3.4).

Figure 3.4 – (a) Digital micrometer used to measure the thickness of wood veneer and kraft paper strips; (b) close-up of the micrometer head on a yellow cedar veneer specimen

Tensile strength of weathered and unweathered veneer and paper strips was measured using a paper tester (Pulmac HWS5786, Pulmac Systems, Williston, V.T. U.S.A.) located in a constant climate control room. Tensile tests were carried out at zero-span, as shown in Figure 3.5, to assess the effects of treatment and weathering on the properties of cellulose (Evans and Schmalzl, 1989). Clamping pressure of 206.8 kPa was used for tensile strength testing, and tensile strengths of samples was calculated according to equation (1):
Where, \( TS = \text{tensile strength (kg/mm}^2) \)
\( P = \text{failure load (psi)} \)
\( P_0 = 1.9 \text{ psi (zero pressure values required to unload jaws)} \)
\( K = 0.375 \text{ (instrument constant provided by the manufacturer)} \)
\( S_w = 15 \text{ mm (effective width of specimen)} \)
\( S_t = \text{specimen thickness (µm)} \)

Figure 3.5 – (a) Pulmac paper tester used to measure the tensile strength of wood veneers and kraft paper strips; (b) close-up of the jaws of the Pulmac paper tester. Note that the jaws abut against each other (zero-span)

3.2.8 Scanning electron microscopy

Weathered samples were retrieved from the test site and conditioned in a constant climate control room. Both weathered and unweathered samples were conditioned for a minimum of seven days and cut to length using a small razor saw measuring 114.3 mm x 11.1 mm (blade-dimensions) and kerf of 0.254 mm. Samples, with final dimensions of 3 mm x 2 mm x 2 mm, were fixed to 12 mm diameter aluminum stubs using double-sided adhesive tabs (#76760, Electron Microscopy Sciences Inc., Hatfield, PA, U.S.A.). Samples on aluminum stubs were sputter coated with 8 nm of gold and examined using a Zeiss UltraPlus analytical field electron scanning microscope (Zeiss, Oberkochen, Germany) with an accelerating voltage
of 5kV and a working distance of 13.1 to 16.3 mm. Scanning electron images of samples were saved in TIFF format.

3.3 Results

3.3.1 Yellow cedar veneer and kraft paper strip trial (Experiment 1)

There were highly significant \((p<0.001)\) effects of material type (wood veneer or paper strip) and chemical treatments on colour \((L^*, a^*, b^*)\), and weight and tensile strength losses of veneer and paper strips exposed to the weather for 50 days.

3.3.1.1 Appearance of wood veneers and paper strips after treatment and weathering

The appearance of modified and unmodified yellow cedar veneers and kraft paper strips before and after weathering is shown in Figure 3.6 and Figure 3.7. All images of veneer and paper strip samples are appended to this thesis (Appendix 1). The 10% PF resin solution imparted a light red tint to the modified veneers and paper strips, and as the concentration of PF resin increased to 20% and 30%, the modified veneers and paper strips became dark red to brown, respectively. However, the red colour of modified veneers was blotchy, particularly at higher concentrations of PF resin, but modified paper strips were not blotchy. Veneers modified with PF resin and the lignin stabilizer, Lignostab, were slightly less red than those modified with 30% PF, but Lignostab had no effect on the colour of modified paper strips. The red colour of modified veneers and paper strips became less pronounced after weathering and veneers became less blotchy. Modified veneers and paper strips became yellower during exterior exposure, and fungal staining in the form of black dots and grey streaks developed in both veneers and paper strips modified with 10% PF resin. However, fungal discolouration was less evident in veneers and paper strips modified with higher concentrations of PF resin (Fig. 3.8). Moreover, weathered veneers and paper strips modified with PF resin retained their shape better than the unmodified controls, which became wrinkly
and distorted during exposure. Fungal staining was also more pronounced in the veneer and paper controls. The tan colour of paper controls was lost and they were bleached white during exposure.

Figure 3.6 – Scanned images of modified and unmodified yellow cedar veneers before and after exposure to 50 days of natural weathering. Scale bar is 10 mm
Figure 3.7 – Scanned images of modified and unmodified kraft paper strips before and after exposure to 50 days of natural weathering. Scale bar is 10 mm.
Figure 3.8 – Surface colonization of treated and untreated yellow cedar veneer and kraft paper strip by mould fungi indicated by arrows. Scale bar is 1 mm
3.3.1.2 Colour changes of wood veneers and paper strips

Colour changes of modified and unmodified samples during weathering are shown in Figure 3.9. Wood veneers modified with 20% - 30% PF became lighter during exterior exposure, whereas the controls and veneers treated with 10% PF resin became darker (Fig. 3.9). The veneers treated with 30% PF resin and 2% lignin stabilizer were slightly lighter than those treated with 30% PF resin on its own. A similar trend was observed for paper strips, except the controls were much lighter than treated strips due to bleaching of paper mentioned above. The addition of Lignostab did not affect lightness of PF-modified paper strips.

![Graph showing changes in lightness of treated and untreated yellow cedar veneers (V) and kraft paper strips (P) during exposure to 50 days of weathering. Colour change is expressed as ratio of colour after weathering/colour before weathering. Ratio of 1 indicates no change in lightness of samples during weathering. Ratios above and below 1 indicate increase and decrease in lightness of samples during weathering, respectively. Error bars are ± standard error of difference (p<0.001) from analyses of variance.](image)

Figure 3.9 – Changes in lightness of treated and untreated yellow cedar veneers (V) and kraft paper strips (P) during exposure to 50 days of weathering. Colour change is expressed as ratio of colour after weathering/colour before weathering. Ratio of 1 indicates no change in lightness of samples during weathering. Ratios above and below 1 indicate increase and decrease in lightness of samples during weathering, respectively. Error bars are ± standard error of difference (p<0.001) from analyses of variance.

Veneers treated with PF resin became yellower during weathering (Fig. 3.10). The degree of yellowing increased with concentration of PF resin, but yellowing of PF-modified veneers was unaffected by the addition of lignin stabilizer to the resin. Untreated veneers became slightly less yellow during
weathering. Resin-treated paper strips also yellowed during weathering and the untreated paper strips also became less yellow during weathering. However, in contrast to wood veneers, the addition of lignin stabilizer to 30% PF resin solution increased yellowing of PF treated paper strips.

Figure 3.10 – Changes in yellowness of treated and untreated yellow cedar veneers (V) and kraft paper strips (P) during exposure to 50 days of weathering. Colour change is expressed as ratio of colour after weathering/colour before weathering. Ratio of 1 indicates no change in yellowness of samples during weathering. Ratios above and below 1 indicate increase and decrease in yellowness of samples during weathering, respectively. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance

Veneers became redder during weathering, but PF resin treatment, particularly 20% and 30% PF treatments, restricted changes in redness of the treated veneers (Fig. 3.11). Paper strips treated with PF resin became redder, whereas the controls became less red. Addition of Lignostab did not affect the red colour of PF-treated veneers or paper strips.
Figure 3.11 – Changes in redness of treated and untreated yellow cedar veneers (V) and kraft paper strips (P) during exposure to 50 days of weathering. Colour change is expressed as ratio of colour after weathering/colour before weathering. Ratio of 1 indicates no change in redness of samples during weathering. Ratios above and below 1 indicate increase and decrease in redness of samples during weathering, respectively. Error bars are ± standard error of difference (p<0.001) from analyses of variance

3.3.1.3 Weight loss of wood veneers and paper strips

Figure 3.12 shows weight losses of treated and untreated veneers during exterior exposure. Veneers treated with PF resin lost significantly (p<0.001) less weight than the untreated controls as expected. Weight losses of veneers treated with 20% PF, 30% PF or 30% PF and lignin stabilizer were less than those of veneers treated with 10% PF resin, but differences were not significant (p>0.05). Weight losses of treated paper strips were significantly (p<0.001) less than the untreated controls. There was no correlation between weight losses of treated paper strips during weathering and concentration of PF resin used to treat the strips. Furthermore, there were no significant (p>0.05) differences in weight losses of paper strips treated with the different PF resin solutions.
3.3.1.4 Tensile strength losses of wood veneers and paper strips

Figure 3.12 – Percentage weight loss of treated and untreated yellow cedar veneers (V) and kraft paper strips (P) exposed to 50 days of natural weathering. Error bars are ± standard error of difference (p<0.001) from analyses of variance.

3.3.1.4 Tensile strength losses of wood veneers and paper strips

Figure 3.13 shows tensile strength of treated and untreated yellow cedar veneer before and after exposure to the weather. PF resin treatment significantly (p<0.001) reduced tensile strength of treated veneers. Tensile strengths of veneers treated with higher concentrations of PF resin (20%, 30% or 30% PF resin and lignin stabilizer) were significantly (p<0.001) lower than those of veneers treated with 10% PF resin. During weathering, PF modified veneers became stronger, whereas the controls lost strength. There were no significant (p>0.05) differences in the strengths of weathered PF-treated veneers.
Figure 3.13 - Tensile strength of modified yellow cedar veneers before ($p<0.001$) and after ($p<0.001$) exposure to 50 days of natural weathering. Error bars are ± standard error of difference from analyses of variance.

Treatment with PF resin also caused strength losses of kraft paper strips Figure 3.14. Tensile strength losses of PF treated paper strips were correlated with concentration of PF resin used to treat strips. The tensile strength of strips treated with 20% PF resin did not change during weathering. Conversely, tensile strength of strips treated with 30% or 30% PF resin and Lignostab slightly increased, whereas the controls and strips treated with 10% PF resin became weaker during weathering. The addition of the lignin stabilizer to PF resin had no effect ($p>0.05$) on tensile strengths of strips before or after weathering.
Figure 3.14 - Tensile strength of modified kraft paper strips before ($p<0.001$) and after ($p<0.001$) exposure to 50 days of natural weathering. Error bars are ± standard error of difference from analyses of variance.

The overall effects of weathering on tensile strengths of yellow cedar veneers and kraft paper strips are shown in Figure 3.15. These graphs show the ratio of tensile strength of veneers after weathering to their tensile strengths before weathering. The results confirm trends shown in Figure 3.13 and Figure 3.14 that untreated veneers and paper strips lost strength during exposure, whereas the treated veneers became stronger.
Figure 3.15 - Ratios of tensile strengths of modified and unmodified (a) yellow cedar veneers and (b) kraft paper strips exposed to 50 days of natural weathering. The ratios represent tensile strengths of weathered veneers divided by strengths of unweathered veneers. Ratios greater or less than 1 represent increase or decrease in tensile strengths during weathering, respectively. Ratios equal 1 indicate no change in tensile strengths. Error bars are ± standard error of difference (p<0.001) from analyses of variance.
3.3.2 Yellow cedar and Scots pine veneer trial (Experiment II)

The effects of treatment, species and interaction of treatment x species on colour and weight and tensile strength losses of veneers exposed to the weather for 50 days are shown in Table 3.6. Treatment had significant effects on all measures used to assess weathering of veneers, except for redness ratio. ‘Species’ had significant effects on all measures of weathering resistance, except for redness ratio and lightness. There was only one significant interaction of treatment x species on colour parameters (yellowness), but there were significant interactions on weight and tensile strength losses.

Table 3.6 – Significant effects of PF resin treatment, species and interactions between treatment and species on parameters used to assess the weathering of yellow cedar and Scots pine veneers exposed outdoors for 50 days

<table>
<thead>
<tr>
<th>Weathering parameters</th>
<th>Experimental factors</th>
<th>Treatment</th>
<th>Species</th>
<th>Treatment x species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lightness</td>
<td>***</td>
<td>NS</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>Redness</td>
<td>***</td>
<td>NS</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>Yellowness</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>Ratio of change in lightness</td>
<td>***</td>
<td>***</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>Ratio of change in redness</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>Ratio of change in yellowness</td>
<td>***</td>
<td>***</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>Weight</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Weight loss percentage</td>
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<tr>
<td>Strength</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength unweathered</td>
<td>***</td>
<td>***</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>Tensile strength weathered</td>
<td>*</td>
<td>***</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>Ratio of tensile strength loss</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td></td>
</tr>
</tbody>
</table>

*** = p<0.001; ** = p<0.01; * = p<0.05; NS = p>0.05 (not significant)

3.3.2.1 Appearance of yellow cedar and Scots pine veneers after treatment and weathering

The appearance of modified and unmodified yellow cedar and Scots pine veneers exposed to 50 days of natural weathering is shown in Figure 3.16 and Figure 3.17, respectively. Images of all veneer samples before and after exposure to the weather can be viewed in Appendix 1. Phenolic resin modification made yellow cedar and Scots pine veneers darker and redder, as expected. Scots pine veneers modified with PF resin were a little blotchy. The addition of the lignin stabilizer, Lignostab, to the
PF resin made treated yellow cedar and Scots pine veneers slightly redder. Untreated veneers became grey and distorted, as a result of weathering. Splits developed in unmodified Scots pine veneers during weathering. Modified cedar and pine veneers became darker, redder and yellower after weathering. Fungal staining was less evident on modified veneers and they did not distort during exterior exposure (Fig. 3.18).
Figure 3.16 – Images of modified and unmodified yellow cedar veneers before and after 50 days of natural weathering. Scale bar is 10 mm

Figure 3.17 – Images of modified and unmodified Scots pine veneers before and after 50 days of natural weathering. Scale bar is 10 mm
Figure 3.18 – Surface colonization of treated and untreated yellow cedar and Scots pine veneers by mould fungi. Scale bar is 1 mm

3.3.2.2 Colour change of yellow cedar and Scots pine veneers

Changes in lightness of yellow cedar and pine veneers as a result of weathering are plotted in Figure 3.19. Unmodified veneers became darker after weathering, as expected. PF resin treated veneers also became darker, but the darkening was less pronounced than that of untreated veneers. Darkening of veneers when averaged across treatments was significantly ($p<0.001$) greater for Scots pine compared to yellow cedar veneers. Addition of lignin stabilizer to 20% PF resin significantly ($p<0.001$) reduced darkening of veneers.
There was a significant ($p<0.001$) treatment x species interaction on the yellowness parameter ($b^*$) of weathered veneers, because yellowness of untreated yellow cedar and Scots pine veneers was similar but treated Scots pine veneers (P) became more yellow than treated yellow cedar veneers (C) after exposure to outdoor weathering (Fig. 3.20). Furthermore, the lignin stabilizer significantly ($p<0.001$) reduced the yellowing of Scots pine veneers treated with 20% PF resin, whereas it had no significant ($p>0.05$) effect on the yellowing of yellow cedar veneers (Fig. 3.20).
Figure 3.20 – Yellowness of treated and untreated yellow cedar (C) and Scots pine (P) veneers after 50 days of weathering. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.

Figure 3.21 shows changes in yellowness ratios of treated and untreated veneers after weathering averaged across species. PF resin treated veneers were significantly ($p<0.001$) yellower than the untreated controls. The difference in yellowing of veneers treated with 20% PF or 20% PF and lignin stabilizer was not statistically significantly ($p>0.05$).
Figure 3.21 – Change in yellowness ratios of treated and untreated yellow cedar and Scots pine veneers averaged across species after 50 days of weathering. Colour change is expressed as ratio of colour after weathering divided/colour before weathering. Ratio of 1 indicates no change in yellowness of samples during weathering, respectively. Ratios above and below 1 indicate increase and decrease in yellowness of samples during weathering. Error bars are ± standard error of difference (p<0.001) from analyses of variance.

PF resin treated wood veneers were significantly (p<0.001) redder than those of untreated controls (Fig. 3.22). Veneers treated with PF resin and the lignin stabilizer were significantly (p<0.001) less red than those of veneers treated with PF resin alone.
Figure 3.22 – Redness of treated and untreated wood veneers after 50 days of weathering. Note that results are averaged across species. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.

3.3.2.3 Weight losses of yellow cedar and Scots pine veneers

Figure 3.23 shows the weight losses of treated veneers and untreated controls after 50 days of natural weathering. There was a significant ($p<0.001$) treatment x species interaction, because untreated yellow cedar veneers had greater weight losses than untreated Scots pine veneers but this difference did not occur in cedar and pine veneers treated with 20% PF or 20% PF and Lignostab solutions. Clearly, PF resin treatment reduced weight losses of treated cedar and pine veneers, but the lignin stabilizer did not have a significant ($p>0.05$) effect on weight losses of PF-treated cedar or pine veneers.
Figure 3.23 – Percentage weight losses of treated and untreated yellow cedar (C) and Scots pine (P) veneers exposed to 50 days of natural weathering. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.

3.3.2.4 Tensile strength losses of yellow cedar and Scots pine veneers

Figure 3.24 shows tensile strengths of weathered and unweathered wood veneers averaged across species. Treatment with 20% PF resin or 20% PF resin and lignin stabilizer caused a significant ($p<0.001$) decrease in tensile strength of veneers. However, treated veneers were significantly ($p=0.012$) stronger than the untreated controls after exposure to 50 days of natural weathering. Addition of Lignostab to 20% PF resin did not significantly ($p>0.05$) affect tensile strengths of veneers after treatment or weathering.
Figure 3.24 – Tensile strengths of treated and untreated veneers before \((p<0.001)\) and after \((p=0.012)\) exposure to 50 days of natural weathering. Note that the results are averaged across species. Error bars are ± standard error of difference from analyses of variance.

A significant \((p<0.001)\) treatment x species interaction occurred for tensile strength of veneers after weathering, because treated (PF, PF/Lignostab) yellow cedar veneers were stronger than untreated controls, but the strengths of treated and untreated Scots pine veneers were the same (Fig. 3.25).
Changes to tensile strengths of treated cedar and pine veneers as a result of weathering are plotted as ratios in Figure 3.26. There was a significant ($p<0.001$) treatment x species interaction on tensile strength losses of veneers, because pine veneers lost less strength than cedar veneers, except for veneers treated with PF and lignin stabilizer. Treated (PF, PF/Lignostab) cedar and pine veneers became slightly weaker during weathering, whereas the controls became much weaker.
3.3.4 Microstructural changes of unmodified and PF resin modified wood during natural weathering

The microstructure of tracheid and rays at the surface of untreated yellow cedar, Scots pine and southern pine blocks are shown in Figure 3.27. Middle lamellae can be clearly seen between earlywood and latewood cells in all three softwood species. Latewood cell walls of yellow cedar are thinner than those in Scots and southern pine (Fig. 3.27). Middle lamellae are slightly recessed between earlywood and latewood cell walls, particularly in yellow cedar (Fig. 3.27b). However, in Scots pine latewood, middle lamellae sometimes protruded above the secondary cell wall (Fig. 3.27c, d). Separation of tracheids was more pronounced in latewood (Fig. 3.27 b, d, f). Voids in wood cell walls occurred where microtoming cut through bordered pits (Fig. 3.27a, b, e). Lumens of a few latewood cells of Scots pine were occluded by resin (Fig. 3.27).
Figure 3.27 – SEM images of untreated samples (before weathering), showing: (a) yellow cedar earlywood; (b) yellow cedar latewood; (c) Scots pine earlywood and latewood; (d) Scots pine latewood; (e) southern pine earlywood; (f) southern pine latewood. Arrows indicate: (1) recessed middle lamella; (2) protruding middle lamella; (3) separation of tracheids; (4) bordered pit void; (5) occlusion of lumen by resin.

The microstructure of yellow cedar, Scots pine and southern pine was altered by modification with 20% PF resin, as shown in Figure 3.28. Earlywood cell walls appeared to be thicker than those of earlywood in untreated controls, although thickening was less pronounced in latewood. Resin appeared to coat transverse surfaces of cell walls and lumens of some Scots and southern pine earlywood tracheids: some latewood tracheids were also occluded by resin (Fig. 3.28c-f). PF resin also filled the voids created by pit chambers and rays (Fig. 3.27c).
Figure 3.28 – SEM images of samples treated with 20% PF resin (before weathering), showing: (a) yellow cedar earlywood; (b) yellow cedar latewood; (c) Scots pine earlywood and latewood; (d) Scots pine latewood; (e) southern pine earlywood; (f) southern pine latewood. Arrows indicate: (1) PF resin filled lumen; (2) PF resin occlusion of ray

Similar microstructural changes occurred in woods treated with 20% PF resin and 2% lignin stabilizer (Fig 3.29), although filling of earlywood lumens appeared to be more common in wood treated with PF resin and Lignostab than in wood treated with PF resin on its own (Fig. 3.29b-e).
Exposure to natural weathering caused degradation of untreated yellow cedar, Scots pine and southern pine, as expected, and the damage became more pronounced with increasing exposure. SEM photographs below show macro- and microstructural changes to transverse surfaces of Scots pine after weathering for 79 (Fig. 3.30), 100 (Fig. 3.31), 280 and 606 days (Fig. 3.32). Changes at southern pine surface weathered for 100 and 424 days are shown in Figure 3.33. Changes at transverse surfaces of yellow cedar after 100 and 424 days are shown in Figures 3.34 and 3.35, respectively.
Large radial checks occurred after 79 days of weathering as a result of separation of rays in Scots pine (Fig. 3.30a). Resin canals were still intact (Fig. 3.30b). However, middle lamellae in earlywood and latewood were completely eroded (Fig. 3.30c, d). Earlywood and latewood tracheids were distorted and cell walls of some tracheids delaminated.

![SEM images of untreated Scots pine samples after 79 days of natural weathering](image)

Figure 3.30 – SEM images of untreated Scots pine samples after 79 days of natural weathering, showing: (a) entire SEM sample; (b) earlywood, latewood and a resin canal; (c) distorted earlywood tracheids; (d) distorted latewood tracheids. Note the: (1) checks formed from separation of rays; (2) erosion of middle lamellae; (3) fractured cell wall

After 100 days of weathering, more radial checks developed in Scots pine samples and the checks became bigger (Fig. 3.31a). Resin canals were degraded and some colonization of resin canals and latewood tracheids by fungi occurred (Fig. 3.31b, d).
Figure 3.31 – SEM images of untreated Scots pine samples after 100 days of natural weathering, showing: (a) entire SEM sample; (b) degraded resin canal in latewood; (c) distorted earlywood tracheids; (d) distorted latewood tracheids. Note that: (1) checks formed from separation of rays; (2) erosion of middle lamellae; (3) fractured cell wall; (4) colonization of resin canal by fungus.

Figure 3.32a shows that radial checks had widened and tangential checks formed at boundary of earlywood and latewood in Scots pine samples weathered for 280 days. A resin canal had completely collapsed (Fig. 3.32b). Middle lamellae in earlywood and latewood were completely eroded, which resulted in pronounced distortion of tracheids (Fig. 3.32c, d). Figure 3.32c shows fractured earlywood cell walls. The transverse surface of Scots pine samples after 606 days of weathering had become sponge-like due to massive distortion of earlywood and latewood tracheids and thinning of their cell walls (Fig. 3.32e-h). There was increased colonization by fungi in earlywood and latewood tracheids (Fig. 3.32f, h).

Microstructural changes to southern pine weathered for 100 days were similar to those observed at the surface of similarly exposed Scots pine samples, although earlywood appeared to be more degraded than earlywood in Scots pine. In addition, ray checks appeared to be larger (Fig. 3.33a-d). This trend was also apparent in southern pine samples weathered for 424 days (Fig. 3.33e-h).
Figure 3.32 - SEM images of untreated Scots pine samples after 280 (a-d) and 606 (e-h) days of natural weathering, showing: (a) entire SEM sample; (b) collapsed resin canal; (c) earlywood; (d) latewood; (e) entire SEM sample; (f) fungi-colonizing degraded earlywood tracheids; (g) distorted earlywood; (h) mould colonizing latewood. Arrows indicate: (1) widened radial macro-check; (2) tangential check at earlywood and latewood boundary; (3) distorted tracheids; (4) fractured tracheid cell wall; (5) fungal colonization in voids between latewood tracheids; (6) fungal hyphae.
Figure 3.33 - SEM images of untreated southern pine samples after 100 (a-d) and 424 (e-h) days of natural weathering, showing: (a) large radial check in earlywood and latewood; (b) resin canal in latewood; (c) degraded earlywood tracheids; (d) degraded latewood tracheids; (e) entire SEM sample; (f) earlywood and latewood; (g) degraded earlywood tracheids; (h) latewood. Note that: (1) large radial checks; (2) degraded resin canal; (3) erosion of middle lamellae; (4) distortion of tracheids; (5) fractured tracheid cell walls; (6) colonization of resin canal by fungi.
In comparison to Scots pine and southern pine, the transverse surface of yellow cedar exposed to 100 days of natural weathering appeared sponge-like and disorganized (Fig. 3.34b), because of erosion of middle lamellae and severe degradation of earlywood and latewood tracheids from 100 days of weathering (Fig. 3.34c-d). Figure 3.34b to d show the degradation of yellow cedar samples. Figure 3.34b shows that the sponge-like appearance of weathered yellow cedar is caused by formation of interconnected radial and tangential checks. These checks caused separation of earlywood and latewood tracheids and are smaller than those found in similarly exposed Scots and southern pine samples. Cell wall fracture was more severe in yellow cedar earlywood than in latewood tracheids, and hence, there is greater distortion of earlywood tracheids than latewood tracheids (Fig. 3.34c). Fractured cell wall fragments can be seen to be loosely attached to degraded earlywood tracheids (Fig. 3.34c). Latewood tracheids were also distorted and degraded (Fig. 3.34d).

Figure 3.34 – SEM images of untreated yellow cedar sample after 100 days of natural weathering, showing: (a) entire SEM sample; (b) earlywood and latewood; severely degraded earlywood (c) and latewood (d) tracheids
The transverse surface of yellow cedar became even more sponge-like with increasing exposure due to the formation of numerous radial and tangential micro-checks (Fig. 3.35a). Voids became bigger because of severe distortion of earlywood and latewood tracheids (Fig. 3.35b).

Figure 3.35 – SEM images of untreated yellow cedar sample after 424 days of natural weathering, showing: (a) sponge-like SEM sample; (b) heavily degraded earlywood and latewood tracheids. Note the widening of checks on the transverse surface

Degradation at the transverse surfaces of all softwood species became more pronounced with increasing exposure. Micro-checks in pines were initially formed in the radial direction due to separation of rays, and as exposure progressed, micro-checks in the tangential direction developed due to separation of earlywood and latewood tracheids. Micro-checks in Scots pine were spaced apart and traversed earlywood and latewood: earlywood between these checks had a sponge-like appearance, as shown in Figures 3.30a, 3.31a and 3.32a. Radial checks were closer together in southern pine than those in Scots pine (Fig. 3.33e). These checks were mainly confined to earlywood, which was heavily checked after 424 days of weathering. Radial checks in yellow cedar after 100 days of weathering were small and evenly distributed across both earlywood and latewood, as shown in Figure 3.35a. In addition, the radial checks were intercepted by tangential checks that developed at the earlywood and latewood boundary and voids formed in the earlywood. Thus, the weathered transverse surface of yellow cedar was very sponge-like,
as mentioned above. Smaller checks were observed in cell walls of earlywood and latewood tracheids, and they were more pronounced in southern pine and yellow cedar than in Scots pine.

