

Changes in chemistry, color, dimensional stability and fungal resistance of *Pinus radiata* D. Don wood with oil heat-treatment

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Abstract

Pinus radiata wood specimens were heat-treated at 160–210°C in linseed oil and the effects of treatment on chemical composition, color, dimensional stability, and fungal resistance were examined. The degradation of hemicelluloses was the most remarkable feature, which is the principal reason for alterations in wood properties. Removal or migration of extractives, oil uptake and the accumulation of oil on the wood surface were observed. The color of heat-treated wood became more uniform and darker, and its dimensional stability (i.e., anti-swelling efficiency) and fungal resistance were improved by up to 60% and 36%, respectively. The viscosity of the oil after treatment was elevated with the treatment temperature and was higher in comparison to heated oil without wood present.

Keywords: chemical change; CIEL*a*b* system; color variation; dimensional stability; heat treatment; linseed oil; weight percentage change (WPC).

Introduction

Wood from plantation forests is increasingly important due to depletion of tropical forests and desire to restrict utilization of natural forests. *Pinus radiata* D. Don is one of the most important fast grown plantation species in the Oceania, South America and South Africa. Worldwide, the plantation area of *P. radiata* is about 4.3×10^6 ha (Lungo et al. 2006), which contributes 1.1% of the global and 8.8% of the Asia-Pacific trade in forest products (FAO 2005). *P. radiata* is considered to be the backbone of New Zealand forestry with about 1.6×10^6 ha of plantation area. The annual sustainable harvest of *P. radiata* in New Zealand is 18×10^6 m³ and is

predicted to increase to 24×10^6 m³ by 2015 and 35×10^6 m³ during 2015–2025 (MAF 2010). Its potential as wood supplier is large across the globe.

The *P. radiata* wood has a cream white color, clear wood growth ring pattern, and moderate mechanical properties. Its stability and durability are regarded as inferior to other commercial species, such as ponderosa pine and Douglas-fir (Bamber and Burley 1983; Dickson and Walker 1997; Maclaren 2002). Thus it has a relatively weak position in the global markets in comparison with the species as mentioned above (Walker 2006; Wang et al. 2008).

Wood quality can be improved by heat treatment with temperatures usually below 260°C (Hill 2006). Heat treatment of wood belongs to the most important innovations of the last decade and such products are since a couple of years commercially available. Changes caused by heat treatment in chemical composition and physical properties (with dimensional stability in focus) were intensely investigated (Repellin and Guyonnet 2005; Esteves et al. 2008a; Tuong and Li 2011). Even the dimensional stability of MDF panels can be improved when the fibers are heat-treated (Garcia et al. 2006). The surface composition was investigated by modern analytical instruments, such as XPS and ToF-SIMS by Bryne et al. (2010). Parallels between natural ageing and heat treatment with focus on color changes were addressed by Matsuo et al. (2011). Color change of thermally modified wood was the topic of Gonzáles-Pena and Hale (2009a,b). Rapp et al. (2006) revealed interesting interrelationships between the severity of heat treatments and mechanical properties in impact milling experiments. Brischke et al. (2007) reported on the interrelationship between heat treatment intensities and color data of wood. The improved wettability of heat-treated wood is well known (Pétrissans et al. 2003; Hakkou et al. 2005) and Wolkenhauer et al. (2008) investigated recently the surface free energy of heat treated beech wood. It is obvious from studies based on hydrogen-deuterium exchange and ²H NMR spectroscopy that the number of accessible OH groups in heat treated wood is decreased (Phuong et al. 2007). The wood water relationship of heat treated wood was illuminated by Almeida et al. (2009).

Treatment in hot vegetable oils with boiling points higher than 260°C is one of the alternatives to heating in dry state or in steam (Sailer et al. 2000a,b; Welzbacher and Rapp 2002; Wang and Cooper 2005); for oil properties see Gunstone (2002). The advantages of heat treatment in oil are the absence of oxygen, uniform and fast heat transfer rate to wood, and surface protection by the absorbed oil (Sailer et al. 2000a,b). Stamm et al. (1946) were the pioneers of this type of treatment. The authors treated wood in a bath of