Erosion of middle lamellae was similar in all three softwood species. Earlywood and latewood tracheid cell walls in the pines and yellow cedar thinned, fractured and distorted. However, cell wall degradation of earlywood and latewood tracheids was more pronounced in southern pine and yellow cedar than in Scots pine. Loosely attached fractured cell wall fragments were observed at the surface of earlywood tracheids in southern pine (Fig. 3.33c) and yellow cedar (Fig. 3.34c) after 100 days of weathering. In comparison, cell wall fracture and distortion of earlywood tracheids of Scots pine occurred later and was seen in samples exposed to 280 days of weathering (Fig. 3.32c). Degradation of latewood tracheids in pines after 100 days of weathering (Fig. 3.31d, 3.33d) was less pronounced than that in yellow cedar (Fig. 3.34d). Scots pine latewood tracheids (Fig. 3.31d) were less distorted than those of southern pine (Fig. 3.33d). There was cell wall fracture in latewood tracheids of southern pine (Fig. 3.33d) and yellow cedar (Fig. 3.35b), but cell wall fracture was less pronounced in Scots pine latewood.

Colonization of weathered surfaces by fungi was more pronounced in pines than yellow cedar (Fig. 3.31e, 3.33e, 3.35). In the pines, fungi colonized voids created from distortion of earlywood and latewood tracheids, lumens of degraded tracheids and degraded resin canals.

Microstructural degradation as a result of weathering was less pronounced in PF resin treated Scots pine, southern pine and yellow cedar samples compared to that in untreated controls. The transverse surfaces of PF-treated Scots pine samples weathered for 79 or 100 days were free of macro-checks (Fig. 3.36a, d). There was less degradation of resin canals (Fig. 3.36f). Earlywood and latewood tracheids were free of distortion (Fig. 3.36b, e and f), but micro-checks were formed in latewood cell walls (Fig. 3.36c). Erosion of middle lamellae in earlywood and latewood was minimal.
Figure 3.36 – SEM images of Scots pine samples treated with 20% PF resin and exposed to 79 (a-c) or 100 (d-f) days of natural weathering, showing: (a) entire SEM sample; (b) earlywood; (c) earlywood and latewood; (d) entire SEM sample; (e) earlywood; (f) resin canal in latewood

Small radial checks resulting from separation of rays developed at the transverse surface of PF resin treated Scots pine after 280 days of weathering (Fig. 3.37a). Resin canals were still intact (Fig. 3.37b). Earlywood and latewood tracheids had maintained their structure, although cell walls were thinner (Fig. 3.37c). Erosion of middle lamellae had occurred, but was less pronounced than that in unmodified exposed controls (Fig. 3.37b and c). Cell walls adjacent to lumens that were filled with resin had less pronounced degradation (Fig. 3.37b and c).
Degradation of PF-treated Scots pine samples was more prominent after 606 days of exposure. Earlywood cell walls had thinned and eroded, but cell corners and cell walls adjacent to resin were still intact (Fig. 3.37e). Latewood cells had distorted and some of the lumens were sealed off as a result. Erosion of middle lamellae in latewood formed voids, which were colonized by mould (Fig. 3.37f). However, checking was not pronounced (Fig. 3.37e).

Figure 3.37 – SEM images of Scots pine samples treated with 20% PF resin and exposed to 280 (a-c) or 606 (d-f) days of natural weathering, showing: (a) entire SEM sample; (b) resin canal in latewood; (c) earlywood and latewood; (d) earlywood and latewood, (e) earlywood and (f) latewood at high magnification. Arrows indicate: (1) resin filling; (2) less degraded cell corner; (3) colonization by fungi
Southern pine samples treated with PF resin and exposed to the weather for 100 days looked similar to similarly exposed PF-treated Scots pine samples, although southern pine samples had more micro-checks in cell walls (Fig. 3.38b and c). Only minor checking was present in samples exposed to 424 days of weathering (Fig. 3.38d). Earlywood and latewood cell walls were thinner, fractured, and were separated at middle lamellae (Fig. 3.38e and f). Such degradation did not occur in thicker cell walls that were heavily bulked by PF resin or in cell walls adjacent to lumens that were filled with resin (Fig. 3.38e). Fungi colonized lumens of some earlywood tracheids and lumens and voids in latewood tracheids (Fig. 3.38f).

Figure 3.38 – SEM images of southern pine samples treated with 20% PF resin and exposed to 100 (a-c) or 424 (d-f) days of natural weathering, showing: (a) entire SEM sample; (b) earlywood; (c) resin canal in latewood; (d) entire SEM sample; (e) earlywood; (f) latewood. Arrows indicate: (1) micro-checks; (2) resin filled lumens
PF resin treated yellow cedar samples exposed to 100 days of natural weathering were free of checks (Fig. 3.39a). A PF resin coating was evident at the surface of some samples (Fig. 3.39b). Erosion of middle lamellae was barely discernable (Fig. 3.39c). Micro-checks were formed in latewood cell walls and along middle lamellae (Fig. 3.39b and c). Treated yellow cedar degraded differently to the pines during weathering. There was no checking of samples exposed for prolonged periods of time (424 days), but voids were formed in earlywood from the thinning, distortion and collapse of earlywood tracheids (Fig. 3.39d and e). Erosion of middle lamellae was severe in samples exposed to 424 days of weathering (Fig. 3.39f).
Figure 3.39 – SEM images of yellow cedar samples treated with 20% PF resin and exposed to 100 (a-c) or 424 (d-f) days of natural weathering, showing: (a) entire SEM sample; (b) earlywood and latewood; (c) latewood showing cell wall micro-check; (d) entire SEM sample; (e) earlywood and latewood; (f) earlywood and latewood at high magnification. Note the PF resin filled lumen

The degradation of samples treated with PF resin and lignin stabilizer was very similar to that of samples treated with PF resin. The transverse surface of treated Scots pine samples exposed to 79 days of weathering was largely free of large checks. However, middle lamellae in earlywood and latewood had begun to erode and some cell walls had separated (Fig. 3.40c). Separation of latewood cell walls was more pronounced after 100 days of exposure (Fig. 3.40f).
Figure 3.40 – SEM images of Scots pine samples treated with 20% PF resin and 2% lignin stabilizer and exposed to 79 (a-c) or 100 (d-f) days of natural weathering, showing: (a) entire SEM sample; (b) earlywood and latewood; (c) earlywood and latewood at high magnification; (d) entire SEM sample; (e) earlywood; (f) resin canal in latewood.

Microstructural changes to PF-Lignostab treated Scots pine samples exposed to 280 or 606 days of weathering were similar to those of PF-treated Scots pine samples exposed outdoors for prolonged periods of time (Fig. 3.41a-c), except erosion of earlywood cell walls and distortion of latewood cell walls in PF-Lignostab treated pine appeared to be more severe (Fig. 3.41e and f). However, degradation of earlywood cell corners and cell walls adjacent to lumens filled with resin was less pronounced (Fig. 3.41d and e). Lumens in earlywood cells and voids in latewood were colonized by fungi.
Figure 3.41 – SEM images of Scots pine samples treated with 20% PF resin and 2% lignin stabilizer and exposed to 280 (a-c) or 606 (d-f) days of natural weathering, showing: (a) entire SEM sample; (b) resin canal at earlywood and latewood interface; (c) latewood at high magnification; (d) earlywood and latewood, (e) earlywood; (f) latewood. Arrows indicate: (1) PF resin filled lumens; (2) less degraded cell corners; (3) fungal colonization in voids between distorted latewood tracheids.

There was little difference in the degradation of PF-Lignostab treated southern pine samples exposed to 100 days of weathering compared to that of samples treated with PF resin (Fig. 3.42a-c). Degradation of PF-Lignostab treated southern pine became more pronounced with prolonged exposure to the weather, as expected. Earlywood tracheids became much thinner and erosion of middle lamellae in latewood was pronounced (Fig 3.42e and f).
Figure 3.42 – SEM images of southern pine samples treated with 20% PF resin and 2% lignin stabilizer and exposed to 100 (a-c) or 424 (d-f) days of natural weathering, showing: (a) resin canal in latewood; (b) earlywood; (c) cell wall micro-checks in latewood; (d) entire SEM sample; (e) earlywood; (f) latewood. Arrows indicate: (1) PF resin filling in lumens; (2) less degraded cell corner; (3) colonization of latewood lumens by fungi.

There was more pronounced erosion of earlywood tracheids in PF resin and Lignostab treated yellow cedar samples exposed to 100 days of weathering compared to that of samples treated with PF resin (Fig. 3.42 b and c). Checks were evident at the transverse surface of yellow cedar samples exposed outdoors for 424 days (Fig. 3.42e). Earlywood tracheid walls became very thin, but latewood tracheids were less distorted than those of samples treated with PF resin (Fig. 3.42f). However, there appeared to be more pronounced fungal colonization of earlywood.
Figure 3.43 – SEM images of yellow cedar samples treated with 20% PF resin and 2% lignin stabilizer and exposed to 100 (a-c) or 424 (d-f) days of natural weathering, showing: (a) entire SEM sample; (b) earlywood and latewood; (c) earlywood at high magnification; (d) latewood under high magnification; (e) entire SEM sample; (f) earlywood and latewood. Arrows indicate: (1) PF resin filled lumens; (2) colonization of voids in tracheids by fungi.

In summary, degradation at the transverse surfaces of Scots pine, southern pine and yellow cedar treated with 20% PF resin became more prominent with increasing exposure to the weather. Checks were formed in treated pines after 100 days of exposure (Fig. 3.36d, 3.38a). Compared to the pines, the transverse surface of PF resin treated yellow cedar was less severely checked even after 424 days of weathering, but voids were formed in earlywood (Fig. 3.39). However, there was micro-checking of cell walls in all three PF-treated softwood species.
Cell wall degradation was more pronounced in PF resin treated yellow cedar samples than in treated and weathered southern pine samples (Fig. 3.39e, f). For example, there was severe thinning and distortion of earlywood and latewood tracheids in yellow cedar samples, whereas PF-treated southern pine samples showed fracture of earlywood cell walls, but less thinning and distortion of cell walls (Fig. 3.38e, f). Erosion of middle lamellae was minute in all species treated with PF resin, until outdoor exposure exceeded 100 days (Fig. 3.37b, c, 3.38e, f, 3.39e, f). Fungi were observed in lumens and voids in earlywood and latewood tracheids, respectively, in all three softwoods (Fig. 3.37f, 3.38f, 3.39f).

The addition of lignin stabilizer to PF resin had little protective effect on the microstructure of treated pines. On the contrary, there was some evidence that microstructural degradation was more pronounced in samples treated with PF-Lignostab than in samples treated with PF resin (Fig. 3.41, 3.42d-f, 3.43d-f). For example, distortion of latewood tracheids in Scots pine and erosion of middle lamellae in southern pine was slightly greater in samples treated with PF-Lignostab than in samples treated with PF resin. Adverse effects of lignin stabilizer were also observed in treated yellow cedar.

3.4 Discussion

In the introduction to this chapter, I hypothesized the addition of the lignin stabilizer, Lignostab, to PF resin would have beneficial effects on the photostability of wood or paper treated with PF resin. My results do not support this hypothesis, with one exception. The lignin stabilizer reduced photo-induced darkening of yellow cedar and Scots pine veneers treated with 20% PF resin, and had a positive effect at reducing yellowing of PF-treated Scots pine veneers. My finding that Lignostab restricts darkening of PF-treated veneers accords with that of Evans et al. (2013), who found that Lignostab restricted darkening of PF-treated radiata pine veneers exposed to the weather for 83 days, and the findings of Liu (2011) that Lignostab restricted darkening of PF-treated yellow cedar veneers exposed to 50 days of natural weathering. However, my finding that yellowing of PF-treated Scots pine veneers was restricted by
Lignostab did not accord with the findings of Evans et al. (2013) or Liu (2011). The lignin stabilizer, Lignostab, is designed to reduce production of coloured chromophores produced by photodegradation of lignin, according to Hayoz et al. (2003) and Schaller and Rogez (2007). Hence, the ability of Lignostab to reduce darkening of PF-treated wood veneers accords with its photoprotective properties. PF resin is an antioxidant and a good UV absorber, so the resin is susceptible to photodegradation, and produces coloured compounds that discolour PF-treated wood (Morawetz, 1949; Tarkow et al., 1966; Kol’tsov et al., 1985; Kielmann & Mai, 2016a, 2016b).

My results indicated that Lignostab was unable to restrict tensile strength losses of PF-treated wood veneers, a finding that accords with those of Evans et al. (2013), who observed that Lignostab did not reduce strength losses of PF-treated yellow cedar veneers exposed outdoors to 50 days. However, Evans et al. (2013) found that Lignostab was able to restrict reddening of PF-treated (10%) radiata pine veneers and weight losses of PF-treated (30%) yellow cedar veneers. In comparison, I found that the lignin stabilizer had no significant effect on these properties of veneers when they were treated with 20% or 30% PF resin and exposed to natural weathering. However, there was a positive effect of Lignostab on the weight losses of veneers treated with 20% PF resin. The differences between my findings and those of Evans et al. (2013) may be due to different outdoor weathering conditions that my samples were exposed to compared to those of Evans et al. (2013). Other additives are available to reduce polymer degradation, and they might be more successful than Lignostab at reducing photodegradation of PF-treated wood. I screen such additives in Chapter 5.

My results accord with previous observations that PF resin can photostabilize wood, and they extend such observations in two important ways. I tested species that have not been examined before, and my SEM observations include results for PF-treated wood that had been exposed to the weather for prolonged periods of time. My SEM observations provide some new insights into the photoprotective
effects of PF resin on wood. Firstly, PF resin slows down the erosion of the middle lamella and thinning of cell walls, possibly because cell walls are bulked with a polymer (PF resin) that is less susceptible to photodegradation than wood. This observation indicates that effective PF resin treatments should maximize bulking of cell walls, while minimizing potential damage caused by the treatment. There are also potential species x treatment interactions. PF resin treated Scots pine became more yellow and was more resistant to tensile strength loss after weathering compared to PF-treated yellow cedar, even though treated pine veneers had lower weight gain due to treatment than cedar veneers. SEM observations showed that treated southern pine samples were more resistant to microstructural degradation than treated yellow cedar. These observations suggest that the effects of PF resin treatment against weathering may depend on wood species. I further examine species x treatment interactions for PF-treated Scots and southern pine boards in the next chapter.

The ability of PF resin treatments to restrict colonization of treated veneer and paper by mould was unexpected, because PF resin is not biocidal. It is possible that bulking of wood cell walls and kraft fiber with PF resin prevented cell wall penetration by fungal hyphae and halted the spread of mould (Duncan, 1963). In addition to the ability of the ‘hard’ resin to prevent colonization of weathered surface by mould fungi, it may have reduced support for fungal colonization at treated surfaces due: (1) to reduction in voids where water can collect; (2) restricting availability of nutrients, such as sugars, resulting from photodegradation of wood (Brischke & Melcher, 2015; Schoeman & Dickinson, 1997).

3.5 Conclusions

I conclude that the lignin stabilizer, Lignostab, had limited ability to improve effectiveness of PF resin as a photoprotective treatment for wood or paper. Lignostab was able to restrict wood veneers treated with 20% PF resin from becoming darker, when they were exposed to natural weathering. Such an effect was less pronounced when veneers were treated with 30% PF resin (and Lignostab). Hence, it is
more beneficial to employ a lignin stabilizer for the treatment of wood with lower (20%) rather than higher (30%) concentrations of PF resin. Other photostabilizers, for example, UV absorbers, hindered amine light stabilizers or pigments may be better than Lignostab at enhancing the photoprotective effects of PF resin treatment, and they will be investigated in Chapter 5.

I have extended observations of the effectiveness of PF resin as a photoprotective treatment for wood and provided explanations for how the treatment protects wood from photodegradation and colonization by mould fungi. There was no additional benefit of treating paper with PF resin above 10% concentration. Therefore, I conclude that treatment with 10% PF resin is optimum for the photoprotection of paper overlays used outdoors, but higher concentrations are better for wood.
Chapter 4: Surface Protection of Scots pine and Southern Pine Deck Boards with Phenol Formaldehyde Resin and Lignin Stabilizer

4.1 Introduction

A previous study found that the lignin stabilizer, Lignostab, improved the ability of low molecular weight PF resin (10%) to reduce colour changes of veneers exposed to the weather (Evans et al., 2013). This finding was confirmed by some of my results in Chapter 3. My results also showed that treatment of wood veneers with solution containing 20% PF resin provided better photoprotection than treatment with 10% PF resin, and that outdoor performance of PF resin treated veneers was affected by wood species. I hypothesize that the lignin stabilizer, Lignostab, will have the same effect on the discolouration of solid deck boards treated with modified PF resin. To test this hypothesis, I treated southern pine and Scots pine deck board samples with modified and unmodified PF resins (20% PF and 2% Lignostab v. 20% PF) using two treatment methods (dip and vacuum) and exposed samples to natural weathering. The effectiveness of PF resin treatments at protecting wood from the deleterious effects of weathering are related to level of treatment, as mentioned above. Therefore, I further hypothesized that the effectiveness of treatments at reducing checking would vary with retention of PF resin in treated boards resulting from the use of two different treatment method (momentary dip v. vacuum impregnation).

4.2 Materials and methods

4.2.1 Experimental design and statistical analyses

My experiment examined the ability of different PF resin envelope treatments (dip 20% PF, dip 20% PF and 2% Lignostab, vacuum 20% PF, vacuum 20% PF and 2% Lignostab) to photostabilize deck boards machined from two different pine species (Scots pine, southern yellow pine) and exposed to 80 days of natural weathering. Decking samples were cut from five Scots pine and five southern pine boards to
provide replication at the higher level, and to account for random variation between wood boards and decking samples. Decking samples from each block were randomly assigned to the different treatments.

Analysis of variance (ANOVA) was used to examine the effects of treatments on various measures of the performance of deck boards exposed to the weather for 80 days: (1) colour change; (2) surface checking; (3) surface roughness; (4) contact angle; (5) cupping of samples. Results were analyzed using Genstat Version 12.1, 17.1, 18.1, 18.2 (VSN International, 2009, 2014, 2016). Some data were transformed to meet the assumptions of ANOVA (normality of residuals, homogeneity of variance, independence of sampling, independent observations). Statistically significant ($p<0.05$) results are plotted and comparison of individual means can be carried out using error bars (± standard error of difference) derived from ANOVA, or least significant difference (LSD) bars derived from Fisher’s least significant difference test (Williams & Abdi, 2010).

4.2.2 Preparation and characterization of Scots and southern pine deckboards samples

Scots pine and southern pine decking samples were each prepared from five different kiln dried flat-sawn boards. The boards were ripped to width using a sliding table saw (Martin T75 PreX, Otto Martin Maschinenbau GmbH & Co. KG, Otteobeuren, Germany), planned to thickness using a rotary planer (Martin T54, Otto Martin Maschinenbau GmbH & Co. KG, Otteobeuren, Germany) and cross-cut to length using a chop saw (Omga® T55-300, OMGA, Inc., South Bend, I.N., U.S.A.). The final dimensions of deck board samples were 150 mm (longitudinal) x 85 mm (tangential) x 19 mm (radial). End grain of samples was sealed with a marine epoxy resin (PC Products PC-11®, Protective Coating Company, Allentown, P.A. U.S.A.). The deck board samples were conditioned in a constant climate room (20 ± 1 °C and 65 ± 5% r.h.) for a minimum of seven days.
Deck board samples were weighed after they were conditioned for 10 days. A 150 mm x 25 mm x 19 mm offcut from each conditioned board was oven dried at 105 ± 5 °C for 24 hours, weighed using a digital analytical balance (PG5002-S, Mettler Toledo, Switzerland), and its moisture content was calculated. The weights of treated and conditioned boards were adjusted accordingly to obtain weight gains due to treatment.

4.2.3 Synthesis and preparation of modified PF resin

Phenol formaldehyde treatment solutions were diluted with tap water to 20% from parent PF resin (45.89% solids) solutions supplied by Arclin USA Inc. (Springfield, O.R. U.S.A.). The chemical composition of a typical batch of PF resin is described in Chapter 3 (Section 3.2.2.2). Lignin stabilizer, Lignostab® 1198, provided by CIBA Specialty Chemicals Corp (Tarrytown, N.Y. U.S.A.) was dissolved in tap water and added to diluted PF resin solutions.

4.2.4 Treatment of deckboard samples

Deck board samples were individually dip- or vacuum-impregnated with PF resin at room temperature. Dip-impregnation involved submerging samples in treatment solutions for 10 minutes at atmospheric pressure. For vacuum-impregnation, individual samples were placed in a glass vacuum cylinder, measuring 130 mm (diameter) x 18 mm (height). A rotary vane vacuum pump (ED200A, Edwards High Vacuum International Ltd., Crawley, U.K.) was used to pull a vacuum (-90 kPa) in the vacuum cylinder for 10 minutes. Vacuum within the cylinder was used to draw in the treatment solution. The sample remained submerged in the solution for an additional 10 minutes. Impregnated samples were removed from the cylinder, placed inside a beaker for 30 seconds to drain off excess solution, air-dried in a climate control room for 16 hours, and cured in a convection oven (G01305A, Lindberg/Blue M™, Riverside, M.I., U.S.A.) at 128 ± 5 °C for 3 hours (a modified curing schedule used by Liu (2011)). Treatments for all three experiments are summarized in Table 4.1 below.
Samples that were vacuum-treated with PF resin had significantly ($p=0.015$) greater weight gains due to treatment than those dipped in resin, as expected. Weight gains of southern pine samples that were vacuum-impregnated with PF resin were significantly ($p=0.015$) greater than similarly treated Scots pine samples, but there was little difference in the weight gains of samples from the two species that were dip-treated. There were no consistent differences in weight gain of samples treated with 20% PF resin and those treated with 20% PF and Lignostab.

Table 4.2 – Weight gains of Scots pine and southern pine deck boards as a result of dipping or vacuum impregnation

<table>
<thead>
<tr>
<th>Impregnation</th>
<th>Treatment solution</th>
<th>Treatment weight gain (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Scots pine (SD)</td>
<td>Southern pine (SD)</td>
<td></td>
</tr>
<tr>
<td>Dip</td>
<td>20% PF</td>
<td>0.8 (0.2)</td>
<td>1.0 (0.3)</td>
<td></td>
</tr>
<tr>
<td>Dip</td>
<td>20% PF + 2% Lignostab</td>
<td>0.8 (0.2)</td>
<td>1.1 (0.2)</td>
<td></td>
</tr>
<tr>
<td>Vacuum</td>
<td>20% PF</td>
<td>1.5 (0.6)</td>
<td>3.0 (0.6)</td>
<td></td>
</tr>
<tr>
<td>Vacuum</td>
<td>20% PF + 2% Lignostab</td>
<td>1.7 (0.7)</td>
<td>2.7 (0.7)</td>
<td></td>
</tr>
</tbody>
</table>

A 19 mm x 19 mm x 5 mm cross-section was cut from the side of each sample. Depth of envelope penetration was measured from the tangential and radial sides of cross-sections using a digital caliper (CD-6”ASX, Mitutoyo Corp., Kawasaki, Japan). Weight gain of pine decking was recalculated according to the depth of treatment penetration. Table 4.3 shows the adjusted treatment weight gains.
4.2.5 Weathering trials

Scots and southern pine deck board samples were predrilled using a 4.76 mm diameter drill bit driven by a 419.1 mm swing drill press (Delta Machinery Inc., Hollandale, M.S., U.S.A.). Each drill hole was located 40 mm from the ends of the samples and 12 mm from the sides. The surface of each hole was widened using a 3/8” (9.52 mm) countersunk drill bit. Six Scots pine and six southern pine deck board samples (treated and untreated) from each experimental block were fastened using 8 x 2.5” (203 mm x 63.5 mm) Paulin Dura Grip Duradized II deck screws (H. Paulin & Co., Toronto, O.N. Canada) to preservative-treated strips of wood measuring 1400 mm (length) x 50 mm (width) x 50 mm (thickness). For each block of 12 samples, an untreated wooden board measuring 150 mm (length) x 60 mm (width) x 19 mm (thickness) was fastened to each end of a row of 12 samples to prevent the sides of samples on the ends of the rows from being exposed to the weather. Each of the five blocks of samples were fastened using decking screws to different decking racks, each with sub-frame and legs made from untreated yellow cedar and maple (Acer spp.), respectively. The deck boards were spaced 10 mm apart and had 12 mm of overhang from sub-frame (Fig. 4.1). The order of deck boards within each rack was randomized. Each board was mounted bark side up (convex). Deck boards were exposed horizontally to the weather on the UBC campus for 80 days from March 4th to May 22nd, 2013. Weathering conditions during the weathering trial are shown in Table 4.4.

Table 4.3 – Weight gain of treated pine deck boards in the surface layer of wood that was penetrated by PF resin

<table>
<thead>
<tr>
<th>Impregnation</th>
<th>Treatment solution</th>
<th>Treatment weight gain (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Scots pine</strong> (SD)</td>
<td><strong>Southern pine</strong> (SD)</td>
</tr>
<tr>
<td>Dip</td>
<td>20% PF</td>
<td>24.1 (10.0)</td>
<td>17.3 (5.3)</td>
</tr>
<tr>
<td>Dip</td>
<td>20% PF + 2% Lignostab</td>
<td>27.6 (12.3)</td>
<td>29.8 (14.6)</td>
</tr>
<tr>
<td>Vacuum</td>
<td>20% PF</td>
<td>19.0 (6.0)</td>
<td>16.3 (4.5)</td>
</tr>
<tr>
<td>Vacuum</td>
<td>20% PF + 2% Lignostab</td>
<td>33.5 (13.1)</td>
<td>42.2 (8.0)</td>
</tr>
</tbody>
</table>
Table 4.4 – Weather conditions in Vancouver, British Columbia, Canada during the 80-day exposure trial of PF-treated and untreated Scots and southern pine deck board samples

<table>
<thead>
<tr>
<th>Month</th>
<th>Temperature (°C)</th>
<th>Total Precipitation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum(^1)</td>
<td>Mean</td>
</tr>
<tr>
<td>March</td>
<td>2013</td>
<td>10.45</td>
</tr>
<tr>
<td>April</td>
<td>2013</td>
<td>12.79</td>
</tr>
<tr>
<td>May</td>
<td>2013</td>
<td>17.08</td>
</tr>
</tbody>
</table>

\(^1\)Average maximum and minimum daily temperatures
Data collected for Vancouver International Airport, [http://climate.weather.gc.ca/historical_data/search_historic_data_e.html](http://climate.weather.gc.ca/historical_data/search_historic_data_e.html)

Figure 4.1 – Treated and untreated Scots and southern pine deck board samples at the start of the weathering trial: (a) samples from the five different blocks; (b) samples mounted on weathering racks; (c-d) close up of weathering racks
4.2.6 Assessment of the photoprotective effects of PF resin treatments on the properties of Scots and southern pine deck board samples

Weathered deck board samples were retrieved from the test site and conditioned in a constant climate control room for a minimum of seven days. Samples were scanned at 1200 dpi resolution, 256 colours and 100% scale using a flatbed scanner (Microtek® Scanmaker® i800, Microtek International Inc., Hsinchu, Taiwan). Samples were scanned before and after treatment, and again after weathering for 80 days. Samples weathered for 2 years were gently rubbed using a damp cloth to remove the grey weathered layer and re-scanned.

Colour measurements of deck board samples used the ‘specular component included’ (SCI) mode of a spectrophotometer (Minolta CM-2600D, Konica Minolta, Tokyo, Japan). Colour is expressed using the CIE 1976 L*a*b* Space System, as described in Chapter 3 (Section 3.2.4.2). Colour of deck boards was measured before treatment, after treatment and after weathering (Liu, 2011). A paper mask containing 4.7 mm diameter holes was made for each deck board sample to ensure colour measurements were made at precisely the same place at each of the measurement intervals (Fig. 4.2) (Vollmer, 2011). Changes in colour at exposed surfaces of samples during weathering are expressed as the ratio of colour parameters (L*, a*, b*) after weathering divided by parameters before weathering. A ratio above or below 1 indicates increase or decrease in colour parameter during weathering, respectively. Colour of samples weathered for 25 months was measured at the surface that was not cleaned.
Initial contact angle ($C_i$) of water droplets on surfaces of deck boards was used as a measure of the hydrophobicity of surfaces. Contact angle was measured using the sessile drop method and a goniometer (KSV CAM 101, KSV Instruments Ltd., Espoo, Finland) (Fig. 4.3). All measurements were carried out at room temperature. A 5 µL droplet of distilled water was placed at a random location on the surface of each sample. The spread of each droplet was imaged every 48 milliseconds, and droplets were imaged at 0.288, 0.336 and 0.384 seconds after they stabilized and formed stable and sharp images. The images were used to calculate the initial contact angle of droplets on each sample. Contact angles were calculated using a Young-Laplace algorithm within CAM 200 software (KSV Instruments Ltd., Espoo, Finland) (KSV Instruments, 2007). Initial left and right contact angles were averaged for each droplet and contact angles for each of the three images were averaged to obtain a mean for each sample.
The length and width of the ten largest surface checks that developed at the surface of each weathered deck board sample was measured. Checks originating in end grain, fasteners or around knots were not measured. Length and width of checks were measured using a transparent 30 cm long Perspex ruler and a calibrated optical magnifying glass, respectively, as previously described by Evans et al. (2010). Length and width measurements were used to calculate the area of each check.

The surface roughness of weathered deck board samples was measured using an AltiSurf® 500 confocal profilometer (Altimet SAS, Thonon-les-bains, France) (Fig. 4.4). A linear profile 75 mm from end grain and across the entire width of each sample (perpendicular to the grain) was obtained. Line-profiling used a 3 mm (3000 µm to 92 nm) probe at 10 µm spacing between measurement points and a scan speed of 1 mm/s. The following roughness parameters were obtained using AltiMap® Premium version 6.2 image analysis software (Altimet SAS, Thonon-les-bains, France): $R_a$, arithmetic average of surface roughness; $R_{RSM}$, root mean squared of surface roughness; and $R_z$, maximum profile valley depth.
Figure 4.4 – (a) Confocal profilometer used to measure the surface roughness of Scots and southern pine deck board samples; (b) image showing surface of a southern pine board being scanned with a 3 mm probe

Cupping of deck boards was measured using a Mitutoyo ID-C1012EB digital dial gauge (Mitutoyo Corp. Kawasaki-shi, Japan) after boards were treated and again after they were weathered. The wide tangential surface and one side of each sample were held against a flat horizontal table and a vertical reference fence, respectively. Cupping of samples was measured at three locations, 30 mm, 75 mm and 120 mm from end grain.

4.3 Results

The effects of treatment, species and interaction of treatment x species on the various measures used to assess the weathering of deck board samples are shown in Table 4.5. ‘Treatment’ had significant effects on all weathering parameters, with the exception of cupping, roughness and contact angle. ‘Species’ had significant effects on all weathering parameters, except for lightness and yellowness, lightness ratio, cupping and roughness. Interaction of treatment x species was significant for one colour parameter (lightness) and all checking parameters (length, width and area).
Table 4.5 – Significant effects of PF resin treatment, species and interactions between treatment and species on weathering parameters used to assess the performance of Scots and southern pine decking samples exposed to 80 days of natural weathering

<table>
<thead>
<tr>
<th>Weathering parameters</th>
<th>Experimental factors</th>
<th>Treatment</th>
<th>Species</th>
<th>Treatment x species</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Colour</strong></td>
<td></td>
<td>***</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Ratio of change in lightness</td>
<td></td>
<td>***</td>
<td></td>
<td>NS</td>
</tr>
<tr>
<td>Ratio of change in redness</td>
<td></td>
<td>***</td>
<td>***</td>
<td>NS</td>
</tr>
<tr>
<td>Ratio of change in yellowness</td>
<td></td>
<td>***</td>
<td>**</td>
<td>NS</td>
</tr>
<tr>
<td><strong>Ten largest checks</strong></td>
<td></td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Average area</td>
<td></td>
<td>***</td>
<td></td>
<td>NS</td>
</tr>
<tr>
<td>Average length</td>
<td></td>
<td>**</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Average width</td>
<td></td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td><strong>Cupping</strong></td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td><strong>Roughness</strong></td>
<td></td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td><strong>Contact angle</strong></td>
<td></td>
<td>NS</td>
<td>**</td>
<td>NS</td>
</tr>
</tbody>
</table>

*** = p<0.001; ** = p<0.01; * = p<0.05; NS = p>0.05 (not significant)

Table 4.6 shows significant treatment x species interaction on lightness ratio (p=0.036) and average check width (p=0.038) of deck boards exposed to 25 months of natural weathering. In addition, treatment and species had significant (p<0.05) effects on all other parameters.

Table 4.6 – Significant effects of PF resin treatment, species and interactions between treatment and species on weathering parameters used to assess the performance of Scots and southern pine decking samples exposed to 25 months of natural weathering

<table>
<thead>
<tr>
<th>Weathering parameters</th>
<th>Experimental factors</th>
<th>Treatment</th>
<th>Species</th>
<th>Treatment x species</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Colour</strong></td>
<td></td>
<td>***</td>
<td>**</td>
<td>*</td>
</tr>
<tr>
<td>Ratio of change in lightness</td>
<td></td>
<td>***</td>
<td>**</td>
<td>NS</td>
</tr>
<tr>
<td>Ratio of change in redness</td>
<td></td>
<td>***</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Ratio of change in yellowness</td>
<td></td>
<td>***</td>
<td>**</td>
<td>NS</td>
</tr>
<tr>
<td><strong>Ten largest checks</strong></td>
<td></td>
<td>***</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Average area</td>
<td></td>
<td>***</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Average length</td>
<td></td>
<td>NS</td>
<td>**</td>
<td>NS</td>
</tr>
<tr>
<td>Average width</td>
<td></td>
<td>***</td>
<td>NS</td>
<td>*</td>
</tr>
</tbody>
</table>

*** = p<0.001; ** = p<0.01; * = p<0.05; NS = p>0.05 (not significant)

4.3.1 Appearance of Scots and southern pine deck boards after treatment and weathering

Envelope treatment with PF resin on its own or containing lignin stabilizer made Scots pine and southern pine deck boards redder. This red colouration was blotchy and more prominent in Scots pine.
samples (Fig. 4.5, 4.6), whereas treated southern pine deck boards had milder and more uniform red colouration (Fig. 4.7, 4.8). Earlywood of Scots pine sapwood was redder and darker than latewood or earlywood in heartwood. Vacuum impregnation imparted a red tint to Scots pine latewood. There were also differences in the colour of earlywood and latewood due to treatment (Fig. 4.6). Addition of lignin stabilizer to PF resin did not affect the colour of either treated Scots pine or treated southern pine deck boards.

Treated samples became less red and developed a yellow colouration as a result of weathering, as expected. Yellowing occurred in earlywood and latewood of treated Scots pine and southern pine deck boards. The appearance of deck board samples before and after weathering can be assessed using scanned images in Figure 4.5 to Figure 4.8. The red colour in the earlywood in sapwood in treated Scots pine samples was lost after 80 days of weathering. Weathered samples treated with PF resin and lignin stabilizer were very similar to those treated with PF resin on its own. Some black staining due to mould was present in treated and weathered Scots pine and southern pine samples. Black staining due to fastener corrosion also occurred. Checking was more pronounced in untreated controls, as expected. Checks in untreated southern pine samples were larger than those in untreated Scots pine samples. Checks were also larger and more numerous in controls that were vacuum-impregnated with water than controls that were dip-impregnated. Weathered surfaces of untreated boards were grey in colour.

Appearance of deck board samples after 25 months of natural weathering can be seen in Figure 4.11 and Figure 4.12. Surface checks in PF resin treated pine boards were narrow compared to those in untreated boards. There was no difference in the surface checking of dip- and vacuum-treated Scots pine samples, but checks in vacuum-treated southern pine samples were narrower than those in boards treated by dipping. Weathered surface of PF resin treated Scots pine and southern pine deck boards were colonized by mould, and the treated surfaces became darker as a result. The yellowing of PF-treated
surfaces could be seen through the mould (Fig. 4.11b, c, e, f, 4.12b, c, e, f). Weathered surfaces of untreated pine boards were also covered in mould, but the surface was bleached from weathering and the untreated boards were grey. The mould could be wiped off with a damp cloth. Bottom sections of scanned images in Figure 4.11 and Figure 4.12 show areas of boards that were cleaned. Colour of envelope treated samples was retained, which was unexpected. Cleaned surfaces of PF-treated Scots pine were yellower than those treated with PF resin and lignin stabilizer. Yellowing was more pronounced in southern pine boards that were vacuum-impregnated than those that were dip-treated. Earlywood of treated Scots pine and southern pine was yellower than latewood, which greyed during weathering. Furthermore, fibers at the surface of treated Scots pine and southern pine boards were resistant to erosion and grain raising, unlike those at the surface of untreated samples. Scanned images of all samples are appended to this thesis (Appendix 2).
Figure 4.5 – Scanned images of dip-treated and untreated Scots pine decking samples before and after weathering for 80 days: (a) unweathered control; (b) unweathered sample treated with PF resin; (c) unweathered sample treated with PF resin and Lignostab; (d) weathered control; (e) weathered sample treated with PF resin; (f) weathered sample treated with PF resin and Lignostab. Scale bar is 10 mm
Figure 4.6 – Scanned images of vacuum-treated and untreated Scots pine decking samples before and after weathering for 80 days: (a) unweathered control; (b) unweathered sample treated with PF resin; (c) unweathered sample treated with PF resin and Lignostab; (d) weathered control; (e) weathered sample treated with PF resin; (f) weathered sample treated with PF resin and Lignostab. Scale bar is 10 mm.
Figure 4.7 – Scanned images of dip-treated and untreated southern pine decking samples before and after weathering for 80 days: (a) unweathered control; (b) unweathered sample treated with PF resin; (c) unweathered sample treated with PF resin and Lignostab; (d) weathered control; (e) weathered sample treated with PF resin; (f) weathered sample treated with PF resin and Lignostab. Scale bar is 10 mm
Figure 4.8 – Scanned images of vacuum-treated and untreated southern pine decking samples before and after weathering for 80 days: (a) unweathered control; (b) unweathered sample treated with PF resin; (c) unweathered sample treated with PF resin and Lignostab; (d) weathered control; (e) weathered sample treated with PF resin; (f) weathered sample treated with PF resin and Lignostab. Scale bar is 10 mm.
Figure 4.9 – Scanned images showing dip and vacuum-treated Scots pine decking samples weathered for 80 days: (a) dip-impregnated with PF resin; (b) dip-impregnated with PF resin and Lignostab; (c) vacuum-impregnated with PF resin; (d) vacuum-impregnated with PF resin and Lignostab. Scale bar is 10 mm
Figure 4.10 - Scanned images showing dip and vacuum-treated southern pine decking samples weathered for 80 days: (a) dip-impregnated with PF resin; (b) dip-impregnated with PF resin and Lignostab; (c) vacuum-impregnated with PF resin; (d) vacuum-impregnated with PF resin and Lignostab. Scale bar is 10 mm
Figure 4.11 – Scanned images of treated and untreated Scots pine decking samples before and after weathering for 25 months: (a) dip-impregnated with water; (b) dip-impregnated with PF resin; (c) dip-impregnated with PF resin and Lignostab; (d) vacuum-impregnated with water; (e) vacuum-impregnated with PF resin; (f) vacuum-impregnated with PF resin and Lignostab. Scale bar is 10 mm
Figure 4.12 – Scanned images of treated and untreated southern pine decking samples before and after weathering for 25 months: (a) dip-impregnated with water; (b) dip-impregnated with PF resin; (c) dip-impregnated with PF resin and Lignostab; (d) vacuum-impregnated with water; (e) vacuum-impregnated with PF resin; (f) vacuum-impregnated with PF resin and Lignostab. Scale bar is 10 mm
4.3.2 Colour parameters (L*, a*, b*)

Samples dip- or vacuum-treated with PF resin became darker as a result of outdoor exposure (Fig. 4.13). The untreated controls also darkened, and there was no significant (p>0.05) difference in the darkening of the untreated controls and samples treated with 20% PF resin. The lignin stabilizer, Lignostab, reduced the darkening of boards that were vacuum- or dip-treated with PF resin, but Lignostab was more effective in boards that were vacuum-treated.

Figure 4.13 – Change in lightness of dip and vacuum (vac) treated and untreated decking samples exposed to 80 days of natural weathering. Lightness is expressed as ratio of L* parameter after weathering/L* parameter before weathering. Ratio of 1 indicates no change in lightness of samples after weathering. Ratios below 1 indicate darkening of samples after weathering. Note that the results are averaged across species. Error bars are ± standard error of difference (p<0.001) from analyses of variance.
Treated samples became yellower after natural weathering, whereas the controls became less yellow (Fig. 4.14), which accounts for the significant ($p<0.001$) effect of treatment on the $b^*$ parameter (Table 4.5). Yellowing of treated samples containing Lignostab was greater than that of samples treated with 20% PF resin alone. When results are averaged across all treatments, weathered Scots pine boards were yellower than southern pine boards, which accounts for the significant ($p<0.001$) effect of species on the $b^*$ parameter (Table 4.5).

Figure 4.14 – Change in yellowness of dip and vacuum (vac) treated and untreated decking samples exposed to 80 days of natural weathering. Yellowness is expressed as ratio of $b^*$ parameter after weathering/$b^*$ parameter before weathering. Ratio of 1 indicates no change in yellowness of samples after weathering. Ratios above and below 1 indicate an increase or decrease in yellowness of samples after weathering, respectively. Note that the results are averaged across species. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.
PF resin treated deck boards became redder ($a^*$) during weathering, whereas the controls showed little change in redness (Fig. 4.15). Increases in redness were prominent in PF-treated samples that were vacuum-treated with PF resin. The addition of Lignostab significantly ($p<0.001$) reduced changes in redness of samples that were vacuum-treated with PF resin. Changes in redness of Scots pine boards during weathering were less pronounced than those of southern pine boards, when averaged across all treatments, Table 4.5.

Figure 4.15 – Change in redness of dip or vacuum (vac) treated and untreated decking samples exposed to 80 days of natural weathering. Redness is expressed as ratio of $a^*$ parameter after weathering/$a^*$ parameter before weathering. Ratio of 1 indicates no change in redness of samples after weathering. Ratios above 1 indicate an increase in redness of samples after weathering. Note that the results are averaged across species. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance
A significant ($p<0.001$) treatment x species interaction occurred for the changes in lightness of deck boards exposed to 2 years of natural weathering. This was because the decrease in lightness of Scots pine boards that were vacuum- or dip-treated with PF resin was more pronounced than those of southern pine boards treated with PF resin, and the same species/treatment difference did not occur with the other treatments (water or PF+Lstab).

Figure 4.16 – Change in lightness of dip and vacuum (vac) treated and untreated southern (SYP) and Scots pine (SP) decking samples exposed to 25 months of natural weathering. Lightness is expressed as ratio of $L^*$ parameter after weathering/$L^*$ parameter before weathering. Ratio of 1 indicates no change in lightness of samples after weathering. Ratios below 1 indicate darkening of samples after weathering. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.
The yellowness ratio of treated deck boards was significantly ($p<0.001$) less than that of untreated boards after 25 months of exposure, with the exception of those dip-treated with PF resin and Lignostab (Fig. 4.17). There was no difference in vacuum- or dip-treated boards, except for those treated with PF/Lignostab. Scots pine boards had significantly ($p=0.001$) lower yellowness ratios than southern pine boards, when averaged across all treatments.

Figure 4.17 – Change in yellowness of dip and vacuum (vac) treated and untreated decking samples exposed to 25 months of natural weathering. Yellowness is expressed as ratio of $b^*$ parameter after weathering/$b^*$ parameter before weathering. Ratio of 1 indicates no change in yellowness of samples after weathering. Ratios below 1 indicate decrease in yellowness of samples after weathering. Note that the results are averaged across species. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.
Loss in redness of treated deck boards was significantly \( p<0.001 \) lower than that of untreated boards after 25 months of weathering, except for boards dip-treated with PF resin and Lignostab (Fig. 4.18). Redness loss in vacuum-treated boards was significantly \( p<0.001 \) less than those of dip-treated boards.

![Graph showing change in redness of dip and vacuum (vac) treated and untreated decking samples exposed to 25 months of natural weathering. Redness is expressed as ratio of \( a^* \) parameter after weathering/\( a^* \) parameter before weathering. Ratio of 1 indicates no change in redness of samples after weathering. Ratios below 1 indicate a decrease in redness of samples after weathering. Note that the results are averaged across species. Error bars are ± standard error of difference \( p<0.001 \) from analyses of variance.]

4.3.3 Surface checking of weathered Scots and southern pine deck boards

A significant \( p<0.001 \) treatment x species interaction for check width occurred for deck boards that were weathered for 80 days. Checks formed in PF resin or PF and Lignostab-treated Scots pine boards were narrower than those in similarly treated southern pine boards, whereas there was little difference in the widths of checks in southern pine or Scots pine boards treated with water (Fig. 4.19).
Figure 4.19 – Average width of ten largest checks in dip and vacuum (vac) treated and untreated southern (SYP) and Scots pine (SP) decking samples exposed to 80 days of natural weathering. Least significant difference (LSD) bar is ± standard error of difference ($p<0.001$) from analyses of variance.

There was a significant ($p<0.001$) treatment x species interaction on the length of checks in boards exposed to 80 days of weathering. This interaction occurred because length of checks in PF-treated decking samples varied with species: checks were shorter in southern pine (SYP) treated with PF resin or PF/Lignostab than in other resin-treated boards. However, there was no significant ($p>0.05$) difference in the length of checks in water-treated Scots and southern pine boards (Fig.4.20).
Figure 4.20 – Average length of ten largest checks in dip and vacuum (vac) treated and untreated southern (SYP) and Scots pine (SP) decking samples exposed to 80 days of natural weathering. Least significant difference (LSD) bar is ± standard error of difference (p<0.001) from analyses of variance

A significant (p=0.021) treatment x species interaction occurred for area of checking in deck boards weathered for 80 days. This interaction occurred because the area of checks in boards treated with PF resin, PF resin and Lignostab or water varied with treatment method and species, whereas there was no such variation in boards treated with water (Fig. 4.21).
Figure 4.21 – Average area of dip and vacuum (vac) ten largest checks in treated and untreated southern (SYP) and Scots pine (SP) decking samples exposed to 80 days of natural weathering. Least significant difference (LSD) bar is ± standard error of difference (\(p=0.021\)) from analyses of variance.

There was no effect (\(p>0.05\)) of treatment on length of checks in deck board samples after 25 months of weathering, but there was a significant effect (\(p=0.008\)) of species on check length because southern pine boards had longer checks than those of Scots pine boards. There was a significant (\(p=0.038\)) treatment x species interaction on width of checking in envelope treated Scots pine and southern pine samples. This interaction occurred because check widths in PF resin treated deck boards varied with species and treatment (checks in vacuum-treated boards tended to be smaller than those in dip-treated boards, although the difference was not always significant). In contrast, there was no such variation in boards treated with water (Fig. 4.22).
Figure 4.22 – Average width of ten largest checks in dip and vacuum (vac) treated and untreated southern (SYP) and Scots pine (SP) decking samples exposed to 25 months of natural weathering. Least significant difference (LSD) bar is ± standard error of difference ($p=0.038$) from analyses of variance

Check areas in deck board samples that were treated by dipping or vacuum impregnation with PF resin and lignin stabilizer was significantly different ($p<0.001$), whereas no such variation occurred in samples treated with PF resin or water (Fig. 4.23).
4.3.4 Contact angle of treated and untreated Scots and southern pine decking samples

Contact angle was significantly ($p=0.005$) greater on southern pine boards than on Scots pine boards after the boards were exposed to 80 days of weathering (when results are averaged across all treatments). Otherwise, there was no significant ($p>0.05$) effect of experimental factors on contact angle of weathered boards.

4.3.5 Roughness and cupping of treated and untreated Scots and southern pine decking samples

The effects of treatment and species on the surface roughness or cupping of deck board samples exposed to 80 days of weathering were not significant ($p>0.05$) (Table 4.5).
4.4 Discussion

I hypothesized that the lignin stabilizer, Lignostab, would restrict discolouration of PF resin treated deck board samples. I also hypothesized that the effectiveness of the PF resin treatments would be affected by treatment of samples. My hypotheses are partially supported by my results. Firstly, my results show that the lignin stabilizer reduced darkening and red colour of boards that were vacuum-impregnated with PF resin. However, samples treated with PF-Lignostab yellowed more than those treated with PF on its own. I hypothesized that the ability of PF treatments to reduce checking would be related to treatment weight gains resulting from the use of different treatment methods. Vacuum impregnation of samples resulted in higher weight gains of samples, and southern pine samples had significantly higher weight gains than Scots pine samples. In accord with my hypothesis, checks were shorter in southern pine treated by vacuum impregnation than those treated by dipping, but the differences in the other check parameters were less pronounced, except for check area. There was little difference in treatment weight gains of Scots pine samples treated by dipping or vacuum impregnation and differences in checking of two types of Scots pine samples were less pronounced.

There have only been two studies by Evans et al. (2013) and Liu (2011) that examined the effects of Lignostab on the discolouration of PF-treated wood. My observations on the ability of Lignostab to partially restrict discolouration of PF-treated pine decking accords with their findings and also my results in Chapter 3. Evans et al. (2013) exposed PF-treated radiata pine veneers to 83 days of natural weathering and found that Lignostab (2%) reduced darkening and reddening of veneers modified with 10% PF resin. Liu (2011) also found that Lignostab (2%) restricted darkening of yellow cedar veneers treated with 12% PF resin and exposed to 50 days of outdoor weathering. The adverse effect of lignin stabilizer on the yellowing of PF-treated pine boards during outdoor exposure, also accords with the findings of Evans et al. (2013) and Liu (2011).
There have only been a few studies on the photodegradation and surface checking of PF resin treated wood. My results on the checking resistance of PF-treated pine deck board samples accords with findings of Stamm and Seborg (1939), Tarkow et al. (1966), Sudiyani et al. (1999) and Cheng and Evans (2012). Stamm and Seborg found that treatment of Douglas fir plywood veneers with 30% PF resin reduced checking when the treated plywood was naturally weathered for 2 years. Tarkow et al. (1966) found that surface treatment of ponderosa pine and redwood boards with 15% PF resin, and dip or pressure treatment of southern pine boards with PF resin to 1% and 6% WPG, respectively, prevented checking of boards when they were exposed to artificial weathering. Sudiyani et al. (1999) found that treatment of small samples of albizzia and sugi with 7.5% or 10% low molecular weight PF resin restricted checking when samples were artificially weathered for 1080 hours or naturally weathered for 1 year. Cheng and Evans (2012) found that pressure treatment of white spruce deck boards with LMW PF resin to 15.5% WPG restricted width, length and area of surface checks formed in the treated boards when they were exposed to 24 weeks of natural weathering. However, contrary to the findings of Cheng and Evans (2012), I found that treatment of pine decking with PF resin did not have any effect on cupping of boards. This difference in my results and those of Cheng and Evans (2012) may be due to higher treatment uptake in their pressure-treated samples compared to my envelope-treated boards.

The lignin stabilizer, Lignostab, was able to reduce the darkening and reddening of PF resin treated pine deck boards during outdoor weathering, as mentioned above. PF resin discolours during exposure to the weather, because it absorbs UV radiation and photodegrades, producing chromophoric compounds (Tarkow et al., 1966; Kol'tsov et al., 1985; Mijangos et al., 2006). I showed that the colour of cleaned surfaces of boards treated with PF-Lignostab was brighter and more vibrant than those of boards treated with PF resin on its own, suggesting that Lignostab can provide long-term colour stability to PF-resin treated wood.
My results showed that envelope treatment of pine deck boards with PF resin and lignin stabilizer protects them against the deleterious effects of outdoor weathering. However, there are limitations to the treatment that leave room for improvement. Most notably, Lignostab was unable to completely restrict the discoloration of PF resin. In particular, it was associated yellowing of PF-treated boards exposed to the weather. A better additive is needed to improve the ability of PF resin to photostabilize modified wood. Ferric ions have been found to react with phenols to form photostable phenolic complexes, according to Schmalzl et al. (1995) and Mijangos et al. (2006). In addition, ferric chloride can impart mould resistance to wood (Pandey & Pitman, 2002). Ferric chloride may be able to improve the outdoor performance of PF-treated wood. Moreover, surface checking of envelope treated wooden boards could be reduced by adding a hydrophobe to the PF resin, because wax or oils are commonly used in preservative treatments to improve wood’s resistance to checking during outdoor exposure (Zahora, 2000).