molten metal between 160°C and 320°C and called the dimensionally stabilized wood Staybwood. The degree of reduction in hygroscopicity and anti-swelling efficiency (ASE) almost doubled with every 10°C temperature rise. In the last decade, the Menz Holz Process was developed in Germany, in which wood is heat-treated at 180–220°C in refined rapeseed and linseed oils in a closed process vessel (Sailer et al. 2000a,b). Welzbacher and Rapp (2002) examined the biological properties of the heat-treated wood originating from four different European industrial heat-treatment plants. The decay resistance of wood heat-treated in oil was better than that heat-treated in air under identical treatment conditions. The improvement was attributed to exclusion of oxygen. Of course, the results of heat-treatment are also dependent on the wood species (Hill 2006) and the type of heating oil (Wang and Cooper 2005). Tjeerdsma et al. (2005) examined the performance of maleinized linseed oil, while Wang and Cooper (2005) focused on non-drying oils, such as palm oil, soy oil and slack wax. The latter was most suitable in terms of dimensional stability improvement. Manalo and Acda (2009) treated three bamboo species at 160–200°C in coconut oil. The principal reason for property changes in wood heat-treated in gaseous atmosphere is due to changes in chemical composition (Tjeerdsma et al. 1998b; Tjeerdsma and Militz 2005; Windeisen et al. 2007). For oil heat-treated wood, oil uptake also contributes to quality improvement.

There are no reports on oil heat treatment for *P. radiata*, thus the present study intends to close this gap. The linseed oil treated wood will be investigated for changes in chemical composition, color and weight changes, dimensional stability, and fungal resistance. The viscosity change of the oil during heating both with and without wood specimens in it will also be addressed.

Materials and methods

Specimen preparation

Clear *Pinus radiata* D. Don specimens, 300×90×20 mm³ (L×T×R), were cut from kiln dried, flatsawn sapwood boards. Eight specimens were prepared for each treatment. Specimens were oven-dried for 48 h at 102°C, cooled over silica gel desiccator before being placed in conditioning chamber at 65% relative humidity (RH) and 20°C for two to three weeks to attain equilibrium.

Heat treatment

Conditioned specimens at 10–12% moisture content (MC) were immersed in a preheated oil bath at set temperatures of 160°C, 180°C, or 210°C for 1 h, 3 h, or 6 h in commercial grade raw linseed oil. The oil bath was covered but no external pressure was applied. The oil was continuously recirculated, maintaining the operating temperature within one degree of the set point. After treatment, the lid of the oil bath was removed and the oil was left to cool for the desired period of time; then the oil was drained off and the specimens removed. Treated specimens were wiped, oven-dried at 102°C for 24 h, then cooled down over silica gel in a desiccator and weighed. Finally, the specimens were placed in a conditioning

chamber at 65% RH and 20°C for two to three weeks until equilibrium was attained.

Properties measurements

Wet chemical analysis The wood samples were ground to a sieve size of 25–40 mesh (0.25–0.4 mm). Extraction by ethanol-benzene (1:2) and hot water were conducted according to TAPPI Standard (TAPPI-T264 1995). Acid insoluble lignin (Klason lignin) was determined from extracted wood according to TAPPI-T222 (1988). Determination of holocellulose: according to the sodium hypochlorite method (Rowell 2005); α -cellulose in holocellulose: according to NaOH method (Rowell 2005). The hemicellulose content was calculated by subtracting the α -cellulose content from that of holocellulose. All the reported percentages of chemical constituents in this paper are averaged values from three replicates to the nearest of $\pm 0.1\%$.

FTIR spectrometry Perkin Elmer System 2000 FTIR spectrometer. The wood samples were powdered and screened through a 12 mesh sieve (0.12 mm), extracted according to TAPPI-T264 (1995), and vacuum-dried at $70 \pm 3^\circ\text{C}$ for 48 h. The usual KBr pellet technique was applied for accumulation of 64 scans at the resolution of 4 cm^{-1} . The FTIR spectra were baseline-corrected and normalized at the absorption band of maximum and minimum spectra according to the procedure given in the manual of Essential FTIR analysis software.

Color Measured by the CIEL*a*b* system (St-Onge et al. 2005; Esteves et al. 2008b; Ahajji et al. 2009). Instrument: Minolta spectrophotometer (model cm2500d). Diameter of measured circle: 10 mm. Light source: Standard Illuminant D 65 which represents the average daylight including UV region and 10° standard observer. The specimens were stabilized at $20 \pm 2^\circ\text{C}$ and 65% RH before the measurements. For each specimen, six measurement points were marked and the measurements were taken both before and after the treatment. Color comparison was also made between two opposite flat surfaces and between core and surface of each specimen.