Vacuum impregnation was a more effective treatment method than dipping. For example, colour stability and checking resistance was better for vacuum-treated samples, and these beneficial effects were more pronounced after the treated boards were weathered for 2 years. However, the WPG of vacuum-treated Scots and southern pine boards was still low compared to those of PF-treated veneers in Chapter 3. However, they are similar to those of Tarkow et al. (1966) who obtained 1% - 6% WPG for 19 mm thick dip or pressure treatment of southern pine boards, respectively. Vacuum impregnation will be modified in Chapter 6 to increase WPGs.

The grey weathered layer at the surface of treated pine deck boards was shallow and could be easily removed by gentle rubbing. Furthermore, the surfaces of treated boards were less eroded and there was less grain raising after surfaces were rubbed with a damp cloth. These findings were unexpected (and noteworthy), because deck owners could easily use a gentle cleaning procedure to remove the weathered
layer from envelope-treated deck board surface (without excessively eroding or roughening treated board surfaces). The improved checking resistance of pine boards treated with PF-Lignostab compared to PF resin alone after 2 years of natural weathering was also unexpected.

4.5 Conclusions

I conclude that envelope treatment of pine deck boards with PF resin or PF resin and lignin stabilizer, Lignostab, is reasonably effective modification to protect treated board surfaces from the deleterious effects of natural weathering. Photodegradation was shallow at the surfaces of treated boards, and the degraded layer could be easily removed. Treatment using vacuum impregnation was more effective than dipping, but the vacuum impregnation schedule needs to be modified to increase treatment weight gain in Scots and southern pine boards.

Lignin stabilizer imparted some long-term colour stability and resistance to checking of PF-treated pine boards, however, Lignostab was not able to completely restrict all of the deleterious effects of weathering from occurring at board surfaces. Therefore, I conclude that PF resin used to treat deck boards need other additives that are more effective at restricting the discolouration of PF resin, checking and cupping of treated boards.
Chapter 5: Additives to Enhance the Weather Resistance of Wood Treated with Low Molecular Weight Phenol Formaldehyde Resin

5.1 Introduction

Scots and southern pine deck boards exposed outdoors for 2 years were partially protected from weathering by an envelope treatment with 20% low molecular weight phenol formaldehyde resin (Chapter 4). Treated pine boards had reduced surface checking, and the depth of photodegradation was shallower than that of untreated controls. Treated deck boards became yellow as a result of photodegradation of PF resin, and the addition of a lignin stabilizer, Lignostab, did not restrict yellowing. Clearly, other photostabilizers need to be tested to determine if they can prevent the yellowing of PF resin and also restrict the checking of PF-treated wood exposed outdoors to weathering.

Previous studies have shown that wood surfaces can be protected from the adverse effects of UV radiation with pigments, that reflect or absorb UV light. Pigments are mainly inorganic compounds, but lignosulphonates, lignin by-products from pulping, can also colour wood, absorb UV radiation and act as antioxidants (Feist, 1983; Bigger & Delatycy, 1989; Boeriu et al., 2004). Inorganic compounds, such as ferric chloride can photostabilize lignin, provide treated wood with colour and resistance against surface staining fungi (Evans & Schmalzl, 1989; Pandey & Pitman, 2002). Ferric chloride was used as an additive for PF resin to control pot life and improve heat and flame resistance of the resin (Erickson, 1967). The resistance of wood to surface checking can be enhanced using water-repellants that slow the absorption of water into treated wood (Zahora, 2002). All of the aforementioned compounds could enhance the ability of PF resin treatments to protect wood from the adverse effects of weathering. This chapter tests the ability of an iron (III) salt, organic photostabilizers (HALS, UV absorber) and inorganic and organic pigments to restrict photodegradation of PF resin treated wood veneers. I also assess the protective effects of a wax emulsion additive on PF resin treated veneers exposed to natural weathering. I
hypothesize that these additives or combinations of them will improve weather resistance of treated wood veneers.

5.2 Materials and methods

5.2.1 Experimental design and statistical analyses

I designed an experiment to examine the effects of the 19 different additive combinations (Table 5.1) on the photostability of yellow cedar veneers exposed to 50 days of natural weathering. A total of 840 veneers were cut from four yellow cedar blocks. This sampling approach provided replication at the higher (block) level. Statistical analyses took into account random variation between wood blocks and batches of veneers. Ten veneers from each block were gathered into a batch and randomly assigned to the treatment or untreated control, (10 [replicates] x 4 [blocks] x 21 [treatments] = 840 veneers).

Analysis of variance (ANOVA) assessed the effects of treatment on the following measures of the resistance of wood veneers to weathering: (1) colour change; (2) weight loss; (3) tensile strength loss. Statistical analyses of experimental results used Genstat, Version 12.1, 18.2 (VSN International, 2009, 2016). Some data were transformed to meet assumptions of ANOVA (normality of residuals, homogeneity of variance, independence of sampling, independent observations). Statistically significant \( p<0.05 \) results are plotted, and individual means can be compared using error bars (± standard error of difference from ANOVA) or least significant difference (LSD) bars, both obtained from ANOVA (Williams & Abdi, 2010).

5.2.2 Preparation of yellow cedar veneers and SEM samples

Veneers were cut from heartwood of four yellow cedar boards as described in Section 3.2.2 (Chapter 3). Veneers were conditioned in a constant climate room at 20 ± 1 °C and 65 ± 5% r.h. for 5 days and weighed.
5.2.3 Synthesis and preparation of modified PF resin

Low molecular weight phenol formaldehyde resin solutions were diluted with tap water to 20% concentration from parent PF resin (46.67% solids) solutions provided by Arclin USA Inc. (Springfield, O.R., U.S.A.). Chemical composition of a batch of parent PF resin is described in Section 3.2.3 (Chapter 3).

Water-soluble ‘lignin stabilizer’ (LIGNOSTAB® 1198) was supplied by CIBA Specialty Chemicals Corp (Tarrytown, N.Y., U.S.A.). A water-soluble hindered amine light stabilizer (Tinuvin® 123-DW) and water-soluble UV absorber (Tinuvin® 477-DW) were purchased from BASF Corp (Ludwigshafen, Germany). Water-soluble sodium salt of chemically modified low molecular weight lignosulphonate, (REAX® SN); water-soluble kraft lignin with low degree of sulphonation (POLYFON® O); less water-soluble unsulphonated pine kraft lignin (INDULIN® AT) were provided by MeadWestvaco Corporation (Richmond, VA, U.S.A.). Micronized iron oxide (PW601, yellow) was supplied by Johnson Matthey Ceramics, Inc. (Downingtown, Pennsylvania). Ferric chloride was purchased from EM Science (now Merck Millipore, Billeria, M.A., U.S.A.). A water-soluble black dye (CNA70) was purchased from ICA Group (Civitanova Marche, Macerata, Italy). Carbon black was supplied by Alfa Aesar (Ward Hill, M.A., U.S.A.). A wax emulsion (UW5F, 40% solids) and a brown pigment suspended in wax (PD SC1) were provided by Viance LCC (Charlotte, North Carolina, U.S.A.). All additives, except PD SC1, were dissolved in tap water, and then dissolved in diluted PF resin treatment solutions. PD SC1 was not water-soluble and premixing with UW5F was necessary to dissolve it in PF resin solution. All treatment formulations are shown in Table 5.1.
Table 5.1 – PF resin treatment solutions, concentration of additives and abbreviated treatment names

<table>
<thead>
<tr>
<th>No.</th>
<th>Treatment</th>
<th>PF resin concentration (% w/w)</th>
<th>Additive 1 concentration (% w/w)</th>
<th>Additive 2 concentration (% w/w)</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Control</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Water</td>
</tr>
<tr>
<td>2.</td>
<td>PF resin</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>PF</td>
</tr>
<tr>
<td>3.</td>
<td>PF resin + lignin stabilizer</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+Lstab</td>
</tr>
<tr>
<td>4.</td>
<td>PF resin + HALS</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+HALS</td>
</tr>
<tr>
<td>5.</td>
<td>PF resin + UV absorber</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+UVA</td>
</tr>
<tr>
<td>6.</td>
<td>PF resin + lignosulphonate</td>
<td>20</td>
<td>10</td>
<td>0</td>
<td>PF+LIGS</td>
</tr>
<tr>
<td>7.</td>
<td>PF resin + kraft lignin</td>
<td>20</td>
<td>10</td>
<td>0</td>
<td>PF+LIGK1</td>
</tr>
<tr>
<td>8.</td>
<td>PF resin + unsulphonated kraft lignin</td>
<td>20</td>
<td>10</td>
<td>0</td>
<td>PF+LIGK2</td>
</tr>
<tr>
<td>9.</td>
<td>PF resin + ferric chloride</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+Fe</td>
</tr>
<tr>
<td>10.</td>
<td>PF resin + iron oxide</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+IO</td>
</tr>
<tr>
<td>11.</td>
<td>PF resin + black dye</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+Bdye</td>
</tr>
<tr>
<td>12.</td>
<td>PF resin + carbon black</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+Cblack</td>
</tr>
<tr>
<td>13.</td>
<td>PF resin + wax</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+wax</td>
</tr>
<tr>
<td>14.</td>
<td>PF resin + wax + lignin stabilizer</td>
<td>20</td>
<td>2 - wax</td>
<td>2 - Lstab</td>
<td>PF+wax+Lstab</td>
</tr>
<tr>
<td>15.</td>
<td>PF resin + wax + lignosulphonate</td>
<td>20</td>
<td>2 - wax</td>
<td>10 - LIGS</td>
<td>PF+wax+LIGS</td>
</tr>
<tr>
<td>16.</td>
<td>PF resin + wax + ferric chloride</td>
<td>20</td>
<td>2 - wax</td>
<td>2 - FC</td>
<td>PF+wax+Fe</td>
</tr>
<tr>
<td>17.</td>
<td>PF resin + wax + carbon black</td>
<td>20</td>
<td>2 - wax</td>
<td>2 - Cblack</td>
<td>PF+wax+Cblack</td>
</tr>
<tr>
<td>18.</td>
<td>PF resin + wax + brown pigment</td>
<td>20</td>
<td>2 - wax</td>
<td>2 - BPIG</td>
<td>PF+wax+BPIG</td>
</tr>
<tr>
<td>19.</td>
<td>PF resin + lignosulphonate + lignin stabilizer</td>
<td>20</td>
<td>10 - LIGS</td>
<td>2 - Lstab</td>
<td>PF+LIGS+Lstab</td>
</tr>
<tr>
<td>20.</td>
<td>PF resin + lignosulphonate + HALS</td>
<td>20</td>
<td>10 - LIGS</td>
<td>2 - HALS</td>
<td>PF+LIGS+HALS</td>
</tr>
<tr>
<td>21.</td>
<td>PF resin + lignosulphonate + UV absorber</td>
<td>20</td>
<td>10 - LIGS</td>
<td>2 - UVA</td>
<td>PF+LIGS+UVA</td>
</tr>
</tbody>
</table>

Weight gains of treated yellow cedar veneers are shown in Table 5.2. Treatment with 20% PF resin on its own increased weight gain of veneers. Weight gains of veneers treated with PF and lignin additives
were higher than those of veneers treated with PF on its own. Weight gains of veneers treated with PF solutions containing lignin stabilizer, HALS, UVA, ferric chloride or iron oxide were similar to those of veneers treated with PF resin, whereas weight gains of veneers treated with PF solutions containing wax and the black pigments (black dye and carbon black) were lower than those of PF-treated veneers.

Table 5.2 – Weight gains of yellow cedar veneers treated with modified and unmodified PF resin

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Treatment weight gain</th>
<th>Percentage (%)</th>
<th>(SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF resin</td>
<td>34.6</td>
<td>(2.7)</td>
<td></td>
</tr>
<tr>
<td>PF resin + lignin stabilizer</td>
<td>35.2</td>
<td>(2.9)</td>
<td></td>
</tr>
<tr>
<td>PF resin + HALS</td>
<td>33.9</td>
<td>(3.4)</td>
<td></td>
</tr>
<tr>
<td>PF resin + UV absorber</td>
<td>34.7</td>
<td>(2.6)</td>
<td></td>
</tr>
<tr>
<td>PF resin + lignosulphonate</td>
<td>37.7</td>
<td>(5.5)</td>
<td></td>
</tr>
<tr>
<td>PF resin + kraft lignin</td>
<td>37.5</td>
<td>(3.2)</td>
<td></td>
</tr>
<tr>
<td>PF resin + unsulphonated kraft lignin</td>
<td>37.2</td>
<td>(4.2)</td>
<td></td>
</tr>
<tr>
<td>PF resin + ferric chloride</td>
<td>34.1</td>
<td>(3.2)</td>
<td></td>
</tr>
<tr>
<td>PF resin + iron oxide</td>
<td>34.3</td>
<td>(5.1)</td>
<td></td>
</tr>
<tr>
<td>PF resin + black dye</td>
<td>31.9</td>
<td>(2.6)</td>
<td></td>
</tr>
<tr>
<td>PF resin + carbon black</td>
<td>31.1</td>
<td>(6.3)</td>
<td></td>
</tr>
<tr>
<td>PF resin + wax</td>
<td>27.1</td>
<td>(2.5)</td>
<td></td>
</tr>
<tr>
<td>PF resin + wax + lignin stabilizer</td>
<td>28.0</td>
<td>(2.6)</td>
<td></td>
</tr>
<tr>
<td>PF resin + wax + lignosulphonate</td>
<td>31.4</td>
<td>(2.6)</td>
<td></td>
</tr>
<tr>
<td>PF resin + wax + ferric chloride</td>
<td>27.3</td>
<td>(3.8)</td>
<td></td>
</tr>
<tr>
<td>PF resin + wax + carbon black</td>
<td>27.8</td>
<td>(3.1)</td>
<td></td>
</tr>
<tr>
<td>PF resin + wax + brown pigment</td>
<td>26.3</td>
<td>(7.7)</td>
<td></td>
</tr>
<tr>
<td>PF resin + lignosulphonate + lignin stabilizer</td>
<td>38.1</td>
<td>(2.8)</td>
<td></td>
</tr>
<tr>
<td>PF resin + lignosulphonate + HALS</td>
<td>37.0</td>
<td>(3.3)</td>
<td></td>
</tr>
<tr>
<td>PF resin + lignosulphonate + UV absorber</td>
<td>37.2</td>
<td>(2.9)</td>
<td></td>
</tr>
</tbody>
</table>

5.2.4 Treatment of wood veneers

Treatment solutions were chilled to -2 °C, and thawed at room temperature for 1 h before they were used to treat veneers. The veneers were submerged in a 150 mL beaker of PF resin solution for 10 minutes, held against the wall of a 400 mL beaker for 5 minutes to drain off excess solution, fixed at one end to a wire rack and air-dried in a fume hood for 30 minutes. The air-dried veneers laid on a 290 mm x 125 mm cardboard liner which was secured on a 646 mm x 123 mm x 14 mm softwood plywood panel,
and each end was held down on to the panel cotton string. The wooden panel containing treated veneers was placed horizontally 230 mm below halogen lamps within an infrared oven (Prime Heat Inc., El Cajon, C.A., U.S.A.). The veneers were cured with IR radiation at a temperature of 146.5 ± 1.5°C for 2 minutes and 50 seconds (Fig. 5.1). An exhaust fume hood in the ceiling of the laboratory evacuated fumes produced during curing of the PF resin. The infrared oven faced away from the fume hood to restrict air flow from the fume hood from affecting curing of the PF resin.

Figure 5.1 – (a) infrared oven used to cure treated yellow cedar veneers; (b) photo showing halogen lamps used to emit infrared light; (c) veneers secured by tensioned cotton strings to a plywood panel and placed on a steel mesh platform
5.2.5 Weathering trial

Procedures for weathering of treated and untreated veneers are described in Section 3.2.5 of Chapter 3. Five treated and untreated veneers from each batch were exposed horizontally at a test site on the campus of the University of British Columbia for 50 days. The veneers were first exposed for 31 days from August 15\textsuperscript{th} to September 15\textsuperscript{th} and then re-exposed for the remaining 19 days from October 1\textsuperscript{st} to October 20\textsuperscript{th} in 2014. Figure 5.2 shows a block of veneers being on 1\textsuperscript{st} and 39\textsuperscript{th} days of the outdoor weathering trial.

Table 5.3 – Weathering conditions in Vancouver, British Columbia, Canada during the 50-day exposure trial of PF resin treated yellow cedar veneers

<table>
<thead>
<tr>
<th>Month</th>
<th>Temperature (°C)</th>
<th>Total Precipitation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum\textsuperscript{1}</td>
<td>Mean</td>
</tr>
<tr>
<td>August 2014</td>
<td>23.2</td>
<td>19.2</td>
</tr>
<tr>
<td>September 2014</td>
<td>19.9</td>
<td>15.9</td>
</tr>
<tr>
<td>October 2014</td>
<td>15.8</td>
<td>13.1</td>
</tr>
</tbody>
</table>

\textsuperscript{1}Average maximum and minimum daily temperatures
Data collected for Vancouver International Airport, [http://climate.weather.gc.ca/historical_data/search_historic_data_e.html](http://climate.weather.gc.ca/historical_data/search_historic_data_e.html)

Figure 5.2 – Images showing treated and untreated veneers from the same block after exposure to the weather for (a) 1 day and (b) 39 days

5.2.6 Assessment of the photoprotective effects of PF resin treatments on the properties of yellow cedar veneers

After weathering, treated and untreated yellow cedar veneers were conditioned in a constant climate room (as above) for a minimum of seven days and post-weathering measurements were carried
out. Procedures used for assessing weight and tensile strength losses of veneers, and their colour before and after outdoor weathering were the same as those described in Section 3.2.4.1 and 3.2.4.2 (Chapter 3).

5.2.7 Scanning electron microscopy

Weathered veneer samples were conditioned in a constant climate control room for a minimum of seven days. Small (9 mm [longitudinal] x 3 mm [radial]) rectangular strips were cut with a pair of scissors from unweathered and weathered veneers and fixed to 12 mm diameter aluminum stubs using 11 mm diameter double-sided adhesive tabs (#76760, Electron Microscopy Sciences Inc., Hatfield, PA, U.S.A.). Samples on aluminum stubs were coated with a thin layer (8 nm) of gold and observed using a Zeiss UltraPlus analytical field electron scanning microscope (Zeiss, Oberkochen, Germany) at an accelerating voltage of 5kV and a working distance of 13.3 to 15.1 mm. SEM images of the surface of weathered and unweathered samples (treated and untreated) were saved as TIFF files.

5.3 Results

There were highly significant ($p<0.001$) effects of treatments on colour ($L^*$, $a^*$, $b^*$), weight and tensile strength losses of veneers exposed outdoors for 50 days, as expected.

5.3.1 Appearance of wood veneers after treatment and weathering

Images of veneers after treatment and exposure to weathering are shown in Figure 5.3. Images of all veneer samples are appended to this thesis (Appendix 3). Treatment with 20% PF resin gave treated veneers a red and blotchy colour. PF containing lignin stabilizer, HALS, UVA, iron oxide or wax did not change the colour of veneers. PF containing lignosulphonate or kraft lignin imparted a light brown colour to treated veneers, whereas PF containing unsulphonated kraft lignin imparted a darker brown colour to veneers. Ferric chloride imparted a uniform dark brown colour to veneers. PF containing black dye made
veneers a uniform black colour, whereas veneers treated with PF and carbon black were a blotchy black colour. Veneers treated with PF containing wax and brown pigment was partially covered in patches of brown pigments. Veneers treated with PF resin, wax and ferric chloride were brighter than veneers treated with PF resin and ferric chloride, and wax reduced the blotchiness of veneers treated with PF resin and carbon black. However, wax had no effect on the appearance of veneers treated with PF resin and lignin stabilizer or lignosulphonate. Veneers treated with PF resin, lignosulphonate and different organic photostabilizers were a similar light brown colour.

After 50 days of natural weathering, untreated veneers were wrinkled and gray, whereas all treated veneers maintained their shape and became yellower, except for those treated with PF and ferric chloride, black dye or carbon black. Veneers treated with PF and ferric chloride darkened and became brown after weathering, but their brown colour was less pronounced than that of veneers treated with PF, ferric chloride and wax. Veneers treated with PF and black dye were a blotchy yellow colour, and a similar trend was observed in veneers treated with PF and carbon black or carbon black and wax. Figure 5.3 shows scanned images of treated and untreated veneers before and after weathering.
PF+Lstab  
PF+HALS  
PF+UVA  
PF+LIGS  
PF+LigninK1  
PF+LigninK2  
PF+Fe

Unweathered  
Weathered
A uniform grey colour due to photodegradation of wood and colonization of wood by mould can be seen at the surface of untreated and weathered veneers in Figure 5.3. Black dots (mould colonies) were present at the surface of PF resin treated veneers, but there were fewer dots at veneer surfaces treated with PF and UVA, unsulphonated kraft lignin, ferric chloride, black dye or carbon black additives. In contrast, more mould colonies were found on veneers treated with PF containing Lstab, HALS, wax and the other two lignin additives. Lignosulphonate in combination with PF resin and Lstab reduced the
occurrence of mould colonies on veneers, whereas the opposite occurred when lignosulphonate was combined with PF resin and UVA or HALS. Wax generally reduced mould resistance of veneers treated with PF resin and the different additives. Figure 5.4 shows magnified images of treated and untreated veneers after weathering, and shows the blotchy appearance of some of the treated veneers.

Figure 5.4 – Fungal colonization at the surface of treated and untreated veneers after 50 days of natural weathering: (a) untreated control; (b) PF resin; (c) PF resin and Lignostab; (d) PF resin, lignosulphonate and Lignostab; (e) PF resin, ferric chloride; (f) PF resin, wax and ferric chloride. Arrows indicate mould fungi. Scale bar is 1 mm

5.3.2 Colour parameters ($L^*$, $a^*$, $b^*$) of treated and untreated wood veneers after weathering

Changes to lightness of treated and untreated yellow cedar veneers as a result of natural weathering for 50 days are shown in Figure 5.5. Veneers treated with PF resin on its own became darker after exposure, but they were still significantly ($p<0.001$) lighter than the untreated controls. Darkening
of PF-treated veneers was significantly \((p<0.001)\) reduced by PF resin treatments containing Lignostab, unsulphonated kraft lignin or lignosulphonate and HALS, but the effects of these additives were not significantly \((p>0.05)\) different. Black dye, carbon black, or combinations of wax and carbon black or lignosulphonate and Lignostab in PF resin were significantly \((p<0.001)\) more effective than Lignostab at restricting darkening of PF-treated veneers.

![Graph showing change in lightness of treated and untreated yellow cedar veneers exposed to 50 days of natural weathering. Lightness is expressed as ratio of \(L^*\) parameter after weathering/\(L^*\) parameter before weathering. Ratio of 1 indicates no change in lightness of veneers after weathering. Ratios below 1 indicate darkening of veneers after weathering. Error bars are ± standard error of difference \((p<0.001)\) from analysis of variance.]

Veneers treated with PF resin became yellower after weathering, whereas untreated controls lost their yellowness and became bluer (Fig. 5.6). Lignostab did not restrict yellowing of PF resin treated veneers. Ferric chloride or ferric chloride and wax were the most effective additives at reducing yellowing of PF resin treated veneers, but there was no significant \((p>0.05)\) difference in yellowness of veneers treated with these different additive combinations. The lignin additives, iron oxide, wax or additive combinations containing lignosulphonate and HALS or UVA, wax and lignosulphonate or wax and brown
pigment were significantly ($p<0.001$) more effective than Lignostab at restricting yellowing of PF-treated veneers during weathering. However, the yellowness of veneers treated with PF resin and these additives and additive combinations were not significantly ($p>0.05$) different from each other.

![Figure 5.6 - Change in yellowness of treated and untreated yellow cedar veneers exposed to 50 days of natural weathering. Yellowness is expressed as ratio of $b^*$ parameter after weathering/$b^*$ parameter before weathering. Ratio of 1 indicates no change in yellowness of veneers after weathering. Ratios above and below 1 indicate increase or decrease in yellowness of veneers after weathering, respectively. Error bars are ± standard error of difference ($p<0.001$) from analysis of variance.](image)

PF-treated veneers became redder after exposure to the weather, and their red colour was similar to that of the weathered untreated controls (Fig. 5.7). Veneers treated with PF resin with lignin stabilizer, lignin additives, black dye, carbon black, lignosulphonate and organic photostabilizers or wax and brown pigment significantly ($p<0.001$) were less red than PF-treated veneers, but there was no significant ($p>0.05$) difference in the red colour of veneers treated with PF containing any of these additives. Veneers treated with PF and iron oxide or wax and ferric chloride became greener after weathering, but their colours were not significantly ($p>0.05$) different.
Figure 5.7 - Change in redness of PF resin treated and untreated yellow cedar veneers exposed to 50 days of natural weathering. Redness is expressed as ratio of $a^*$ parameter after weathering/$a^*$ parameter before weathering. Ratio of 1 indicates no change in redness of veneers after weathering. Ratios above and below 1 indicate increase or decrease in redness of veneers after weathering, respectively. Error bars are ± standard error of difference ($p<0.001$) from analysis of variance.

5.3.2 Weight losses of treated and untreated wood veneers during weathering

Figure 5.8 shows weight losses of treated and untreated veneers after 50 days of natural weathering. Treatment with PF resin restricted weight losses of veneers, and their weight losses were significantly ($p<0.001$) lower than those of the untreated veneers, as expected. Addition of Lstab to PF resin did not reduce weight losses of PF-treated veneers. The black dye, carbon black or wax and carbon black were the most effective additives at reducing weight losses of PF-treated veneers, but differences in weight losses of veneers treated with PF containing these different additives were not significant ($p>0.05$). The UVA or ferric chloride additives also significantly ($p<0.001$) reduced weight losses of veneers treated with PF resin, but the difference in weight losses of veneers treated with PF containing these additives was not significant ($p>0.05$).
5.3.3 Tensile strength losses of wood veneers modified with PF resin and additives

Tensile strengths of yellow cedar veneers after treatment and outdoor weathering are shown in Figure 5.9. Treatment with PF resin on its own increased tensile strengths of veneers, and treated veneers were significantly ($p<0.001$) stronger than the untreated controls. Veneers treated with PF resin containing unsulphonated kraft lignin, iron oxide, lignosulphonate and HALS or UVA were significantly ($p<0.001$) stronger than PF-treated veneers, but differences in tensile strength of veneers treated with PF and these different additives were not significant ($p>0.05$). Wax additive when combined with carbon black, HALS or UVA significantly ($p<0.001$) increased the strength of PF treated veneers. However, wax did not have any significant ($p>0.05$) effect on strength of veneers treated with PF and Lignostab additive. Furthermore, wax on its own had a negative effect on strength of veneers treated with PF resin, and veneers treated with PF, ferric chloride and wax were weaker than veneers treated with PF resin and ferric chloride. The lignin stabilizer, Lignostab, did not significantly ($p>0.05$) affect tensile strengths of PF-treated.
veneers. Veneers treated with PF resin and the two black additives were significantly ($p<0.001$) weaker than most of the other treated veneers (Fig. 5.9a).

Weathering weakened both treated and untreated veneers, but tensile strength losses of veneers treated with PF resin were significantly ($p<0.001$) less than those of untreated controls. Weathered veneers treated with PF resin and lignosulphonate and Lignostab were significantly ($p<0.001$) stronger than the ones treated with PF resin on its own. Figure 5.9b shows the effects of weathering on tensile strength ratios of treated and untreated yellow cedar veneers and confirms some trends shown in Figure 5.9a. In addition, it shows that veneers treated with PF resin and black dye, carbon black, wax and carbon black or wax and Lignostab lost little strength, or became stronger during weathering. In three out of four cases, the exception being PF/wax/Lignostab, all of the treatments that were most effective at apparently reducing tensile strength losses of veneers during weathering were ones that were associated with strength losses as a result of treatment.
Figure 5.9 – Graphs showing (a) tensile strengths of PF resin treated and untreated yellow cedar veneers before ($p<0.001$) and after ($p<0.001$) exposure to 50 days of natural weathering; (b) tensile strength ratios ($p<0.001$) of treated and untreated yellow cedar veneers. Ratios indicate change in tensile strength of veneers after exposure to 50 days of natural weathering. Ratios greater or less than 1 represent increase or decrease in tensile strengths of veneers after weathering, respectively. Ratios equal to 1 indicate no change in tensile strengths. Error bars are ± standard error of difference from analysis of variance.
5.3.4 Microstructural changes of unmodified and modified wood veneer during natural weathering

The microstructure of untreated and unweathered yellow cedar veneers is shown in Figure 5.10a and b. Untreated veneers showed minor surface damage caused by microtoming or infrared heating, but bordered pit apertures were round and showed no diagonal micro-checks.

The surfaces of unweathered veneers treated with PF resin were smoother than those of untreated veneers (Fig. 5.10), because they were coated with PF resin (Fig. 5.11a). Pit apertures were often filled or covered with PF resin, although some pit apertures were open and uncoated (Fig. 5.11b).

The microstructure of unweathered veneers treated with PF resin and Lignostab, was similar to that of veneers treated with unmodified PF resin, although the coating appeared to be a little thinner. The coating of veneer surfaces by resin was also less pronounced in veneers treated with PF resin and lignosulphonate and Lignostab (Fig. 5.11).
Figure 5.11 – SEM images showing treated yellow cedar veneer (before weathering): (a, b) veneer treated with 20% PF resin; (c, d) veneer treated with 20% PF resin and 2% lignin stabilizer; (e, f) veneer treated with 20% PF resin, 2% lignin stabilizer and 2% lignosulphonate. Arrows indicate bordered pits.
Veneers treated with PF resin and ferric chloride showed little evidence of degradation as a result of treatment apart from some longitudinal micro-checks (arrowed in Fig. 5.12a). Bordered pit apertures in veneers treated with PF resin and ferric chloride were circular and unchecked (Fig. 5.12b). The appearance of veneers treated with PF resin, ferric chloride and wax was similar to that of veneers treated with PF resin and ferric chloride (Fig. 5.12c and d).

Figure 5.12 – SEM images showing treated yellow cedar veneer (before weathering): (a, b) veneer treated with 20% PF resin and 2% ferric chloride; (c, d) veneer treated with 20% PF resin, 2% ferric chloride and 2% wax. Arrows indicate: (1) longitudinal check; (2) bordered pits; (3) resin filling of pit apertures

In contrast to the appearance of veneers treated with PF resin or PF resin containing Lignostab, Lignostab and lignosuphonate, ferric chloride or ferric chloride and wax, veneers treated with PF resin and the black dye showed more evidence of surface degradation (as a result of treatment). In particular,
tracheid walls contained both longitudinal and transverse micro-checks (arrowed in Fig. 5.13a). However, pit apertures were free of checks. The veneer surface was not coated with PF resin (Fig. 5.13a, b).

Figure 5.13 – SEM images showing yellow cedar veneer treated with 20% PF resin and 2% black dye (before weathering): (a) radial surface; (b) radial surface under higher magnification. Arrows indicate: (1) micro-checking; (2) pit aperture free of a check

Untreated veneers exposed to 50 days of natural weathering were wrinkled, and their surfaces were rougher than those of unweathered controls (Fig. 5.14a). Some, but not all of the bordered pit apertures contained micro-checks (Fig. 5.14b). Mould colonized the degraded and untreated surface, arrowed in Figure 5.14b.

Veneers treated with PF resin and exposed to natural weathering were smoother, and tracheids were less distorted than similarly exposed untreated controls (Fig. 4.14c, d). Some bordered pits were covered with resin, but others were uncoated. Many others, however, contained diagonal micro-checks (arrowed in Fig. 5.14c, d). Degradation and colonization of PF-treated veneer surfaces by mould were less pronounced than those of untreated veneers.
Figure 5.14 – SEM images showing radial surfaces of untreated yellow cedar veneer (a, b) and veneer treated with 20% PF resin (c, d) exposed to 50 days of natural weathering. Arrows indicate: (1) circular pit aperture; (2) pit micro-checks; (3) enlarged pit micro-checks; (4) colonization by mould

The weathered surface of veneer treated with PF resin and Lignostab or lignosulphonate (REAX) was similar to that of surfaces treated with PF resin on its own, except there was less micro-checking of bordered pits (Fig. 5.15a, b). The surface of veneer is clean and largely free of degraded cell wall fragments and mould.
Figure 5.15 – SEM images showing radial surfaces of treated yellow cedar veneer exposed to 50 days of natural weathering: (a, b) veneer treated with 20% PF resin and 2% lignin stabilizer; (c, d) veneer treated with 20% PF resin, 2% lignin stabilizer and 10% lignosulphonate.

Micro-checking of bordered pits in veneers treated with PF resin and ferric chloride was more pronounced than that in untreated and weathered veneers, and some of the micro-checks were larger than those in veneers treated with PF resin, PF resin containing Lignostab or Lignostab and lignosulphonate. The surfaces of veneers treated with the PF resin and ferric chloride and wax combination were largely free of mould. However, wax appeared to have little effect on the micro-checking of veneers treated with PF resin and ferric chloride.
Figure 5.16 – SEM images showing radial surfaces of treated yellow cedar veneer exposed to 50 days of natural weathering: (a, b) veneer treated with 20% PF resin and 2% ferric chloride; (c, d) veneer treated with 20% PF resin, 2% ferric chloride and 2% wax. Arrow indicates large diagonal micro-check

Veneers treated with PF resin and the black dye (CNA70) contained numerous pit micro-checks, some of which were quite large (arrowed in Fig. 5.17). However, the surface was clean and free of mould.
Figure 5.17 – SEM images showing yellow cedar veneer treated with 20% PF resin and 2% black dye and exposed to 50 days of natural weathering: (a) radial surface; (b) radial surface under higher magnification. Arrows indicate: (1) wide pit micro-checks; (2) circular pit aperture; (3) large micro-check formed by joining up of two pit micro-checks

5.4 Discussion

In the introduction of this chapter, I hypothesized that the modification of PF resin with organic photostabilizers, pigments/dyes, or water-repellant additives would improve the ability of PF resin to protect yellow cedar veneers from the effects of natural weathering. My results support this hypothesis. The additives enhanced the weathering resistance of PF-treated veneers to various degrees depending on the ‘measure’ used to assess weathering resistance. Overall, ferric chloride was the most effective additive at improving the weathering resistance of PF-treated veneers. In addition, ferric chloride readily dissolved in diluted PF resin solution, converting it from a light orange to a dark brown/reddish colour. Wood veneers treated with PF resin and ferric chloride were dark brown in colour, which was partially retained when treated veneers were weathered. These observations accord with those of Kielmann et al. (2017), who artificially weathered European beech panels treated with 25% low molecular weight PF resin and 0.15% ferric chloride. The protective effect of ferric chloride and PF resin may be related to the ability of ferric ions to oxidize phenols and form photostable phenolic complexes (Mijangos et al., 2006). It is possible that these complexes restricted the discolouration and weight and tensile strength losses of PF-
treated veneers during weathering. However, PF containing ferric chloride did not reduce micro-checking of bordered pits during weathering, possibly because ferric chloride ions caused degradation of wood, in accord with results of previous studies (Evans & Schmalzl, 1989). Ferric chloride is an inexpensive chemical, whereas organic stabilizers (HALS, and particularly UV absorbers) are more expensive and are used at low concentration to photostabilize polymers.

The HALS (123DW) and Lignostab were generally better than the UV absorber, 477DW, at photostabilizing PF-treated veneers. Lignostab imparted partial colour stability to veneers and had a positive effect on restricting tensile strength loss of treated veneers after weathering, in accord with findings from Chapter 2 and the results of previous studies (Liu, 2011; Evans et al., 2013). In contrast to Lignostab, HALS (123DW) did not restrict discolouration. On the other hand, HALS (123DW) and UVA (477DW) were more effective than Lignostab at restricting weight losses of PF-treated veneers. The lignin additives provided some protection to PF-treated wood veneers exposed to weathering, but their protective effects varied with the type of additive. The ability of lignin additives to scavenge free radicals involved in photodegradation depends on their structure and the stability of phenolic radicals (Boeriu et al., 2004). However, studies on the effect of the structures of lignin additives and their ability to photostabilize wood have not been carried out. Therefore, it is difficult to compare my results on the effects of lignin additives on the photostability of PF-treated wood with those of other studies. Unsulphonated kraft lignin was slightly better than other lignin additives at restricting colonization of PF-treated veneers by mould. Kraft lignin appeared to develop more mould, possibly because sulphonated lignin contains sugar impurities from hemicellulose that are degraded during sulphite pulping (Forss et al., 1985). My results on the effects of lignosulphonate additives on the photostability of PF resin treated veneers partially accord with the findings of Liu (2011), who exposed yellow cedar veneers treated with 12% LMW PF resin and 10% lignosulphonate to 50 days of outdoor weathering. My results on the adverse effects of lignin additives on colour stability, weight and tensile strengths of PF-treated veneers during
outdoor exposure also accord with those of Liu (2011). However, she found that lignosulphonate increased yellowing and weight and tensile strength losses of PF-treated veneers after weathering, whereas I found that yellowing of PF-treated veneers was reduced by kraft lignin, but it was unaffected by lignosulphonate and unsulphonated kraft lignin; weight loss was unaffected by kraft lignin and unsulphonated kraft lignin; and tensile strength loss was unaffected by lignosulphonate and unsulphonated kraft lignin. These differences in my findings and those of Liu (2011) may be due to the lower PF resin concentration and different type of lignin additive employed by Liu (2011) and the ones used here.

Pigments also enhanced the photostability of PF-treated veneers. Pigments protect wood surfaces against photodegradation by absorbing or scattering UV and visible light (Robinson et al., 2006; Wypych, 2015). Darker pigments are better photostabilizers than lighter pigments, because they absorb light better than light-coloured pigments (Robinson et al., 2006). This was evident in my results. Carbon black and the black dye (CNA70) imparted greater photoprotection to PF-treated veneers than yellow iron oxide or a brown pigment. Carbon black and CNA70 provided similar levels of photoprotection to treated veneers during weathering, as shown in the colour change and weight and tensile loss results. Carbon black restricts photodegradation of lignin during weathering by scavenging free radicals and blocking UV and visible light and oxygen from reaching exposed wood surfaces. In contrast, black or other coloured iron oxide pigments can only screen UV light (Heskins & Guillet, 1968; Bigger, 1989; Pappas & Wicks, 2007; Shauwecker et al., 2014). It is noteworthy that carbon black and the black dye were the only pigments that restricted weight losses of PF-treated veneers, and they had similar ability to restrict colour change and weight losses of veneers during weathering. However, carbon black is acidic and a black surface strongly absorbs infrared radiation (heat), which may have caused tensile strength losses and microstructural changes in veneers that were treated with PF resin and carbon black or black dye when they were subject to IR curing (Matsumura et al., 1976; Pappas & Wicks, 2007). Carbon black is unable to
reduce yellowing of white coatings, because it absorbs all wave lengths of light, according to Pappas and Wicks (2007), which may account for why veneers treated with PF and carbon black or black dye yellowed, whereas yellowing did not occur to the same extent in veneers treated with PF and yellow iron oxide. The iron oxide additive was not very effective at protecting PF-treated veneers, which does not accord with findings of Liu (2011). Again, difference in treatments may account for this discrepancy.

The wax emulsion additive in combination with PF and PF and other additives had limited effects on the photostability of veneers, in accord with the findings of Liu (2011). The wax additive increased weight losses of veneers treated with PF resin and ferric chloride, but it restricted yellowing. However, Zahora (2000) found that the treatment of southern pine boards with CCA preservative solution containing this wax additive was able to restrict surface checking of treated boards when they were exposed to 9 years of natural weathering in North Carolina, U.S.A. The effects of this wax additive on the performance of boards treated with PF resin and ferric chloride will be assessed in the following chapter.

This study screened different types of photostabilizers and hydrophobe additives for PF resin treatment, and cured treatments with IR radiation. This approach has not been used before. Wood veneers were heated directly by halogen lamps, so the veneer could quickly reach curing temperatures of 146.5 ± 1.5°C. They were fully cured in 2 minutes and 50 seconds, which is much shorter than 120 minutes of curing in a convection oven, as used in Chapter 3.

Ferric chloride provided some resistance to PF-treated veneers against mould, a finding that accords with Pandey and Pitman (2002). They found that rubberwood treated with 5% ferric chloride resisted mould growth when exposed outdoors for a year. However, they noted that ferric chloride did not reduce photodegradation of lignin. One unexpected finding was the synergistic effect of PF resin, lignosulphonate (REAX) and organic stabilizers. Lignosulphonate improved the ability of Lignostab to restrict darkening and weight losses of veneers and had a positive effect on tensile strength of PF-treated
veneers after weathering. Lignosulphonate also improved the ability of HALS (123DW) to restrict darkening of veneers and improved the ability of UVA (477DW) to reduce yellowing.

5.5 Conclusions

I conclude that ferric chloride is a more effective additive for PF resin than the lignin stabilizer, Lignostab. Lignostab is designed to photostabilize wood rather than PF resin. Ferric chloride restricted discolouration of PF resin treated veneers, reduced colonization of veneers by mould and restricted weight and tensile strength losses. However, ferric chloride appeared to increase micro-checking of PF-treated veneers, although this adverse effect was reduced by the addition of a wax emulsion to PF resin and ferric chloride solution. Wax additive may provide PF resin and ferric chloride pine deck boards with resistance to surface checking during outdoor exposure. This additive combination will be tested in Chapter 6.

Infrared curing showed promise as an efficient approach to curing PF resin treated veneers. Infrared curing could be used to cure PF resin envelope treated decking timber. IR curing technology is used by the finishing industry to cure water-based coatings in a continuous process (Prime Heat Inc., 2014). The use of IR curing to commercially cure PF resin envelope treated timber could be a time and energy efficient alternative to curing with a convection kiln.
Chapter 6: Envelope Modification of Preservative-Treated Pine Decking with Low Molecular Weight Phenol Formaldehyde Resin

6.1 Introduction

In the previous chapter, I found that PF resin and ferric chloride was more effective than PF resin and the ‘lignin stabilizer’, Lignostab, at photostabilizing wood veneers exposed to the weather. Veneers modified with PF resin and ferric chloride had better resistance to discolouration than veneers modified with PF resin and other additives. Modification with PF resin and ferric chloride, however, encouraged micro-checking of cell walls and tensile strength losses of modified veneers were greater than those of PF-modified veneers. These adverse effects, however, were less pronounced when veneers were modified with a PF resin and ferric chloride solution containing wax emulsion. Veneers are used to screen chemicals for photoprotective effects (Evans & Schmalzl, 1989), but more realistic tests are needed to determine if PF resin modifications containing ferric chloride and wax can protect solid wood from photodegradation.

In this chapter, I focus on the use of the PF resin formulations that performed well in Chapter 5 as surface modifications for preservative-treated wood. I hypothesize that PF resin and ferric chloride will be better at protecting preservative-treated Scots and southern pine deck boards from weathering than PF resin/Lignostab combination. I further hypothesize that addition of a wax emulsion to PF resin and ferric chloride solutions used to modified deck boards will provide further beneficial effects, particularly resistance of deck boards to checking. To test these hypotheses, I conducted two experiments. The first one compared the ability of unmodified PF solution and PF resin solutions containing Lignostab (2%), ferric chloride (2%) or ferric chloride (2%) and wax (2%) to protect Scots pine boards treated with copper azole or a metal-free azole-based clear preservative from the adverse effects of weathering. The second experiment was very similar and assessed the ability of unmodified and modified PF resin solutions to
protect untreated southern pine boards or southern pine boards treated with copper azole type c, micronized copper azole type c or metal-free azole-based clear preservatives.

6.2 Materials and methods

6.2.1 Experimental design and statistical analyses

I designed an experiment to assess the ability of envelope modifications with different PF resin solutions (20% PF, 20% PF and 2% Lignostab, 20% PF and 2% ferric chloride, 20% PF, 2% ferric chloride and 2% wax) to protect treated (copper azole, azole) Scots pine boards from the adverse effects of natural weathering. Sixty Scots pine samples were cut from 10 boards treated with copper azole (CA) and 10 boards treated with clear metal-free azole formulation. A second experiment assessed the ability of envelope modifications with different PF resin solutions (20% PF, 20% PF and 2% Lignostab, 20% PF and 2% ferric chloride, 20% PF, 2% ferric chloride and 2% wax) to protect untreated southern pine and southern pine boards treated with different preservatives (copper azole type c, micronized copper azole type c, azole). Sixty southern pine samples were cut from 5 untreated boards, 5 boards treated with copper azole type c (CA-C), 5 boards treated with micronized copper azole type c (mCA-C) and 5 boards treated with a clear metal-free (clear-organic) azole formulation. Replication mainly occurred at the (sample) level in both experiments. Statistical analyses accounted for random variation between samples. Decking samples in both experiments were randomly assigned to the different modifications or unmodified control.

Analysis of variance (ANOVA) assessed the effects of modification on the following measures of the resistance of deck board samples to weathering: (1) colour change; (2) surface checking; (3) contact angle; (4) surface erosion. Experimental results were analyzed using Genstat Version 18.1, 18.2 (VSN International, 2015, 2016). Some transformations were carried out to ensure data met the assumptions
of ANOVA (normality of residuals, homogeneity of variance, independence of sampling, independent observations). Statistically significant ($p<0.05$) results are graphed, and individual means can be compared using error bars ($\pm$ standard error of difference from ANOVA) or least significant difference (LSD) bars derived from Fisher’s least significant difference test (Williams & Abdi, 2010).

6.2.2 Preparation and characterization of pine deck board samples and SEM samples

Scots pine decking samples in the first experiment were cut from 20 different boards that measured 500 mm (longitudinal) x 90 mm (tangential) x 30 mm (radial). The Scots pine boards contained sapwood or heartwood and were treated in a commercial plant with a copper azole (Tanalith® E) or an azole-based organic (Tanalith® M) preservative. The boards were ripped to width using a sliding table saw (Martin T75 PreX, Otto Martin Maschinenbau GmbH & Co. KG, Otteobeuren, Germany) and cross-cut to length using a chop saw (Omga® T55-300, OMGA, Inc., South Bend, I.N., U.S.A.). The final dimensions of the Scots pine decking samples were 150 mm (longitudinal) x 90 mm (tangential) x 30 mm (radial). Southern pine deck board samples in the second experiment were cut mainly from sapwood, and were obtained from 20 different boards that measured 603 mm (longitudinal) x 91 mm (tangential) x 30 mm (radial). The southern pine boards were untreated or commercially treated with a copper azole type c, micronized copper azole type c or azole based (Wolman® AG) preservative. The boards were machined to size with a table saw and chop saw, as above. The final dimensions of the southern pine samples were 175 mm (longitudinal) x 91 mm (tangential) x 30 mm (radial). End grain of samples was sealed with a marine epoxy resin (PC Products PC-11®, Protective Coating Company, Allentown, P.A., U.S.A.) to restrict the formation of end-checks. The decking samples were conditioned in a constant climate room (20 ± 1 °C and 65 ± 5% r.h.) for 30 days before their weight, colour and hydrophobicity were measured.

Conditioned deck board samples were each weighed using a digital analytical balance (PG5002-S, Mettler Toledo, Switzerland). A 90 mm x 30 mm x 5 mm offcut from each conditioned board was oven
dried at 105 ± 5 °C for 24 hours, weighed, and calculated for its moisture content. The weights of modified and conditioned samples were adjusted accordingly to calculate treatment weight gains.

Small samples for scanning electron microscopy (SEM) were prepared from unmodified and untreated Scots and southern pine and yellow cedar boards, as described in Section 3.2.2 (Chapter 3). Yellow cedar SEM samples were included, because experiments in Chapter 3 and 5 assessed the effects of PF resin modifications on weathering of yellow cedar, Scots pine and southern pine samples (SEM blocks and veneers) and I wanted to compare the effects of PF resin modification on the microstructure of pine with results obtained in Chapter 3 and 5.

6.2.3 Synthesis and preparation of modified PF resin

Aqueous low molecular weight phenol formaldehyde resin was supplied by Arclin USA Inc. (Springfield, O.R., U.S.A.), as described in Chapters 3 to 5. Three batches of PF resin were supplied, each contained 46.69% (Experiment 1) and 26.67% (Experiment 2) solids. The chemical composition of a typical batch of parent PF resin is described in Chapter 3 (Section 3.2.3). PF resin concentrate was diluted with tap water to obtain the desired concentration (20%) of PF resin. Water-soluble lignin stabilizer (LIGNOSTAB® 1198) was supplied by CIBA Specialty Chemicals Corp (Tarrytown, N.Y., U.S.A.). Ferric chloride was purchased from EM Science (now Merck Millipore, Billeria, M.A., U.S.A.). A wax emulsion (UW5F, 40% solids) wax supplied by Viance LCC (Charlotte, North Carolina, U.S.A.). All modification formulations are shown in Table 6.1.
Table 6.1 – PF resin modification solutions, concentration of additives and abbreviated treatment names

<table>
<thead>
<tr>
<th>No.</th>
<th>Modification</th>
<th>PF resin concentration (% w/w)</th>
<th>Additive 1 concentration (% w/w)</th>
<th>Additive 2 concentration (% w/w)</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment 1: Preservative-treated Scots pine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Control</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Water</td>
</tr>
<tr>
<td>2.</td>
<td>PF resin</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>PF</td>
</tr>
<tr>
<td>3.</td>
<td>PF resin + LIGNOSTAB 1198</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+Lstab</td>
</tr>
<tr>
<td>4.</td>
<td>PF resin + ferric chloride</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+FeCl₃</td>
</tr>
<tr>
<td>5.</td>
<td>PF resin + ferric chloride + UW5F</td>
<td>20</td>
<td>2 - FeCl₃</td>
<td>2 - wax</td>
<td>PF+FeCl₃+wax</td>
</tr>
<tr>
<td></td>
<td>Experiment 2: Preservative-treated and untreated southern pine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Control</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Water</td>
</tr>
<tr>
<td>2.</td>
<td>PF resin</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>PF</td>
</tr>
<tr>
<td>3.</td>
<td>PF resin + LIGNOSTAB 1198</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+Lstab</td>
</tr>
<tr>
<td>4.</td>
<td>PF resin + ferric chloride</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td>PF+FeCl₃</td>
</tr>
<tr>
<td>5.</td>
<td>PF resin + ferric chloride + UW5F</td>
<td>20</td>
<td>2 - FeCl₃</td>
<td>2 - wax</td>
<td>PF+FeCl₃+wax</td>
</tr>
</tbody>
</table>

Weight gains of copper azole and azole-treated Scots pine decking samples arising from different envelope modifications are shown in Table 5.2. There was a significant ($p=0.036$) preservative x wood type effect on treatment weight gain of Scots pine samples, when averaged across PF resin modifications. This interaction occurred because CA-treated samples containing sap and heartwood had greater weight gains than those of similarly treated heartwood or sapwood samples, but differences between wood types were not observed in clear-organic-treated boards. Furthermore, CA-treated heartwood samples had lower weight gain than heartwood samples treated with a clear preservative, whereas weight gains in samples containing sapwood or sap and heartwood were similar. The ferric chloride and wax additive had a significant ($p<0.001$) negative effect on weight gain of PF-modified samples compared to the wax additive, when results are averaged across preservative treatments and wood type.
Table 6.2 – Weight gains of copper azole or azole-treated Scots pine deck board samples resulting from envelope modification with modified or unmodified PF resin solutions

<table>
<thead>
<tr>
<th>Envelope modification</th>
<th>Preservative treatment</th>
<th>Treatment weight gain</th>
<th>Percentage (%)</th>
<th>(SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF resin</td>
<td>Copper azole</td>
<td>1.7</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Azole</td>
<td>1.4</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>PF resin + Lignostab</td>
<td>Copper azole</td>
<td>1.9</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Azole</td>
<td>1.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>PF resin + ferric chloride</td>
<td>Copper azole</td>
<td>1.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Azole</td>
<td>1.3</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>PF resin + ferric chloride + wax</td>
<td>Copper azole</td>
<td>1.3</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Azole</td>
<td>1.2</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3 shows weight gains of southern pine boards after modification with PF resin solutions.