Weight percentage change (WPC) WPC of the specimens after treatments are presented on the oven-dry basis. Oven-drying: $102 \pm 2^\circ\text{C}$ for 48 h; cooling: over a silica gel in desiccators; accuracy of weighting: $\pm 0.001\text{ g}$. $\text{WPC} (\%) = 100 \times (W_a - W_b) / W_b$, in which, W_b is the oven-dry weight before treatment (g), and W_a is the oven-dry weight after the treatment (g).

Dimensional stability Measured by exposing the treated and untreated samples in three environments: 1. in water bath at $20 \pm 2^\circ\text{C}$, 2. in high humidity condition ($85 \pm 5\%$ RH, $20 \pm 2^\circ\text{C}$), and 3. with three cycles of dry-freeze-wet (DFW) conditions. Each DFW cycle consisted of three days of dry condition in an oven at $35 \pm 2^\circ\text{C}$ followed by a day of freezing at -20°C and three days of water immersion at $20 \pm 2^\circ\text{C}$. In the environment tests of one and two, the specimens were weighed and measured in L (length), T (width) and R (thickness) directions after different intervals until they reached equilibrium. Results were calculated on weight and dimensional changes against over-dry state. In the DFW cycle test, the weight and dimensions of the specimens were measured to the nearest 0.01 mm and 0.001 g at the end of three cycles, totally after 21 days. $\text{ASE} (\%) = 100 \times (S_c - S_i) / S_c$ (Stamm 1964), where S_i is the volumetric or dimensional swelling ratio of treated wood compared to its oven-dry volume or dimension, and S_c is the corresponding ratio of untreated wood. S_c or $S_i (\%) = 100 \times (X_2 - X_1) / X_1$, in which

Table 1 Chemical composition of untreated and heat-treated wood. Average values are the mean of three replicates. Standard deviations are in parentheses. Values followed by a different letter within a column are statistically different at $P=0.05$ (ANOVA Single Factor and t-test).

Treatment	Acid insol. residue (%)	Holocel-lulose (A) (%)	α -Cellulose (B) (%)	Hemicelluloses (A-B) (%)
Control	26.0 ^X (0.5)	72.2 ^X (1.9)	42.0 ^X (1.3)	30.2
160°C-3 h	25.5 ^X (1.6)	70.2 ^X (1.5)	43.1 ^X (1.0)	27.1
180°C-3 h	36.0 ^Y (1.8)	61.3 ^Y (0.9)	41.6 ^X (0.9)	19.7
210°C-3 h	48.4 ^Z (1.8)	49.4 ^Z (0.5)	39.8 ^Y (0.9)	9.5

X_1 is the oven-dry volume (cm^3) or dimension (cm) before test and X_2 is the volume (cm^3) or dimension (cm) of the specimens after test.

The biological efficacy of the treated wood Evaluated by the Wood Mycology Laboratory at Scion, Rotorua, New Zealand, based on the agar block decay test following the standard ‘‘Sutter jar’’ method (Sutter 1978). This method is similar to that of European Standard EN-113 and British Standard BS 6009:1982 (Callahan and Chittenden 2009). However, it differs in exposure time to the decay organism, and in the present study, plastic Petri-dish containers were used instead of glass Kolle flasks (Stahlhut et al. 2008). Eight replicates of treated and untreated specimens, $35 \times 20 \times 7 \text{ mm}^3$ ($T \times R \times L$), were tested. The specimens were first leached for two weeks and air-dried for several days in the laboratory followed by oven-drying at $102 \pm 2^\circ\text{C}$ for 18 h. After this, the specimens were cooled down in silica gel desiccators and weighed. Then the specimens were sterilized by ethylene oxide gas. Finally, the specimens were placed into prepared Sutter agar containers. Incubation was at 26°C and 75% RH for six weeks. The fungus used was *Oilgoporus placenta*, a common brown rot fungus found in leaky buildings in New Zealand (Stahlhut et al. 2008). After incubation, specimens were cleaned, oven-dried and weighed. The percentage weight losses (WL) of the specimens were calculated from the oven-dry weight of the specimens before the incubation (M_b) and after the incubation (M_a) according to the equation: $\text{WL} (\%) = 100 \times (M_b - M_a) / M_b$.