Weight gains of CA-C treated southern pine samples after modification with PF resin solutions, when averaged across all PF resin modifications, were significantly ($p=0.01$) greater than those of mCA-C or untreated samples. Weight gains of clear-organic preservative-treated southern pine samples were not significantly ($p>0.05$) different from those of mCA-C treated or untreated samples. Additives (Lignostab, ferric chloride, wax) did not affect weight gains of PF-modified southern pine boards (averaged across preservative treatments).
Table 6.3 – Weight gains of preservative-treated or untreated southern pine deck board samples resulting from envelope modification with modified or unmodified PF resin solution

<table>
<thead>
<tr>
<th>Envelope modification</th>
<th>Preservative treatment</th>
<th>Treatment weight gain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Percentage (%) (SD)</td>
</tr>
<tr>
<td>PF resin</td>
<td>Untreated</td>
<td>4.7 (0.8)</td>
</tr>
<tr>
<td></td>
<td>Copper azole - type C</td>
<td>8.5 (2.8)</td>
</tr>
<tr>
<td></td>
<td>Micronized copper azole – type C</td>
<td>4.8 (1.4)</td>
</tr>
<tr>
<td></td>
<td>Azole</td>
<td>5.0 (3.0)</td>
</tr>
<tr>
<td>PF resin + Lignostab</td>
<td>Untreated</td>
<td>5.2 (1.4)</td>
</tr>
<tr>
<td></td>
<td>Copper azole - type C</td>
<td>8.8 (2.5)</td>
</tr>
<tr>
<td></td>
<td>Micronized copper azole – type C</td>
<td>5.0 (1.4)</td>
</tr>
<tr>
<td></td>
<td>Azole</td>
<td>6.1 (1.6)</td>
</tr>
<tr>
<td>PF resin + ferric chloride</td>
<td>Untreated</td>
<td>5.0 (2.1)</td>
</tr>
<tr>
<td></td>
<td>Copper azole - type C</td>
<td>6.9 (1.6)</td>
</tr>
<tr>
<td></td>
<td>Micronized copper azole – type C</td>
<td>3.5 (0.3)</td>
</tr>
<tr>
<td></td>
<td>Azole</td>
<td>6.1 (2.7)</td>
</tr>
<tr>
<td>PF resin + ferric chloride + wax</td>
<td>Untreated</td>
<td>2.4 (0.5)</td>
</tr>
<tr>
<td></td>
<td>Copper azole - type C</td>
<td>4.9 (1.0)</td>
</tr>
<tr>
<td></td>
<td>Micronized copper azole – type C</td>
<td>3.5 (1.8)</td>
</tr>
<tr>
<td></td>
<td>Azole</td>
<td>5.3 (2.5)</td>
</tr>
</tbody>
</table>

6.2.4 Modification of pine deck board samples

PF resin solutions were stored below -20 °C and thawed at room temperature in a fumehood for 2.5 hours before they were used to impregnate Scots and southern pine decking samples. Individual samples were sealed in a chilled (-20 °C for 115 minutes) 130 mm (diameter) by 18 mm (height) glass vacuum cylinder. Excess volume in the cylinder was reduced by filling it with chilled glass marbles (15 mm in diameter). The glass cylinder was inserted into an ice jacket mold inside a 177 mm (length) x 177 mm (width) x 173 mm (height) acrylic lab storage container (Thermo Fisher Scientific, Waltham, M.A., U.S.A.). A vacuum (-90 kPa) was pulled in the cylinder for 15 minutes using a rotary vane vacuum pump (ED200A, Edwards High Vacuum International Ltd., Crawley, U.K.). The vacuum was used to draw the modification solution into the cylinder from a 1 litre capacity HDPE laboratory bottle (Thermo Fisher Scientific, Waltham, M.A., U.S.A.) that was placed in a 150 mm (length) x 150 mm (width) x 152 mm (height) acrylic vessel containing ice (Thermo Fisher Scientific, Waltham, M.A., U.S.A.). The vacuum cylinder was sealed
and the deck board sample remained submerged in the solution for an additional 15 minutes, and the vacuum was then released. The impregnated deck board sample was removed from the cylinder, placed inside a beaker for 1 minute to drain off excess PF resin solution and weighed using a digital analytical balance (PG5002-S, Mettler Toledo, Columbus, O.H., U.S.A.). The impregnated decking sample was air-dried in a fumehood for 72 hours, and conditioned in a constant climate room (20 ± 1 °C, 65 ± 5% r.h.) for an additional 48 hours. It was then cured for 120 minutes in a convection oven (G01305A, Lindberg/Blue M™, Riverside, M.I., U.S.A.), where thermocouples attached on surface of samples indicated that temperature ramped up from 20 °C to 155 ± 5 °C in 80 minutes and remained at 155 ± 5 °C for a further 40 minutes.

SEM samples were prepared as described in Chapter 3. Samples were conditioned for 5 days and submerged in a 30 mL beaker containing PF resin, ferric chloride or PF resin ferric chloride and wax solution at room temperature for 10 minutes. After modification, they were held against the wall of a 150 mL beaker for 5 minutes to drain off excess solution, clipped at one end to a wire rack and air dried in a fumehood for 30 minutes, and then cured in a convection oven at 130 ± 5 °C for 120 minutes.

6.2.5 Weathering trial

Modified decking samples were predrilled at 4 locations 10 mm from endgrain and 10 mm from the sides of the samples using a 3.97 mm diameter drill bit driven by a drill press (75-260M1, General International MFG. Co. LTD., Whitehouse, O.H., U.S.A.). Twelve Scots pine decking samples (Experiment 1) were fastened using 8 x 2” (20.32 cm x 5.08 cm) deck screws (Paulin Dura Grip Duradized II, H. Paulin & Co., Toronto, O.N., Canada) to preservative-treated strips of wood, measuring 1400 mm (length) x 50 mm (width) x 50 mm (thickness). A set of twenty southern pine samples (Experiment 2) were fastened to preservative-treated strips of wood, measuring 2500 mm (length) x 50 mm (width) x 50 mm (thickness). For each set of samples, an untreated wooden board was fastened to the ends of each set (row) of samples.
to prevent weathering of the sides of samples at the ends of the rows. These untreated wooden boards in Experiments 1 and 2 measured 150 mm (length) x 30 mm (width) x 30 mm (thickness) and 603 mm (length) x 30 mm (width) x 30 mm (thickness), respectively. Five replicate sets of Scots pine samples (Exp. 1) were fastened using decking screws to a sub-frame (rack) constructed from preservative-treated timber. Three replicate sets of southern pine samples (Exp. 2) were also fastened as above to a subframe (rack) made from preservative-treated spruce-pine-fir timber. The order of deck boards within each rack was randomized. Decking samples were spaced 10 mm apart and mounted bark side up (convex) with their ends flush against the sides of the preservative-treated wood strips. Samples in Experiments 1 and 2 were exposed horizontally to the weather on UBC’s Vancouver campus in two 91-day (3 months) trials for a total of 182 days (6 months). Scots pine samples (Exp. 1) were exposed from March 2nd to June 1st, 2016, and July 1st to September 30th, 2016. Southern pine samples (Exp. 2) were exposed from August 17th to November 16th, 2015, and March 31st to June 30th, 2016. Weathering conditions during the exposure trials are shown in Table 5.3. The weathering schedule for SEM samples is described in Chapter 3 (Section 3.2.5).

Table 6.4 – Weathering conditions in Vancouver, British Columbia, Canada during the 6-month exposure trials of PF-modified, preservative-treated Scots pine (Exp. 1) or southern pine (Exp. 2) decking samples

<table>
<thead>
<tr>
<th>Month</th>
<th>Temperature (°C)</th>
<th>Total Precipitation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum¹</td>
<td>Mean</td>
</tr>
<tr>
<td>August</td>
<td>22.3</td>
<td>18.4</td>
</tr>
<tr>
<td>September</td>
<td>17.7</td>
<td>14.1</td>
</tr>
<tr>
<td>October</td>
<td>14.9</td>
<td>11.8</td>
</tr>
<tr>
<td>November</td>
<td>8.5</td>
<td>5.0</td>
</tr>
<tr>
<td>March</td>
<td>11.6</td>
<td>8.3</td>
</tr>
<tr>
<td>April</td>
<td>15.7</td>
<td>11.8</td>
</tr>
<tr>
<td>May</td>
<td>18.5</td>
<td>14.2</td>
</tr>
<tr>
<td>June</td>
<td>20.2</td>
<td>16.1</td>
</tr>
<tr>
<td>July</td>
<td>22.0</td>
<td>18.3</td>
</tr>
<tr>
<td>August</td>
<td>22.3</td>
<td>18.4</td>
</tr>
<tr>
<td>September</td>
<td>18.0</td>
<td>14.2</td>
</tr>
</tbody>
</table>

¹Average maximum and minimum daily temperatures

Data collected for Vancouver International Airport, [http://climate.weather.gc.ca/historical_data/search_historic_data_e.html](http://climate.weather.gc.ca/historical_data/search_historic_data_e.html)
6.2.6 Assessment of the photoprotective effects of PF resin modifications on the properties of Scots and southern pine deck board samples

After weathering, deck board samples were conditioned in a constant climate room at 20 ± 1 °C and 65 ± 5% relative humidity for a minimum of ten days. Decking samples were scanned using a desk-top scanner as described in Chapter 4 (Section 4.2.5.1) before and after modification and after 13 weeks and 6 months of natural weathering. Paper templates similar to those described in Chapter 4 (Section 4.2.5.1) were used to ensure that the location of colour and contact angle measurements on earlywood and latewood surfaces was randomized and consistent at each measuring interval.

Figure 6.1 – Images showing (a) preservative-treated and PF-modified Scots pine deck board samples; (b) preservative-treated and PF-modified southern pine deck board samples. Image shows samples on the first day of the weathering trials.
Procedures for colour measurement of deck boards before and after weathering are the same as those described in Chapter 4 (Section 4.3.2). Overall colour change at exposed surfaces of samples after natural weathering is expressed using the Delta E parameter, calculated using CIE 1976 colour-difference formula (CIE Colorimetry Committee, 1974):

\[
\Delta E_{ab} = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}
\]

The method used to measure the surface hydrophobicity of samples is different to that used earlier in Chapter 4 (Section 4.2.5.2). Initial contact angle \(C_i\) was averaged across both sides of water droplets. The time for water droplets to spread across the surface of samples and attain a contact angle of 90° (\(C_{<90°}\)) or less was also measured. Both parameters were used as measures of hydrophobicity of modified and unmodified deck board surfaces. Sessile drop method and a goniometer (KSV CAM 101, KSV Instruments Ltd., Espoo Finland) was used to measure contact angle, as described in Chapter 4 (Section 4.2.5.2). A 5 µL droplet of distilled water was placed on the earlywood and latewood of samples and images of the droplet were recorded every 16 milliseconds for 313 images and every 1 second for 2500 images thereafter. Contact angle between the water droplet and the wood surface was measured from images taken 0.016, 0.032 and 0.048 seconds after the droplet stabilized at the wood surface. Contact angles were calculated from images using a Young-Laplace algorithm within the CAM 200 software (KSV Instruments Ltd., Espoo, Finland) (KSV Instruments, 2007). Initial contact angles of droplets on earlywood and latewood on each sample were calculated from three images. The time for the left and right contact angle of water droplets to become less than 90° (time \(CA_{<90°}\)) was recorded. This measure was chosen, because a contact angle of 90° or less indicates that the wood surfaces are hydrophilic, and capillary pressure allows absorption of liquid into the wood’s microstructure (Adam, 1963; Lotter, 2014).

The lengths, widths and areas of the ten largest checks that formed at the surfaces of deck board samples during natural weathering were measured as described in Chapter 4 (Section 4.2.5.3).
Erosion at the surface of decking samples was measured after samples were weathered for 6 months. A stainless-steel mask measuring 40 mm x 15 mm x 0.76 mm was fastened to a corner of each sample with #6 x 1/4” (6.35 mm) stainless steel pan head screws. A 10 mm diameter hole in each mask exposed a circular area of the sample to weathering, while masking adjacent wood. Earlywood and latewood within the unmasked areas and the adjacent unweathered areas was scanned using a non-contact confocal white light profilometer (Altisurf® 500, Altimet SAS, Thonon-les-bains, France). Earlywood and latewood (unmasked and masked) was profiled. Each line scan measured the heights of the weathered and unweathered surface at 13000 points. The line scan was performed using a 3 mm (3000 µm to 92 µm) probe at 1 µm spacing with a scan speed of 250 µm/s. The difference in heights of masked (higher) and unmasked (lower) surfaces represent the erosion of samples (Fig. 6.2).

Figure 6.2 – A linear profile of earlywood of azole-preservative treated Scots pine sample after 6 months of natural weathering, showing the heights of masked (L1-R1) and unmasked (L2-R2) surfaces

6.2.7 Scanning electron microscopy

Weathered and unweathered SEM samples were conditioned in a constant climate control room for a minimum of seven days and cut to thickness using a razor saw, whose blade measured 114.3 mm (length) x 11.1 mm (height) and 0.254 mm (kerf). SEM samples measured 3 mm x 2 mm x 2 mm, and were fixed to 12 mm diameter aluminum stub using 11 mm diameter double-sided adhesive tabs (#76760,
Electron Microscopy Sciences Inc., Hatfield, PA, U.S.A.). Samples were thinly coated with 8 nm of gold and examined at a working distance of 13.3 to 16.0 mm using a Zeiss UltraPlus analytical field emission scanning electron microscope (Zeiss, Oberkochen, Germany) with an accelerating voltage of 5kV. Scanning electron images of weathered and unweathered samples were saved as TIFF files.

6.3 Results

6.3.1 Preservative-treated Scots pine deck boards

Table 6.5 summarizes the effects of modifications and wood characteristics on the parameters used to assess the performance of deck boards exposed to natural weathering. Most of the individual factors (preservative treatment, envelope modification, tissue type) had significant effects on weathering parameters. There were numerous two-factor interactions, and one three-factor interaction.

Table 6.5 – Significant effects of preservative treatment, PF resin modification, wood tissue, and interactions between treatments, modifications and wood tissues on weathering parameters used to assess the performance of Scots pine decking samples exposed to 6 months of natural weathering.

<table>
<thead>
<tr>
<th>Weathering parameters</th>
<th>Experimental factors</th>
<th>Preservative treatment</th>
<th>Envelope modification</th>
<th>Tissue type</th>
<th>Preservative x envelope</th>
<th>Preservative x tissue</th>
<th>Envelope x tissue</th>
<th>Preservative x envelope x tissue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall colour change</td>
<td>**</td>
<td>**</td>
<td>NS</td>
<td>**</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td>Ten largest checks</td>
<td>Average area</td>
<td>NS</td>
<td>**</td>
<td>N/A</td>
<td>NS</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Average length</td>
<td>NS</td>
<td>**</td>
<td>N/A</td>
<td>NS</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Average width</td>
<td>NS</td>
<td>**</td>
<td>N/A</td>
<td>*</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Contact angle</td>
<td>Initial Unweathered</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Weathered</td>
<td>***</td>
<td>***</td>
<td>**</td>
<td>***</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Duration (time) Unweathered</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>**</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Weathered</td>
<td>NS</td>
<td>**</td>
<td>NS</td>
<td>**</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

*** = p<0.001; ** = p<0.01; * = p<0.05; NS = p>0.05 (not significant); N/A = not available
6.3.1.1 Appearance of preservative-treated Scots pine decking samples after envelope modification and weathering

Clear-organic preservative-treated Scots pine earlywood was a blotchy red colour after modification with PF resin, while there was little colour change in latewood as a result of modification with PF resin (Fig. 6.3-6.6). The blotchy red colour of PF-modified earlywood in clear-organic preservative-treated samples was more pronounced than that in samples modified with PF resin and Lignostab. Earlywood in clear-Scots pine samples became a dark red to brown colour after modification with PF resin and ferric chloride, such a colour change was less pronounced in similarly modified latewood. The colour of wood modified with PF resin, ferric chloride and wax was similar to that of wood modified with PF resin and ferric chloride. Modification with PF resin or PF resin and lignin stabilizer had little effect on the colour of CA-treated wood (Fig. 6.7-6.10). Wood modified with PF resin and ferric chloride was darker than unmodified CA-treated wood. Colour changes of earlywood and latewood in heartwood of clear- or CA-treated samples following modification with different PF resin solutions were less pronounced than those of similarly modified sapwood.

Clear-Scots pine controls became less yellow after weathering. Sapwood of clear-treated controls brightened during weathering, whereas heartwood darkened (Fig. 6.3, 6.5). Clear-samples modified with PF resin became yellower and redder as a result of weathering. Such colour changes were more pronounced in clear-samples modified with PF resin and the lignin stabilizer, Lignostab. Clear-samples modified with PF resin and ferric chloride became bluer and darker during weathering (Fig. 6.4, 6.6). The blotchy colouration of PF-modified samples was unchanged after weathering. The colour of PF resin and ferric chloride modified CA- and clear- Scots pine samples was similar to that of similarly treated samples modified with PF resin, ferric chloride and wax. Exposure to weathering resulted in little colour change in CA-treated Scots pine controls, whereas there was more discolouration of the samples modified with PF resin solutions. Sapwood of CA-treated pine boards modified with PF resin on its own or containing lignin
stabilizer became yellower and redder (Fig. 6.7). Colour changes in heartwood were less pronounced (Fig. 6.9). In comparison, CA-treated pine samples modified with PF resin and ferric chloride became greener and darker after weathering (Fig. 6.8 and 6.10). Again, colour changes were less pronounced in heartwood (Fig. 6.10). Colour differences between earlywood and latewood, in PF-modified clear- or CA-treated Scots pine boards were less pronounced after weathering.

Larger surface checks were present in unmodified CA-treated Scots pine samples than in unmodified samples treated with organic-preservative. PF-modification clearly reduced checking. Checks in PF-modified CA-treated pine boards were narrower than those in clear-boards modified with PF resin. Checking of CA-treated or clear-boards was less pronounced when they were modified with PF resin containing additives. Treated samples modified with PF resin and ferric chloride had longer checks than PF-modified (treated samples), although this adverse effect of modification was mitigated when the PF resin and ferric chloride solution contained wax. Heartwood was more resistant to checking than sapwood, as expected.

Mould was not observed at weathered surfaces of unmodified CA-treated pine samples, but mould was present at the surface of unmodified samples treated with organic preservative. Mould was more pronounced at the surface of heartwood of unmodified wood treated with organic-preservative than in similarly treated and exposed sapwood samples. Mould was absent from CA- or organic preservative-treated samples modified with PF resin solutions. Scanned images of all modified and unmodified preservative-treated Scots pine samples before and after natural weathering can be found in Appendix 4.
Figure 6.3 – Images of organic preservative-treated Scots pine (sapwood) deck boards before and after weathering for 6 months: (a) unweathered control; (b) unweathered sample modified with PF resin; (c) unweathered sample modified with PF resin and lignin stabilizer; (d) weathered control; (e) weathered sample modified with PF resin; (f) weathered sample modified with PF resin and lignin stabilizer. Scale bar is 10 mm
Figure 6.4 – Images of organic preservative-treated Scots pine (sapwood) deck boards before and after weathering for 6 months: (a) unweathered sample modified with PF resin and ferric chloride; (b) unweathered sample modified with PF resin, ferric chloride and wax; (c) weathered sample modified with PF resin and ferric chloride; (d) weathered sample modified with PF resin, ferric chloride and wax. Scale bar is 10 mm
Figure 6.5 – Images of organic preservative-treated Scots pine (sapwood and heartwood) deck boards before and after weathering for 6 months: (a) unweathered control; (b) unweathered sample modified with PF resin; (c) unweathered sample modified with PF resin and lignin stabilizer; (d) weathered control; (e) weathered sample modified with PF resin; (f) weathered sample modified with PF resin and lignin stabilizer. Scale bar is 10 mm
Figure 6.6 – Images of organic preservative-treated Scots pine deck boards (sapwood and heartwood) before and after weathering for 6 months: (a) unweathered sample modified with PF resin and ferric chloride; (b) unweathered sample modified with PF resin, ferric chloride and wax; (c) weathered sample modified with PF resin and ferric chloride; (d) weathered sample modified with PF resin, ferric chloride and wax. Scale bar is 10 mm
Figure 6.7 – Images of copper azole-treated Scots pine (sapwood) deck boards before and after weathering for 6 months: (a) unweathered control; (b) unweathered sample modified with PF resin; (c) unweathered sample modified with PF resin and lignin stabilizer; (d) weathered control; (e) weathered sample modified with PF resin; (f) weathered sample modified with PF resin and lignin stabilizer. Scale bar is 10 mm
Figure 6.8 – Images of copper azole-treated Scots pine (sapwood) deck boards before and after weathering for 6 months: (a) unweathered sample modified with PF resin and ferric chloride; (b) unweathered sample modified with PF resin, ferric chloride and wax; (c) weathered sample modified with PF resin and ferric chloride; (d) weathered sample modified with PF resin, ferric chloride and wax. Scale bar is 10 mm
Figure 6.9 – Images of copper azole-treated Scots pine deck boards (sapwood and heartwood) before and after weathering for 6 months: (a) unweathered control; (b) unweathered sample modified with PF resin; (c) unweathered sample modified with PF resin and lignin stabilizer; (d) weathered control; (e) weathered sample modified with PF resin; (f) weathered sample modified with PF resin and lignin stabilizer. Scale bar is 10 mm
Figure 6.10 – Images of copper azole-treated Scots pine deck boards (sapwood and heartwood) before and after weathering for 6 months: (a) unweathered sample modified with PF resin and ferric chloride; (b) unweathered sample modified with PF resin, ferric chloride and wax; (c) weathered sample modified with PF resin and ferric chloride; (d) weathered sample modified with PF resin, ferric chloride and wax. Scale bar is 10 mm
6.3.1.2 Colour of modified and unmodified preservative-treated Scots pine decking samples

There was a significant ($p<0.001$, Table 6.5) interactive effect of preservative treatment and envelope modification on colour change (Delta E) of samples exposed to natural weathering. This interaction occurred because the effectiveness of PF resin modifications at reducing colour change varied with preservative treatment (Fig. 6.11). In particular, PF resin and ferric chloride modification reduced the overall colour change of samples treated with organic preservative, whereas no such effect was observed in modified copper azole-treated samples. In addition, colour change of copper azole-treated wood modified with PF resin was greater than that of water-modified controls, whereas a similar effect was not observed with samples treated with organic preservative.

Figure 6.11 – Overall colour change of envelope-modified copper azole and organic preservative-treated Scots pine decking samples after 6 months of natural weathering. Note that results are averaged across wood type (earlywood and latewood). Samples with high Delta E have greater colour change than those with a low Delta E. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.
6.3.1.3 Surface checking of modified and unmodified preservative-treated Scots pine decking samples

There was a significant ($p<0.05$, Table 6.5) preservative treatment x envelope modification interaction on check width. In other words, the effectiveness of the envelope treatments at restricting check width varied with the different treated samples (Fig. 6.12). Most notably the organic preservative-treated samples modified with PF resin had wider checks than the copper azole-treated samples, whereas there were no significant ($p>0.05$) differences in width of checks in treated samples that were modified with the other PF resin formulations. In contrast, the copper-treated controls (water) had wider checks than organic preservative-treated controls. Figure 6.13 shows that variability in widths of ten largest checks in preservative-treated Scots pine boards was reduced by modification with PF resin solutions.

![Graph showing average width of ten largest checks in envelope-modified copper azole and organic preservative-treated Scots pine decking samples after 6 months of natural weathering.](image)

Figure 6.12 – Average width of ten largest checks in envelope-modified copper azole and organic preservative-treated Scots pine decking samples after 6 months of natural weathering. Note that results are averaged across samples treated with the different preservatives. Least significant difference (LSD) bar is ± standard error of difference ($p=0.02$) from analyses of variance.
Figure 6.13 – Variability in width of ten largest checks in envelope-modified copper azole and organic preservative-treated Scots pine decking samples after 6 months of natural weathering

There was a significant ($p<0.001$) effect of envelope modification on the length of the 10 largest checks in treated boards exposed to weathering. The effectiveness of the envelope modification with PF resin was unaffected by preservative treatment. PF resin modification significantly ($p<0.001$) reduced length of checks that developed when samples were exposed to natural weathering (Fig. 6.14). Checks were longer in samples modified with PF resin and ferric chloride compared to those modified with PF resin on its own. Addition of wax emulsion reduced the length of checks in samples modified with PF resin and ferric chloride. There was no significant ($p>0.05$) difference in the length of checks in samples modified with PF resin or PF resin and Lignostab.
Figure 6.14 – Average length of ten largest checks in envelope-modified Scots pine decking samples exposed to 6 months of natural weathering. Note that results are averaged across samples treated with the different preservatives. Error bars are ± standard error of difference (p<0.001) from analyses of variance.

Figure 6.15 shows average area of checks in envelope modified samples exposed to natural weathering (averaged across untreated samples and ones treated with different preservatives). Checks in PF-modified samples were significantly (p<0.001) smaller than those in unmodified controls. The additives did not have a significant (p>0.05) effect on the area of checks in PF-modified boards.
Figure 6.15 – Average area of ten largest checks in envelope-modified Scots pine decking samples exposed to 6 months of natural weathering. Note that results are averaged across samples treated with the different preservatives. Error bars are ± standard error of difference (p<0.001) from analyses of variance

6.3.1.4 Contact angle of water droplets on modified and unmodified surfaces of preservative-treated Scots pine decking samples

There were significant (p<0.001, Table 6.5) single factor effects (preservative treatment, envelope modification, tissue type) and no interactions on initial contact angle (CA$_i$) of preservative-treated samples as a result of modification with different PF resin solutions. CA$_i$ of all modified and water-modified samples was greater than 90°. Copper azole-treated samples had greater CA$_i$ than those of organic preservative-treated samples (averaged across envelope modifications and wood tissues), and CA$_i$ on earlywood of samples was greater than that on latewood of decking samples (averaged across preservative treatments and envelope modifications). Modification with PF resin and additives increased CA$_i$ of samples, whereas there was no significant (p>0.05) effect on CA$_i$ on samples modified with PF resin on its own, when they were averaged across samples treated with different preservatives and wood tissues (Fig. 6.16). The addition of ferric chloride and wax was most effective additive combination increasing CA$_i$ of PF-modified
samples. Ferric chloride increased CA$_i$ on PF-modified samples, whereas Lignostab did not have any significant ($p>0.05$) effect.

Figure 6.16 – Initial contact angle of water droplet formed on surfaces of modified and unmodified Scots pine decking samples averaged across preservative treatment (before weathering). Error bars are ± standard error of difference ($p<0.001$) from analyses of variance

There was a significant preservative x envelope modification interaction ($p<0.001$, Table 6.5) on CA$_i$ of samples after weathering, because CA$_i$ of weathered organic preservative-treated boards modified with PF resin, ferric chloride and wax was greater than that of similarly modified copper azole-treated samples (Fig. 6.17). In contrast, CA$_i$ of unmodified and PF resin and ferric chloride modified organic preservative-treated boards were lower than those of unmodified and similarly modified copper azole-treated deck boards. Furthermore, there was no significant difference in CA$_i$ of copper azole or organic preservative-treated samples modified with PF resin or PF resin and Lignostab. Latewood in weathered samples had a significantly ($p=0.001$) greater CA$_i$ than that of similarly weathered earlywood, when averaged across boards treated with different preservatives and modified with various PF resin solutions.
Figure 6.17 – Initial contact angle of water droplet formed on surfaces of modified and unmodified copper azole and organic preservative-treated samples averaged across PF resin modification after 6 months of natural weathering. Error bars are ± standard error of difference (p<0.001) from analyses of variance.

There was a significant interaction of preservative treatment x envelope modification (p=0.009, Table 6.5) on time$_{CA<90^\circ}$ of preservative-treated deck boards before weathering. There was no difference in time$_{CA<90^\circ}$ of copper azole and organic preservative-treated boards modified with water (control). Time$_{CA<90^\circ}$ of PF resin or PF resin and Lignostab modified copper azole-treated boards was greater than those of organic preservative-treated samples (Fig. 6.18). PF resin, ferric chloride and wax modification increased time$_{CA<90^\circ}$ of CA- or clear-treated boards compared to PF resin solutions containing the other additives. PF resin and ferric chloride modification increased time$_{CA<90^\circ}$ of modified CA-samples, but this did not occur for similarly modified clear-preservative treated boards.

A significant preservative treatment x envelope modification interaction (p=0.009, Table 6.5) for time$_{CA<90^\circ}$ occurred for weathered samples. This interaction occurred because organic preservative-treated boards modified with PF resin, ferric chloride and wax solution had greatest time$_{CA<90^\circ}$, while time$_{CA<90^\circ}$ of other modified or water-modified boards were not significantly (p>0.05) different (Fig. 6.19).
Figure 6.18 – Time for contact angle of water droplets to decrease below 90° on modified and unmodified surfaces of copper azole and organic preservative-treated Scots pine decking samples (before weathering). Note that results are averaged across wood tissues (earlywood and latewood). Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.

Figure 6.19 – Time for contact angle of water droplets to decrease below 90° on modified and unmodified surfaces of copper azole and organic preservative-treated Scots pine decking samples after 6 months of natural weathering. Note that results are averaged across wood tissues (earlywood and latewood). Error bars are ± standard error of difference ($p=0.009$) from analyses of variance.
6.3.1.5 Erosion of modified and unmodified preservative-treated Scots pine decking samples

Erosion was more pronounced at surfaces of Scots pine controls and boards treated with organic-preservative than those treated with copper azole (Fig. 6.20). Erosion of CA- or organic-treated boards was less pronounced when they were modified with PF resin solutions. Envelope modified Scots pine boards treated with copper azole eroded less than similarly modified boards treated with metal-free azole. Modification with PF/Lstab was more effective than PF/ferric at restricting erosion of CA-treated samples (Fig. 6.20f, h). However, modification with PF/Lstab was better than PF/ferric/wax at restricting erosion of organic preservative-treated boards (Fig. 6.20e, i). Latewood was less eroded than earlywood in all samples, except for CA-treated samples modified with PF/Lstab (Fig. 6.20f).
There was a significant ($p=0.024$, Table 6.5) preservative treatment x envelope modification x wood tissue interaction on erosion of Scots pine samples exposed to outdoor weathering, because the effects...
of envelope modification on restricting erosion of deck boards varied with different wood tissues and preservative treatments. However, this effect was only significant at 5% level ($p<0.05$), and since three-factor interactions are very difficult to interpret and explain, I present and describe results for significant ($p<0.001$) two-factor interactions (preservative treatment x envelope modification, envelope modification x tissue type, preservative treatment x tissue type), shown in Figures 6.21a – 6.21c. Erosion of organic-treated samples was restricted by PF resin modifications, and the erosion resistance of PF-modified samples was improved with additives (Fig. 6.21a). The effects of ferric chloride and lignin stabilizer on the erosion of PF-modified organic-boards was not different, and wax emulsion did not significantly ($p>0.05$) affect the erosion resistance of PF resin and ferric chloride modified organic-boards. In comparison, only modification with PF resin and lignin stabilizer was able to restrict erosion of CA-samples. PF resin modifications restricted erosion on earlywood of Scots pine samples, and the addition of lignin stabilizer was able to improve erosion resistance on PF-modified earlywood (Fig. 6.21b). However, envelope modification had no significant ($p>0.05$) effect on erosion on latewood. Latewood was more resistant to erosion than earlywood for preservative-treated boards, and latewood and earlywood of CA-treated boards were more resistant to erosion than those of boards treated with organic-preservative (Fig. 6.21c).
Figure 6.21 – Depth of erosion after 6 months of natural weathering on: (a) envelope-modified copper azole and organic preservative-treated Scots pine samples (averaged across wood tissues, earlywood and latewood); (b) earlywood and latewood of envelope-modified samples, averaged across preservative treatments; (c) earlywood and latewood of copper azole and organic-treated samples, averaged across envelope-modifications. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.
6.3.2 Preservative-treated and untreated southern pine deck boards

The effects of modification and wood characteristics on the parameters used to assess outdoor performance of southern pine decking samples exposed to weathering are summarized in Table 6.6. Most of the individual experimental factors (preservative treatment, envelope modification, tissue type) had significant effects on weathering parameters. There were many two-factor interactions. Preservative treatment x envelope modification in particular had significant ($p<0.001$) effects on all weathering parameters. There was also a significant three-factor interaction.

Table 6.6 – Significant effects of preservative treatment, PF resin modification, wood tissue, and interactions between treatments, modifications and wood tissues on weathering parameters used to assess the performance of southern pine decking samples exposed to 6 months of natural weathering

<table>
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<tr>
<th>Weathering parameters</th>
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<td>Preservative treatment</td>
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<td>Erosion</td>
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*** = $p<0.001$; ** = $p<0.01$; * = $p<0.05$; NS = $p>0.05$ (not significant)

6.3.2.1 Appearance of preservative-treated and untreated southern pine decking samples after envelope modification and weathering

Modification with PF resin made untreated southern pine deck boards darker, redder, but less yellow (Fig. 6.22, 6.23). Boards modified with PF resin and lignin stabilizer became darker and redder. Boards modified with PF resin and ferric chloride had dark and reddish-brown colour, but they were less
dark and red when they were modified with PF/ferric chloride and wax emulsion. Organic preservative-treated boards were similar in colour to untreated (modified boards) as a result of modification with different PF resin solutions, except earlywood of organic preservative-treated boards modified with PF resin containing ferric chloride or ferric chloride or wax was blotchy (Fig. 6.24, 6.25). Copper azole-treated boards modified with PF resin became greener (Fig. 6.26, 6.27). CA-boards modified with PF resin and Lignostab became yellower, whereas those modified with PF resin and ferric chloride became darker and bluer, resulting in an olive-green colour. The olive-green colour of PF resin and ferric chloride modified CA-samples was less pronounced when wax emulsion was combined with the PF resin and ferric chloride solution. Similar colour changes occurred in micronized copper azole-treated boards after envelope modification, except the colours of modified mCA-boards were lighter than those of modified CA-boards. Furthermore, ferric chloride modified mCA-boards became light brown rather than an olive-green (Fig. 6.28, 6.29). Colour changes of earlywood in preservative-treated and untreated southern pine samples as a result of envelope modification were more pronounced than those of latewood. Thus, the colour difference between earlywood and latewood in preservative-treated or untreated samples generally became less pronounced after they were modified with different PF resin solutions (except for untreated and CA-boards modified with PF resin, and treated and untreated boards modified with PF resin and ferric chloride).

Weathering changed the appearance of unmodified and untreated samples. They became a blotchy dark grey colour, except for latewood which retained some of its original colour (Fig. 6.22). PF-modified boards became a yellowish orange colour as a result of weathering. The PF-modified earlywood darkened possibly due to mould, whereas latewood became darker and yellower. Samples modified with PF resin and Lignostab were less orange than those modified with PF resin. Boards modified with PF resin and ferric chloride were dark brown, and mould was heavier on earlywood than on latewood (Fig. 6.23). The appearance of boards modified with PF resin, ferric chloride and wax after weathering was similar to that
of samples modified with PF resin and ferric chloride. The colour of organic preservative-treated boards modified with different PF resin solutions and exposed to weathering were similar to those of untreated samples modified with similar PF resin solutions, except mould was less pronounced and the colours were more uniform on the modified organic preservative-treated boards (Fig. 6.24, 6.25). Unmodified CA-treated samples lost their yellow and green colour after weathering (Fig. 6.26). Earlywood became lighter and greyer, whereas latewood became darker and greener. CA-samples modified with PF resin became a dark yellowish green, and earlywood became much darker than latewood. Colours of PF- and PF-Lignostab-modified CA-boards were similar. CA-boards treated with PF resin and ferric chloride were slightly darker and browner after weathering, and they were largely unaffected by mould (Fig. 6.27). The colour of CA-treated boards modified with PF/ferric and wax was similar to that of boards modified with PF resin and ferric chloride. Unmodified micronized CA-samples became darker, bluer and slightly redder as a result of weathering (Fig. 6.28). Mould was present, but it was less pronounced than that on unmodified CA-boards. PF- and PF-Lignostab-modified mCA-boards both became darker and redder. PF resin and ferric chloride modified mCA-boards were olive-green. Micronized CA-boards modified with PF resin and ferric chloride became olive green in colour, and their colours became more saturated (yellower and greener) than those of similarly modified CA-boards (Fig. 6.29). The colour of mCA-treated boards modified with PF resin/ferric and wax or PF resin/ferric chloride after weathering was similar.

Large checks developed in unmodified and untreated and organic-preservative or CA-treated decking samples. PF resin modification on its own restricted size of checks in copper-treated and untreated boards, but it had little effect on checking of boards treated with an organic preservative. PF resin and Lignostab modification reduced checking of organic preservative-treated samples. Modification with PF resin and ferric chloride reduced width and length of checks in samples treated with CA or the organic-preservative, but checks were longer in modified and untreated boards. PF resin, ferric chloride and wax modification reduced width of checking in mCA-samples, but checks in PF/ferric chloride and
wax-modified CA-boards were wider and longer. Scanned images of all modified and unmodified preservative-treated or untreated southern pine samples before and after natural weathering are appended to this thesis (Appendix 4).
Figure 6.22 – Images showing untreated southern pine deck boards before and after weathering for 6 months: (a) unweathered control; (b) unweathered sample modified with PF resin; (c) unweathered sample modified with PF resin and lignin stabilizer; (d) weathered control; (e) weathered sample modified with PF resin; (f) weathered sample modified with PF resin and lignin stabilizer. Scale bar is 10 mm.
Figure 6.23 – Images showing untreated southern pine deck boards before and after weathering for 6 months: (a) unweathered sample modified with PF resin and ferric chloride; (b) unweathered sample modified with PF resin, ferric chloride and wax; (c) weathered sample modified with PF resin and ferric chloride; (d) weathered sample modified with PF resin, ferric chloride and wax. Scale bar is 10 mm
Figure 6.24 – Images showing organic preservative-treated southern pine deck boards before and after weathering for 6 months: (a) unweathered control; (b) unweathered sample modified with PF resin; (c) unweathered sample modified with PF resin and lignin stabilizer; (d) weathered control; (e) weathered sample modified with PF resin; (f) weathered sample modified with PF resin and lignin stabilizer. Scale bar is 10 mm.
Figure 6.25 – Images showing organic preservative-treated southern pine deck boards before and after weathering for 6 months: (a) unweathered sample modified with PF resin and ferric chloride; (b) unweathered sample modified with PF resin, ferric chloride and wax; (c) weathered sample modified with PF resin and ferric chloride; (d) weathered sample modified with PF resin, ferric chloride and wax. Scale bar is 10 mm
Figure 6.26 – Images showing copper azole-treated southern pine deck boards before and after weathering for 6 months: (a) unweathered control; (b) unweathered sample modified with PF resin; (c) unweathered sample modified with PF resin and lignin stabilizer; (d) weathered control; (e) weathered sample modified with PF resin; (f) weathered sample modified with PF resin and lignin stabilizer. Scale bar is 10 mm
Figure 6.27 – Images showing copper azole-treated southern pine deck boards before and after weathering for 6 months: (a) unweathered sample modified with PF resin and ferric chloride; (b) unweathered sample modified with PF resin, ferric chloride and wax; (c) weathered sample modified with PF resin and ferric chloride; (d) weathered sample modified with PF resin, ferric chloride and wax. Scale bar is 10 mm
Figure 6.28 – Images showing micronized copper azole-treated southern pine deck boards before and after weathering for 6 months: (a) unweathered control; (b) unweathered sample modified with PF resin; (c) unweathered sample modified with PF resin and lignin stabilizer; (d) weathered control; (e) weathered sample modified with PF resin; (f) weathered sample modified with PF resin and lignin stabilizer. Scale bar is 10 mm.
Figure 6.29 – Images showing micronized copper azole-treated southern pine deck boards before and after weathering for 6 months: (a) unweathered sample modified with PF resin and ferric chloride; (b) unweathered sample modified with PF resin, ferric chloride and wax; (c) weathered sample modified with PF resin and ferric chloride; (d) weathered sample modified with PF resin, ferric chloride and wax. Scale bar is 10 mm
6.3.2.2 Colour of modified and unmodified preservative-treated and untreated southern pine decking samples

There were significant two-factor interactions (preservative treatment x envelope modification, preservative treatment x wood tissue, envelope modification x wood tissue) on colour change (Delta E) of southern pine samples after weathering (Table 6.6). The significant \( p<0.001 \) preservative treatment x envelope modification interaction occurred, because the effects of envelope treatments varied with the different preservative treatments (Fig. 6.30). PF resin modification greatly reduced colour change of untreated or organic preservative-treated boards, whereas modification had less effect on discolouration of copper-treated boards. The only additives that significantly reduced the discolouration of envelope modified micronized copper-treated boards were ferric chloride and wax. Additives had significant effects on colour change of untreated and organic preservative-treated boards modified with PF resin, except for PF/ferric chloride and PF/ferric chloride/wax modified CA-treated boards; PF/Lignostab or ferric chloride modified mCA-treated boards; and PF/Lignostab modified organic preservative-treated boards.
Figure 6.30 – Overall colour change of envelope-modified, preservative-treated and untreated southern pine samples after 6 months of natural weathering. Note that results are averaged across wood tissue. Samples with high Delta E have greater colour change than those with a low Delta E. Least significant difference (LSD) bar is ± standard error of difference ($p<0.001$) from analyses of variance.

There was a significant ($p=0.001$) preservative treatment x wood tissue interaction on colour change of samples, because latewood of CA-treated samples was less discoloured than earlywood, whereas there was no difference in colour change of earlywood and latewood in untreated boards or ones treated with other preservatives (Fig. 6.31a). A significant ($p=0.04$) envelope modification x wood tissue interaction occurred, because colour change of latewood in unmodified southern pine deck boards was less than that of earlywood, but colour changes of earlywood and latewood were not significantly ($p>0.05$) different in boards modified with PF resin solutions (Fig. 6.31b).
6.3.2.3 Surface checking of modified and unmodified preservative-treated and untreated southern pine decking samples

There was a significant ($p<0.001$, Table 6.6) two-factor interaction (preservative treatment x envelope modification) on checking (width, length, area) of southern pine samples exposed to weathering, because the effects of envelope modification with PF resins on checking varied with preservative treatments, as shown in Figures 6.32 – 6.34. PF resin modification reduced width of checking in untreated and preservative-treated deck boards. The additives affected the width of checks in modified treated boards, but ferric chloride and ferric chloride and wax clearly affected checking of treated deck boards in different ways. Ferric chloride on its own or in combination with wax reduced width of checks in PF-modified organic preservative-treated boards, but the effects of these additives on check width of modified boards was less pronounced for boards treated with other preservatives. PF resin and ferric chloride had no effect on check width of mCA-samples, but the PF resin, ferric chloride and wax modification reduced checking of mCA-treated samples.
Figure 6.32 – Average width of ten largest checks in envelope-modified untreated and preservative-treated southern pine decking samples after 6 months of natural weathering. Least significant difference (LSD) bar is ± standard error of difference (p<0.001) from analyses of variance

PF envelope modification reduced the length of checks that developed in untreated and treated samples, with one exception, boards treated with organic-preservatives. The additives had little effect on the length of checks in PF-modified boards with one notable exception: boards treated with copper azole and modified with PF and ferric chloride had much shorter checks than other treated or modified boards.
The effects of PF resin modification on area of checks that developed in untreated and preservative-treated samples during weathering tend to mirror those described above for check width and length. This is expected, because check area is simply derived from length x width. However, it is worth pointing out that additives, particularly ferric chloride and wax were more effective at reducing check area in organic preservative-treated wood than they were with boards treated with the other preservatives, although PF resin and ferric chloride had a large effect on check area of CA-treated samples, because of its dramatic effect at reducing check length.
Figure 6.34 – Average area of ten largest checks in envelope-modified, preservative-treated and untreated southern pine decking samples after 6 months of natural weathering. Least significant difference (LSD) bar is ± standard error of difference ($p<0.001$) from analyses of variance.

Figures 6.35 and 6.36 show variability in width and length of checks in southern pine samples and confirm the interactive effects of envelope modification and preservative treatment on checking of southern pine deck boards exposed to natural weathering. In particular, the PF-Lignostab treatments work well with the untreated or micronized-treated samples, reducing variability in width of checks (Fig. 6.35). In contrast, the PF resin and ferric chloride modifications work well with organic preservative-treated samples. However, only the PF/ferric chloride modification reduced variability in check width of CA-treated boards.
There was less variability in check lengths as a result of PF resin modification of boards, although two of the modifications that reduced variability in width of checks of treated boards had the same effect on check lengths (Fig. 6.36). These modification/treatment combinations were PF-ferric and CA and PF-ferric-wax and organic-preservative treatment. In addition, the PF-Lignostab modification reduced variability of check length in organic-preservative (clear) treated boards.
6.3.2.4  Contact angle of modified and unmodified, preservative-treated and untreated southern pine decking samples

There was a significant ($p<0.001$, Table 6.6) preservative treatment x envelope modification interaction on initial contact angle of samples. This interaction occurred, because PF resin modification improved CA$_i$ of copper azole or organic preservative-treated boards, but it had no significant ($p>0.05$) effect on CA$_i$ of untreated and micronized CA-treated boards. In addition, modification of CA- or organic preservative-treated boards with PF resin and ferric chloride increased contact angles, but had no significant ($p>0.05$) effect on the contact angles of micronized-treated or untreated boards.

Figure 6.36 – Variability in length of ten largest checks in envelope-modified, preservative-treated or untreated southern pine deck boards after 6 months of natural weathering
Figure 6.37 – Initial contact angle of water droplets on surfaces of envelope-modified untreated and preservative-treated southern pine decking samples (before weathering). Note that results are averaged across wood tissues (earlywood and latewood). Least significant difference (LSD) bar is ± standard error of difference ($p<0.001$) from analyses of variance.

There were significant two-factor interactions (preservative treatment x envelope modification, envelope modification x wood tissue) on CA$_i$ of southern pine decking samples after weathering. A significant ($p<0.001$) preservative treatment x envelope modification interaction occurred, because the effects of modification with PF resin or PF resin containing Lignostab or ferric chloride varied with preservative treatments, whereas the effects of PF resin, ferric chloride and wax modification did not (Fig. 6.38a). Modification with PF resin improved CA$_i$ of modified CA- or mCA-treated boards after weathering, but the modification had a negative effect on CA$_i$ of untreated samples, and had no effect on CA$_i$ of organic preservative-treated samples. The addition of Lignostab or FeCl$_3$ had little effect on CA$_i$ of PF-modified boards, but the combination of PF resin/FeCl$_3$ and wax significantly ($p<0.001$) increased CA$_i$ of untreated or treated boards. There was a significant ($p=0.006$) envelope modification x wood tissue interaction, because CA$_i$ on earlywood and latewood of weathered PF resin, ferric chloride and wax modified samples
were different, and this effect was not observed in samples modified with water or other PF resin solutions (Fig. 6.38b).

Figure 6.38 – Initial contact angle of water droplets on surfaces of southern pine decking samples after 6 months of natural weathering: (a) envelope-modified, preservative-treated and untreated samples ($p < 0.001$), averaged across wood tissues; (b) envelope-modified earlywood and latewood of pine samples ($p = 0.006$), averaged across preservative treatments. Least significant difference (LSD) bar and error bars are ± standard error of difference from analyses of variance.

There were significant ($p < 0.001$, Table 6.6) two-factor interactions (preservative treatment x envelope modification, envelope modification x wood tissue) on the time for contact angle to decrease below 90° in southern pine samples (before weathering). The preservative treatment x envelope modification interaction occurred, because the effects of PF resin, ferric chloride and wax modification on time($\text{CA} < 90^\circ$) of samples varied with different preservative treatments (Fig. 6.39a). Boards treated with copper-based preservative and modified with PF resin, ferric chloride and wax were significantly ($p < 0.001$) more hydrophobic after modification than boards modified with water or the organic-preservative. The envelope modification x wood tissue interaction occurred, because time($\text{CA} < 90^\circ$) of earlywood in samples modified with PF resin solution containing ferric chloride and wax was significantly ($p < 0.001$) greater than that of similarly modified latewood, but this effect was not observed with the other modified samples (Fig. 6.39b).
Figure 6.39 – Time for contact angle of water droplets to decrease below 90° on surfaces of southern pine decking samples (before weathering): (a) preservative-treated or untreated samples modified with PF resin solutions or water (control) averaged across wood tissues; (b) earlywood and latewood of samples modified with PF resin solutions or water (control) averaged across preservative treatments. Least significant difference (LSD) bar and error bars are ± standard error of difference (p<0.001) from analyses of variance.

There was a significant (p<0.001) preservative treatment x envelope modification x tissue type interaction on time$_{CA<90^\circ}$ of envelope modified samples after weathering. This three-factor interaction occurred, because the effects of envelope modification on time$_{CA<90^\circ}$ varied with different preservatives and tissue types (earlywood and latewood) (Fig. 6.40). Time$_{CA<90^\circ}$ on earlywood was greater than that of latewood for CA-boards modified with PF resin and untreated and preservative-treated boards modified with PF resin, ferric chloride and wax. In other cases, time$_{CA<90^\circ}$ of wood tissues was not different. Hydrophobicity (time$_{CA<90^\circ}$) was higher on earlywood of PF resin, ferric chloride and wax modified mCA-boards than on other modified preservative-treated and untreated samples.
Figure 6.40 – Time for contact angle of water droplets to decrease below 90° on surfaces of envelope modified preservative-treated southern pine samples after 6 months of natural weathering. Error bars are ± standard error of difference ($p<0.001$) from analyses of variance.

6.3.2.5 Erosion of modified and unmodified preservative-treated and untreated southern pine decking samples

Erosion at surfaces of untreated or preservative-treated southern pine deck boards modified with PF resin solutions or water (control) are shown in Figures 6.41 and 6.42. Erosion occurred at the surface of untreated southern pine controls (Fig. 6.41a) or boards treated with organic-preservative (Fig. 6.41b) or copper azole (Fig. 6.42a). However, erosion of these boards was mild. Micronized CA-treated boards did not erode, although a circular dent made from the stainless-steel mask can be seen in Figure 6.42b. Erosion at the surface of preservative-treated or untreated boards modified with PF resin solutions was minimal (Fig. 6.41c-j, 6.42c-j).
<table>
<thead>
<tr>
<th>Untreated</th>
<th>Organic preservative-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Water</td>
<td>(b) Water</td>
</tr>
<tr>
<td>(c) PF resin</td>
<td>(d) PF resin</td>
</tr>
<tr>
<td>(e) PF resin + Lignostab</td>
<td>(f) PF resin + Lignostab</td>
</tr>
</tbody>
</table>
Figure 6.41 – Profilometry images of masked areas on envelope modified untreated or envelope modified and organic preservative-treated southern pine decking samples after 6 months of natural weathering
<table>
<thead>
<tr>
<th>Copper azole-treated</th>
<th>Micronized copper azole-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Water</td>
<td>(b) Water</td>
</tr>
<tr>
<td>(c) PF resin</td>
<td>(d) PF resin</td>
</tr>
<tr>
<td>(e) PF resin + Lignostab</td>
<td>(f) PF resin + Lignostab</td>
</tr>
</tbody>
</table>
There was a significant \( p<0.001 \) interaction of preservative treatment x envelope modification on erosion of deck boards during weathering, because erosion of treated and untreated samples varied with PF resin modifications (Fig. 6.37). In particular, there was pronounced erosion of mCA-boards modified with PF and \( \text{FeCl}_3 \) and also untreated boards modified with PF resin. However, the effects of envelope modification on erosion of CA- or organic preservative-treated deck boards during weathering was not significant \( p>0.05 \).
6.3.4 Microstructural changes in Scots, southern pine and yellow cedar during natural weathering

The microstructure of untreated and PF-modified Scots pine, southern pine and yellow cedar (before and after weathering) was described in Chapter 3 (Section 3.3.4). Figure 6.44 shows the microstructure of PF resin and ferric chloride modified samples. They appear similar to those modified with PF resin on its own. Wood surfaces were covered with a coating of PF resin and ferric chloride. Some lumens and rays were filled with resin (Fig. 6.44c). Middle lamellae in earlywood and latewood of Scots pine (Fig. 6.44a, b) and latewood of southern pine (Fig. 6.44d) appeared to be raised above the surface as a result of modification. Earlywood and latewood cells of yellow cedar were slightly damaged during specimen preparation (Fig. 6.44e, f).
Transverse surfaces of softwoods modified with PF resin, ferric chloride and wax solution appeared to be rougher than those modified PF resin and ferric chloride (Fig. 6.45a – f). The PF resin, ferric chloride and wax coating also appeared to be thicker and contained small particles.
Figure 6.45 – SEM images showing samples modified with 20% PF resin, 2% ferric chloride and 2% wax (before weathering): (a) earlywood and (b) latewood of Scots pine; (c) earlywood and (d) latewood of southern pine; (e) earlywood and (f) latewood of yellow cedar

Exposure of unmodified and modified samples to weathering caused surface degradation of earlywood and latewood tracheids, as expected. Figures 6.46 and 6.47 show macro- and microstructural changes to surfaces of modified Scots pine after exposure to 79, 100, 280 and 606 days of weathering. PF resin and ferric chloride modified southern pine (Fig. 6.48) and yellow cedar (Fig. 6.49) were weathered for 100 and 424 days, and changes in their microstructure as a result of weathering are shown.
Very little erosion of middle lamellae in earlywood and latewood in PF resin/ferric chloride modified samples was observed after 79 days of weathering (Fig. 6.46a). Some separation of latewood cell walls from middle lamellae occurred and numerous micro-checks were present (Fig. 6.46c, d).

![SEM images showing Scots pine samples modified with 20% PF resin and 2% ferric chloride and exposed to 79 (a) or 100 (b-d) days of natural weathering, showing: (a) earlywood and latewood; (b) earlywood and (c) latewod at high magnification; (d) resin canal in latewood](image)

The cellular structure of PF resin and ferric chloride modified Scots pine exposed to 280 days of weathering was largely undamaged (Fig. 6.47a-c). However, earlywood cell walls had eroded and become thinner. Latewood cell walls had also become thinner and they contained micro-checks (Fig. 6.47b, c). The middle lamella in latewood was also eroded (Fig 6.47c). Cell walls adjacent to lumens that were filled with resin were less degraded (Fig 6.47b, c). After 606 days of exposure, there was much greater degradation of PF and ferric chloride modified samples. Macro-checks were prominent at the earlywood and latewood boundary and radially along rays (Fig. 6.47d). Earlywood cell walls were very thin and eroded, but cell
corners and cell walls adjacent to voids where there was a lot of resin were still intact (Fig. 6.47e). Latewood cells were twisted and parts of walls were missing in some cases (Fig. 6.47f). Mould was observed in lumens of earlywood cells, but it was mainly found in voids between distorted latewood cells (Fig. 6.47e, f).