The oil viscosities Oil viscosities of fresh unheated linseed oil, and linseed oil heated at 160°C , 180°C and 210°C for 3 h with and without wood specimens in the oil were measured in a Haake viscometer with MV1 sensor at a shear rate of 1000 s^{-1} and temperature of $20.2 \pm 0.1^\circ\text{C}$. The mean of 10 replicates was calculated.

Results and discussion

Chemical analysis

As demonstrated in Table 1, no significant changes in chemical constituents were found for the 160°C treatment, but the overall holocellulose content decreased by 15% and 32%, respectively, at 180°C and 210°C . The most significant change was for hemicellulose content, which decreased by approximately 35% and 69% at treatment temperatures of 180°C and 210°C , respectively. This finding is in agreement

with that of Mazella et al. (2004), who found a rapid hemicelluloses degradation at temperatures above 200°C during heat treatment in air. Hemicelluloses have low thermal stability (Fengel and Wegener 1984; Windeisen et al. 2007). Especially, their acetyl groups are split off in the form of acetic acid (Tjeerdsma et al. 1998a).

The α -cellulose content diminished only slightly at 210°C (by 5%) due to its crystalline structure (Fengel and Wegener 1984). The accessibility of glucosidic bonds in cellulose is also restricted compared to that of the hemicelluloses (Boonstra and Tjeerdsma 2006). Hill (2006) reported that cellulose degradation begins at 210 – 220°C and degradation accelerated above 270°C when levoglucosan and other break-down products are formed. Kim et al. (2001) also noted that severe degradation of the crystalline region occurs in a range of 300 – 340°C .

Lignin is considered to be the most thermal stable wood constituent. At temperatures up to 600°C , mass losses (ML) of hemicelluloses amount to over 95%, and those of cellulose to more than 80%, whereas ML of lignin does not exceed 60% (Bartkowiak and Zakrzewski 2004). Significant lignin degradation occurs only at a temperature above 280°C (Akgül et al. 2007). The relative proportion of lignin in wood remained unchanged for wood treated at 160°C but increased at 180°C and 210°C . The apparent increase in lignin content is partly due to the loss of holocellulose. Moreover, some of the thermally degraded carbohydrates may be incorporated within the lignin during the Klason lignin determination. This can lead to a falsely high estimation of lignin content (Zaman et al. 2000; Yildiz et al. 2006). Condensation reactions of lignin at temperatures higher than 200°C may also contribute to the changes in lignin content (Tjeerdsma and Militz 2005).

FTIR spectral data help to interpret the complex changes in wood upon heat treatment (Pandey 1999; Tjeerdsma and Militz 2005; Windeisen et al. 2007). The IR bands that showed important alterations are 1738 , 1650 , 1510 , 1430 , 1374 , 1267 , 1165 , 1113 , 1060 and 1030 cm^{-1} , but the general aspects of the spectra are very similar (results not shown). The 1738 cm^{-1} band is remarkably reduced after heat-treatment, which can be interpreted as hemicellulose degradation. The decline and shift of the 1650 cm^{-1} band reflects the decrease in absorbed water with increasing treatment temperature. At 210°C treatment the 1510 cm^{-1} band (lignin, aromatic ring) increased slightly, indicating the degradation of hemicelluloses and the relative increment of the lignin content. Based on the literature, it can be assumed that cross-linking density within the lignin network is increased at higher temperatures (Tjeerdsma et al. 1998a; Wikberg and Liisa Maunu 2004; Windeisen et al. 2007). The bands at 1060 cm^{-1} and 1030 cm^{-1} corresponding to C-O stretching in cellulose and hemicelluloses decreased after the treatments which indicate depolymerization of polysaccharides.

Weight and color changes of the treated wood

Figure 1 shows the effect of treatment temperature and time on the mean weight percentage change (WPC) of the treated specimens. In general, the specimens gained a certain

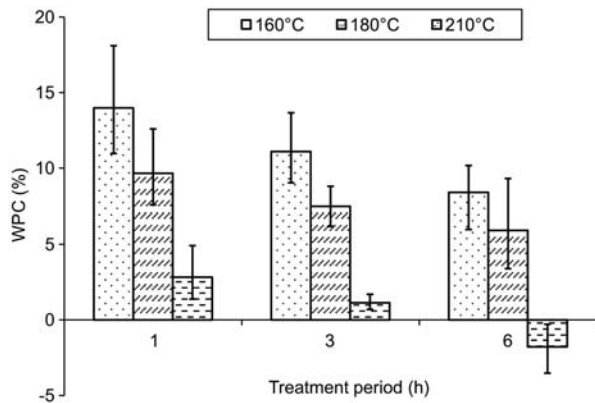


Figure 1 Weight percentage change (WPC, %) of heat-treated *Pinus radiata* wood in oil for different treatment temperatures and treatment durations (number of specimens $n=8$).