Figure 6.47 – SEM images showing Scots pine samples modified with 20% PF resin and 2% ferric chloride and exposed to 280 (a-c) or 606 (d-f) days of natural weathering, showing: (a) resin canal in latewood; (b) earlywood; (c) latewood; (d) earlywood and latewood; (e) earlywood and (f) latewood at high magnification. Arrows indicate: (1) intact ray; (2) resin filling; (3) cell corner; (4) fungal spores
PF resin and ferric chloride modified southern pine samples weathered for 100 days had similar microstructural changes to those observed in similarly modified and weathered Scots pine samples (Fig 6.48a-c). Exposure to 424 days of weathering caused thinning and degradation of earlywood cell walls (Fig. 6.48e). Latewood cell walls were also thinner, distorted and fractured. Many cells had separated at the middle lamella, which was often eroded (Fig. 6.48f). Cell wall degradation was less pronounced in cells adjacent to lumens that were filled with resin, (Fig. 6.48e, f). Fungal spores were observed in lumens of earlywood and latewood cells (Fig 6.48e, f).
Figure 6.48 – SEM images showing southern pine samples modified with 20% PF resin and 2% ferric chloride and exposed to 100 (a-c) or 424 (d-f) days of natural weathering, showing: (a) resin canal in latewood; (b) earlywood and (c) latewood at high magnification; (d) entire SEM sample; (e) earlywood; (f) latewood. Arrows indicate: (1) cell wall degradation; (2) resin filled lumens in latewood.

Microstructural degradation of PF resin and ferric chloride modified yellow cedar samples weathered for 100 days was a little more pronounced than that in similarly modified and weathered pine samples (Fig. 6.49a, b). There was more evidence of thinning and fracture of earlywood cell walls. However, the protective effects of resin lumen-filling was observed in yellow cedar sample (Fig. 6.49b).
The transverse surface of modified yellow cedar samples exposed to 424 days of weathering was largely free of large checks (Fig. 6.49c), unlike pines. However, voids were present in earlywood resulting from the thinning and collapse of earlywood tracheids (Fig. 6.49d). Middle lamellae were severely eroded in samples exposed to the weather for 424 days (Fig. 6.49f).

Figure 6.49 – SEM images showing yellow cedar samples modified with 20% PF resin and 2% ferric chloride and exposed to 100 (a-d) or 424 (e, f) days of natural weathering, showing: (a) entire SEM sample; (b) earlywood; (c) latewood; (d) latewood at high magnification; (e) entire SEM sample; (f) earlywood and latewood. Arrows indicate latewood tracheids protected by resin filling of cell lumens.
Middle lamellae in earlywood and latewood in Scots pine samples modified with PF resin, ferric chloride and wax and exposed to the weather for 79 days had begun to erode. Checks were present in latewood cell walls (Fig. 6.50a, b). Small lumps, possibly wax, were observed in lumens of earlywood tracheids. Exudation of material, possibly wax, from rays was observed (Fig. 6.50a, c, d).

![SEM images showing Scots pine samples modified with 20% PF resin, 2% ferric chloride and 2% wax and exposed to 79 (a, b) or 100 (c, d) days of natural weathering, showing: (a) earlywood; (b) latewood; (c) earlywood; (d) latewood. Arrows indicate deposits at wood surfaces, possibly wax](image)

After 280 days of weathering, the cellular structure of Scots pine samples modified with PF resin-FeCl₃ and wax was intact, but earlywood cell walls were thinner and middle lamellae of latewood were eroded (Fig. 6.51a, b). Earlywood cell walls adjacent to lumens filled with resin were less degraded (Fig. 6.51a). Resin in resin canals appeared to be intact (Fig. 6.51c). Macro-checks were formed at the transverse surface of modified Scots pine samples exposed to 606 days of weathering (Fig. 6.51d). Cell walls of earlywood tracheids were very thin, but corners of earlywood cell walls remained upright and
resin filled structures were still intact (Fig. 6.51e). Latewood tracheids were distorted as was also observed for samples modified with PF resin and FeCl₃ (Fig. 6.51f). Fungus colonized voids at the wood surface.

Figure 6.51 – SEM images showing Scots pine samples modified with 20% PF resin, 2% ferric chloride and 2% wax and exposed to 280 (a-c) or 606 (d-f) days of natural weathering, showing: (a) earlywood; (b) latewood; (c) resin canal in latewood; (d) earlywood and latewood; (e) earlywood and (f) latewood at high magnification. Arrow indicates latewood cell wall adjacent to a cell lumen filled with resin

Latewood cell walls of southern pine samples modified with PF resin, ferric chloride and wax developed numerous checks when they were exposed to 100 days of weathering (Fig. 6.52b). Checks also
developed adjacent to middle lamellae (Fig. 6.52b). Earlywood cell walls exposed to 100 days of weathering were less degraded (Fig. 6.52a). Earlywood cell walls exposed to 424 days of weathering were thinner and more degraded (Fig. 6.52e). Latewood cell walls were severely degraded, possibly because of extensive micro-checking of cell walls. There was also severe erosion of middle lamellae in latewood, which opened up voids between latewood tracheids (Fig. 6.52f). Fungi were observed in lumens of earlywood and lumens and within voids between degraded latewood tracheids.
Figure 6.52 – SEM images showing southern pine samples modified with 20% PF resin, 2% ferric chloride and 2% wax and exposed to 100 (a-c) or 424 (d-f) days of natural weathering, showing: (a) earlywood; (b) latewood; (c) latewood at high magnification; (d) entire SEM sample; (e) earlywood; (f) latewood

Figure 6.53b-d show the microstructure of earlywood and latewood of yellow cedar modified with PF resin, ferric chloride and wax, following 100 days of natural weathering. Photodegradation of yellow cedar appeared to be greater than that in samples modified with PF resin and FeCl₃. Cell walls of earlywood and latewood tracheids were thinner and fractured. Erosion of middle lamellae at corners of
earlywood cells and latewood was pronounced. After 424 days of exposure, large voids were formed at the earlywood-latewood interface (Fig. 6.53e), and fungi colonized voids at the surface (Fig. 6.53f).

Figure 6.53 – SEM images showing yellow cedar sample modified with 20% PF resin, 2% ferric chloride and 2% wax and exposed to 100 (a-d) or 424 (e, f) days of natural weathering, showing: (a) entire SEM sample; (b) PF resin covering latewood; (c) earlywood and (d) latewood at high magnification; (e) entire SEM sample; (f) earlywood and latewood. Arrows indicate cell wall fracture

Degradation of all untreated softwood species modified with PF resin and ferric chloride increased with increasing exposure to the weather, as expected. After 100 days of weathering, checking was more
pronounced at transverse surfaces of modified pines than at similarly exposed yellow cedar surfaces. Micro-checking was more prominent in latewood tracheid walls of pines than in yellow cedar latewood cell walls. However, overall, cell wall degradation of PF resin and ferric chloride modified yellow cedar after 100 days of natural weathering was more severe than those in similarly modified and exposed pines. This trend continued with increasing exposure of samples to natural weathering. Mould was observed in all modified softwoods after weathering.

Addition of wax emulsion to PF resin and ferric chloride solution appeared to accelerate photodegradation of wood cell walls, particularly latewood cell walls in pines. Voids were larger in yellow cedar modified with PF/ferric chloride solution containing wax emulsion after 424 days of weathering than those of samples modified with solutions that did not contain the wax emulsion. Deposits of extraneous materials, possibly wax, were observed at transverse surfaces and in lumens of modified tracheids, but they were lost with exposure of samples to the weather.

6.4 Discussion

I hypothesized in the introduction to this chapter that ferric chloride would be a more effective additive than Lignostab at improving the ability of PF resin to protect preservative-treated Scots and southern pine from the deleterious effects of weathering. I also hypothesized that the addition of a wax emulsion would enhance surface hydrophobicity and checking resistance of PF-modified and preservative-treated and untreated pine deck boards during weathering. My results partially support these hypotheses. Additive combinations for PF resin that contained ferric chloride, ferric chloride and wax were generally better at protecting deck boards from the adverse effects of weathering than the lignin stabilizer, Lignostab. However, the effects of these additives on weather resistance of deck boards varied with preservative treatments.
On one hand, ferric chloride was a better additive than Lignostab at restricting discolouration of PF-modified boards during weathering. This was mainly due to ferric chloride’s ability to restrict change in yellowness and redness of preservative-treated or untreated pine boards modified with PF resin, which accords with findings of Chapter 5. PF resin and ferric chloride modified southern pine boards became darker after weathering, which accords with findings of Kielmann et al. (2017) for darkening of PF-modified European beech exposed to artificial weathering. However, ferric chloride had an adverse effect on the checking of PF-modified boards and accelerated erosion at latewood of CA-treated Scots pine samples during weathering, possibly due to degradation of wood by ferric chloride (Evans and Schmalzl, 1989).

Surfaces of all pine decking samples treated with PF resin ferric chloride and wax became hydrophobic, and the surface hydrophobicity of southern pine boards modified with PF solution containing ferric chloride and wax increased with exposure, which accords with findings of Lesar et al. (2011) who noted an increase in initial contact angle on montan wax-treated surfaces of Norway spruce after exposure to artificial weathering. Furthermore, the ability of wax to restrict discolouration of PF resin and ferric chloride modified clear organic preservative-treated Scots pine and CA-treated southern pine boards accords with findings of Liu (2011) that addition of 2.5% wax emulsion stabilized the colour of yellow cedar veneers treated with 36% PF resin and exposed to 50 days of outdoor weathering. However, PF resin, ferric chloride and wax modified surfaces of Scots pine boards lost their surface hydrophobicity after weathering, possibly a result of photodegradation and leaching of wax from exposed surfaces. The loss of wax during weathering may explain why the wax additive did not enhance checking resistance of PF and ferric chloride modified Scots pine samples. Addition of wax also reduced WPG of modified deck boards, which may explain the increased erosion at latewood of PF resin, ferric chloride and wax modified clear-treated Scots pine boards and increased microstructural degradation observed in modified Scots and southern pine samples.
Ferric chloride, like the lignin stabilizer, Lignostab, did not impart mould resistance to PF-modified southern pine samples. This observation does not accord with findings in Chapter 5. In Chapter 5, PF resin and ferric chloride modified yellow cedar veneers were exposed outdoors for only 50 days. Thus, differences in my findings and those in Chapter 5 may be due to difference in the length of exposure between the two experiments.

The increased microstructural degradation in wax modified Scots and southern pine samples was unexpected. The ability of Lignostab to restrict width of checking in PF-modified southern pine samples did not accord with findings of Chapter 4. Moreover, the ability of Lignostab to restrict erosion at surfaces of PF resin and preservative-treated Scots pine boards does not accord with findings of Liu (2011). However, she assessed the erosion of radiata pine face veneers modified with 10% PF resin and 2% Lignostab after approximately 83 days (2000 hours) of natural weathering. Differences in my findings and those of Liu (2011) are possibly due to her use of lower concentrations of PF resin, different sample species and shorter outdoor exposure.

Some of the interactive effects of preservative treatment on WPG and outdoor performance of samples modified with different PF resin solutions were unexpected. Treated woods often contain internal checks, which could facilitate the absorption of PF resin during pressure-impregnation (McMillen, 1958). Such an effect would explain the high treatment uptake of copper azole-treated southern pine boards. A noteworthy preservative treatment and modification interaction is the positive effect of FeCl₃ modifications on restricting size and variability of checking in samples treated with organic-preservative.

6.5 Conclusions

I conclude that envelope modification with PF resin can protect preservative-treated and untreated pine decking from the deleterious effects of natural weathering. The ability of PF resin modification to
protect the appearance of modified boards can be enhanced by combining the resin with a lignin stabilizer, ferric chloride or a wax emulsion. The effects of PF resin/additive combination on the weather resistance of modified and treated boards varied depending on preservative type, because of PF-modification and preservative treatment interactions. Therefore, a suitable resin/additive combination for treated wood decking needs to be tailored to different preservative treatments. PF resin and ferric chloride appears to be suitable for the modification of copper azole or organic preservative-treated southern pine decking. PF resin, ferric chloride and wax is suitable for modification of micronized copper azole-treated southern pine boards. PF resin alone or PF resin combined with ferric chloride and wax both imparted similar degrees of protection for modified and untreated southern pine boards, but the dark colour of PF-ferric-wax modified wood masked mould. The PF resin or PF resin, ferric chloride and wax solutions also provided similar level of weather resistance to copper azole- or organic preservative-treated Scots pine boards, and the most suitable solution for modification might be determined by the desired colour of the Scots pine decking.

Further research on the reactions of PF resin solutions and copper or triazole compounds, using Fourier-transform infrared spectroscopy would help understand the interactive effects of PF-modifications and preservative treatments on weathering resistance of modified and treated deck boards. The modified/treated boards should undergo additional outdoor exposure to assess if the PF-modification/preservative treatment interactions noted here become more pronounced or diminish with prolonged weathering of the modified/treated samples. This would also provide insights into the long-term effects of modifications on the performance of treated pine boards. The unbalanced replication in this Chapter restricted comparison of the effects of wood species on weathering of modified/treated deck boards exposed to weathering. However, SEM observations showed that PF-modifications provided various degree of microstructural protection to Scots, southern pine and yellow cedar. Research on the
photoprotective effects of PF-modification on a wider range of wood species treated with different preservatives would be worthwhile.
Chapter 7: General Discussion, Conclusions and Suggestions for Further Research

7.1 General Discussion

The overall aim of this thesis was to investigate whether envelope modification with PF resin could protect wooden deck boards from the deleterious effects of the weather. Overall, my results show that such envelope treatments have beneficial effects on the appearance and some other properties of wooden deck boards exposed outdoors. However, the effectiveness of treatments depended on treatment method (dip v. vacuum, Chapter 4), additives blended with the PF resin (Chapters 3 and 6) and preservative treatments applied to deck boards (before resin modification; Chapter 6).

Vacuum treatment with PF resin was more effective at protecting untreated boards from the deleterious effects of weathering, as expected (Chapter 4). However, an unexpected effect of the research in Chapter 4, which compared the effectiveness of envelope treatment at protecting untreated boards exposed outdoors, was the finding that the photodegraded layer was much shallower in PF-treated boards than in untreated boards, and the grey weathered layer could be easily removed with gentle rubbing using a damp cloth. It is noteworthy that underneath the weathered layer, the colour of PF-treated boards was retained even after 2 years exposure. The cleaned surfaces of vacuum impregnated boards were deeply coloured, had less bleaching and were more resistant to grain raising than those that were dip treated, in accord with findings that vacuum impregnated samples maintained their appearance better when they were exposed to the weather than samples dipped in PF resin. The cleaned surfaces of vacuum impregnated Scots pine boards looked similar to those of southern pine boards, despite lower treatment weight gains than southern pine boards. The colour of cleaned surfaces of Scots and southern pine boards treated with PF resin and lignin stabilizer appeared lighter and more vibrant than those treated with PF alone. This finding suggests that the lignin stabilizer, when added to the resin, is able to protect the PF
resin from photodegradation. There were other beneficial effects of the lignin stabilizer on the appearance of deck boards exposed to weathering. For example, the lignin stabilizer restricted width of surface checks in PF-treated Scots pine boards (Chapter 4), width of checks in PF-modified organic-preservative-treated Scots pine boards and length of checks in PF-modified organic-preservative-treated southern pine boards (Chapter 6). These results are contrary to findings that the lignin stabilizer had little effect on the weight and tensile strength losses of PF resin treated wood veneers (Chapter 3 and 5). These results suggest that the use of thin veneers to screen chemicals for their photoprotective effects may not be a good predictor of their ability to reduce the checking of wood. Hence, I conclude that such thin veneer tests should be augmented by trials that use larger dimension samples.

Overall, my research showed that many of the additives I screened could enhance the ability of PF resin to photostabilize wood and protect it from the deleterious effects of weathering. However, no single additive or combination of additives in PF resin was able to prevent all of the undesirable effects of weathering from occurring at the surface of PF-modified deck boards. For example, one of the most effective additives, ferric chloride, had adverse effects on the weathering of thin wood veneers. In addition, SEM observations in Chapter 5 showed that ferric chloride increased micro-checking of pits in PF-treated yellow cedar. Results in Chapter 6 showed that ferric chloride when added to the PF resin had a negative effect on the surface checking of PF-modified southern pine. These adverse effects may have occurred because ferric or chloride ions caused degradation of wood (Evans & Schmalzl, 1989). Additives were only screened for their ability to restrict the photodegradation of wood (Chapters 3 and 5). Therefore, it’s not surprising that they were not particularly effective at reducing the colonization of veneers or deck boards by mould fungi. However, mould was less pronounced when PF resin was used to modify preservative-treated deck boards. Furthermore, there were some other noteworthy interactive effects of preservative-treatment and PF resin modification on the appearance of deck boards exposed to natural weathering.
The interactive effects of PF modification and preservative treatment are described in Chapter 6. One noteworthy interaction was the beneficial effect of PF and ferric chloride modification on the appearance of boards treated with an organic-preservative. Boards treated with organic-preservative lost their visual appeal more quickly than wood treated with copper-based preservatives (Temiz et al., 2007). PF modification slowed the weathering process, as expected. But the PF-ferric chloride modification was more effective at restricting weathering of boards treated with organic-preservative than modification with PF or PF and Lignostab. These results suggest that the modification of wood by metal ions, either in the preservative treatment or in PF resin helps restrict weathering of boards treated with organic-preservatives. Furthermore, there was evidence that PF-ferric chloride modification had beneficial effects on the checking of boards treated with copper-based preservative, although the effects were not as pronounced as those in boards treated with organic-preservative. The beneficial effects of PF modification on the weathering of treated deck boards was expected to increase when the resin was blended with a wax emulsion additive, because such additives are commonly added to wood preservatives to increase the resistance of treated wood to weathering (Greaves, 1992; Zahora, 2002). However, the effects of wax on surface hydrophobicity and parameters used to assess the performance of Scots and southern pine boards modified with PF resin and ferric chloride varied depending on different preservative treatments. There was a notable interactive effect of modification treated with PF resin, ferric chloride and/or wax on checking of micronized CA- or CA-treated southern pine boards. Wax emulsion restricted width of checking in PF resin and ferric chloride modified micronized CA-treated boards, but the wax additive adversely affected width and length of checks in modified CA-treated samples. Furthermore, SEM observations in Chapter 6 suggested that the wax emulsion accelerated microstructural degradation of yellow cedar, Scots and southern pine, modified with PF resin and ferric chloride. These findings suggest that there may be a component of the wax emulsion that accelerated photodegradation of wood. Further research is needed to confirm this suggestion.
7.2 Conclusions

I conclude that PF resin, when used as an envelope treatment, can protect untreated and preservative-treated wooden deck boards from the adverse effects of natural weathering. The effectiveness of the resin at restricting change in appearance of modified boards can be increased by blending the resin with photoprotective and hydrophobic additives, but PF and additive combinations need to be tailored to suit deck boards treated with different preservatives. PF and ferric chloride appears to be suitable for envelope modification of copper azole or organic-preservative-treated southern pine decking. Modification with PF resin, ferric chloride and wax is suitable for micronized copper azole-treated boards, because the addition of wax emulsion restricted checks from becoming wider. PF resin on its own or PF resin containing ferric chloride and wax were both similarly effective for modification of untreated southern pine, but the dark brown colour of PF, ferric chloride and wax modified wood made mould less visible. Likewise, modification with PF resin or PF resin solution containing ferric chloride and wax imparted similar effects on weather resistance of copper azole- or organic-treated Scots pine boards.

Envelope modification with PF resin appears to provide a weather resistant barrier at the surface of modified deck boards. The barrier restricts photodegradation, including the extent of degradation at the surface of wood and the depth of degradation. The envelope treatment was not particularly effective at controlling mould growth at the surface of deck boards, although the dark colour of PF/ferric chloride modified wood masked the presence of mould. I conclude that envelope modification to restrict the weathering of treated wood could be improved further by adding a biocide to the resin, in addition to tailoring the treatment to the wood substrate.

Envelope modification of Scots and southern pine decking using vacuum impregnation was more effective than dip impregnation at protecting deck boards from prolonged (2-year) exposure to natural weathering. Thus, I conclude that vacuum impregnation is more suitable than dipping for envelope
modification of decking. Envelope modification of preservative-treated deck boards adds an additional step during the production of deck boards. Furthermore, the modified deck boards would need to be dried to remove water and the resin would have to be cured at high temperature. I showed that PF resin in veneers could be cured by infra-red radiation, which would greatly reduce the time needed to manufacture modified treated boards. However, further research would be needed to examine whether IR radiation could be used to cure PF resin-treated deck boards. I conclude that PF modification shows promise as a finishing process to enhance the resistance of treated wood to weathering, but the modification process needs refining and, as pointed out above, treatment solutions should be tailored to specific treatments.

7.3 Suggestions for further research

My most noteworthy finding was the interactive effects of PF resin modification and preservative treatments on the outdoor performance of pine decking. The copper azole, micronized copper azole and organic-preservative-treated Scots and southern pine deck boards responded differently to PF modification. Further research to study the chemistry of the reactions of PF solutions and copper or triazole compounds, first starting with Fourier-transform infrared spectroscopy would help to shed light on interactive effects on PF modification and preservative treatments on the outdoor performance of modified/treated deck boards.

Further research should extend the outdoor weathering of envelope modified and preservative-treated deck boards and assess whether the interactive effects of PF resin modification and preservative treatment become more pronounced or diminish with prolonged exposure of boards to the weather. This would also allow better evaluation of the commercial potential of PF resin modification to protect wooden decking used outdoors.
The unbalanced replication of treatments and species in Chapter 6 prevented serious evaluation of the effect of wood species on the weathering of treated and modified deck boards exposed to the weather. SEM observations indicated that PF-modification varied in its ability to protect the microstructure of Scots and southern pine and yellow cedar. It would be worthwhile in future to assess the effects of envelope modification on weathering of a broader range of wood species treated with different preservatives.

Additional research should investigate the weathering performance of wooden decking modified with PF resin and some of the other stabilizers that had beneficial effects on the photostability of PF-modified wood veneers. For example, lignosulphonate and Lignostab combination, in particular, had a positive effect on tensile strengths of PF-treated veneers after weathering, and if the treatments can restrict checking of wooden boards, lignosulphonate and Lignostab might be a better alternative to wax emulsion as a means of restricting checking of PF-treated wood decking.

In addition, as foreshadowed above, further research is needed to develop additives that can restrict mould growth at the surface of PF-modified deck boards. Research is also needed to optimize the treatment process, particularly rapid vacuum treatment and curing of PF resin. Such research if successful could produce more weather-resistant deck boards that are better able to compete with wood plastic composites, and require less maintenance (finishing and refinishing) from the consumer.
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Image: Deprotonation of phenol in a base medium. The phenolate anion has negative charge delocalized at the ortho or para sites (reproduced from ©Laborie, 2002), *Figure 2.1. From Laborie, M. P. G. (2002). Investigation of the wood/phenol-formaldehyde adhesive interphase morphology (Doctoral thesis).* Retrieved from
Image: Diagram displaying the formation of HMPs. From the left, (a) addition of formaldehyde to phenol in sodium hydroxide forms (b) ortho- and para- monohydroxymethyl phenols and additional reaction with formaldehyde forms (c) dihydroxymethyl phenols and (d) trihydroxymethy phenols (reproduced from (c)Gardziella et al., 2000), Figure 2.2. From Gardziella, A., Pilato, L. A. & Knop, A. (2000). Phenolic resins: chemistry, reactions, mechanism. In *Phenolic resins chemistry, applications, standardization, safety and ecology* (2nd completely revised ed.), (pp. 24-36). Berlin, Heidelberg: Springer. Used with permission from Springer.

Image: Images showing Compreg propellers made by Engineering and Research Corporation (ERCO). (a) variable pitch hardwood Compreg propeller blades attached to a 2D30 (10˚ and 15˚) hub; (b) Compreg blank blade; (c) threaded root of Compreg blank blade, where a steel ferrule would be attached (©Not Plane Jane, n.d.), Figure 2.12. From Not Plane Jane. (n.d.). ERCO “compreg” propeller blades. Retrieved from [http://notplanejane.com/erco.htm](http://notplanejane.com/erco.htm) Used with permission from NotPlaneJane.com.

Image: Initial condensation reactions of furfuryl alcohol monomers in acidic medium: (a) methylene bridge formation; (b) methylene ether bridge formation; (c) conversion of methylene ether bridge to methylene bridge (reproduced from (c)Lande et al., 2004c), Figure 2.13. From Lande, S., Eikenes, M., & Westin, M. (2004c). Chemistry and ecotoxicology of furfurylated wood. *Scandinavian Journal of Forest Research, 19*(Suppl. 5), pp. 14-21 Used with permission from Taylor & Francis Group.

Image: Cross-linking of linear furfuryl alcohol polymers occurs according to reactions (a) and (b). (reproduced from (c)Lande et al. 2004c), Figure 2.14. From Lande, S., Eikenes, M., & Westin, M. (2004c). Chemistry and ecotoxicology of furfurylated wood. *Scandinavian Journal of Forest Research, 19*(Suppl. 5), pp. 14-21 Used with permission from Taylor & Francis Group.

Image: Reaction of acetic anhydride with wood (reproduced from (c)Jebrane et al., 2011), Figure 2.18. From Jebrane, M., Pichavant, F., & Sèbe, G. (2011). A comparative study on the acetylation of wood by reaction with vinyl acetate and acetic anhydride. *Carbohydrate Polymers, 83*(2), pp. 339-345 Used with permission from Elsevier.


Image: Images of white spruce deck boards (a) untreated and (b) treated with 10% low molecular weight PF resin exposed to 24 weeks of natural weathering. Scale bar is 60 mm ((c)Cheng and Evans, 2012), Figure 2.23. From Cheng, K. J., & Evans, P. D. (2012). Weathering performance of white spruce decking treated with low molecular weight phenol formaldehyde resin. *Proceedings of the 11th Pacific Rim Bio-based Composites Symposium (November 28-30, Shizuoka, Japan)*, pp. 575-578 Used with permission from International Tropical Timber Organization.
Appendices

Appendix 1 – Yellow Cedar Veneers and Kraft Paper Strips (Chapter 3)

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