amount of weight due to the oil uptake during the treatment, but the gain in specimen weight decreased with the increase in treatment temperature and treatment time. For 3 h treatments, the WPC values at 160°C, 180°C, and 210°C were approximately 11%, 7.5% and 1%, respectively. At a given treatment temperature, the WPC values were the greatest for 1 h treatments and the least for 6 h treatments. In fact, the specimens treated at 210°C for 6 h lost 1.8% weight due to the wood degradation.

The heat-treatment also affected the wood color, as expected, with the wood turning darker, but the wood color became more uniform on the exposed surfaces. The color of the wood treated at 160°C, 180°C, and 210°C for 3 h was, respectively, yellowish brown, reddish-brown and dark-chocolate. No surface cracks, warp or twist were observed in the treated wood. The surface appeared shiny near the rays which may be due to a high uptake of oil by parenchyma cells compared to other wood tissues. The color change was similar on two flat faces of the specimens (Table 2) but the

two faces became identical in color after treatment at high temperatures. When the wood was treated at 180°C and 210°C, the total color difference (ΔE^*) and the brightness variation (ΔL^*) between the two surfaces was less than 1.5 units although the wood surfaces became darker. The human eye can distinguish color change only if ΔL^* is more than 3 units (Phelps et al. 1994) or the value of ΔE^* is >2 (Sundqvist 2002).

Color difference between core and surface for the treated specimens was found to be significant (Table 2, lower part). This difference, both for ΔE^* and for ΔL^* , was reduced with increasing treatment temperature.

Dimensional stability

Table 3 presents the results of volumetric swelling percentage (S) and anti swelling efficiency (ASE) of the treated wood as affected by treatment temperature (Table 3, upper part) and treatment duration (Table 3, lower part). Under all of the three test environments, the volumetric swelling of the treated wood decreased substantially compared to the untreated wood. The highest ASE of 53–60% was found in specimens treated at 210°C whereas the ASE was less for specimens treated at 160°C (31–38%) and at 180°C (37–39%). At a given temperature, the ASE values were the least for the shortest treatment time (1 h). However, no significant difference was observed between specimens treated for 3 h and those for 6 h.

The dimensional stability in T (width) and R (thickness) directions in the water immersion test are shown in Table 4 in which the ASE in T direction was greater than in R direction for all treatment temperatures. The values of ASE at 160°C in T and R directions were 19% and 13%, respectively, while the corresponding values for wood treated as at 210°C were 42% and 40%. This implies that wood becomes more stable and less anisotropic after treatments at high temperatures.

Table 2 CIEL*a*b* values and color differences between the two flat surfaces no. 1 and 2 of treated and untreated specimens, and between surface and core of treated specimens.

Treatment	Surface or core	Color in CIE $L^*a^*b^*$ system			Color difference			
		L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE
Untreated	Surf. 1	68.1	11.51	33.8				
	Surf. 2	64.3	12.2	31.8	3.8	-0.8	2	4.3
160°C-3 h	Surf. 1	65.9	12.3	38.2				
	Surf. 2	62.5	13.2	37	-3.3	0.9	-1.2	3.6
180°C-3 h	Surf. 1	61.2	13.7	36.8				
	Surf. 2	59.8	14.1	36.6	-1.4	0.4	-0.3	1.5
210°C-3 h	Surf. 1	47.1	13.8	26.3				
	Surf. 2	46.1	13.3	25.6	-0.9	-0.5	-0.7	1.2
160°C-3 h	Surf.	55	13.4	31.8				
	Core	70	7.3	27.5	15	-6.1	-4.2	16.7
180°C-3 h	Surf.	61.2	12	33.5				
	Core	74.7	6.9	27	13.6	-5.1	-6.6	15.9
210°C-3 h	Surf.	36.9	11.3	15.9				
	Core	47.3	11.8	26.7	10.4	0.6	10.8	15

Table 3 Volumetric swelling percentage (S) and anti-swelling efficiency (ASE) of untreated and heat-treated wood at different treatment temperatures (upper part) and at different treatment times (lower part). Average values are the mean of seven replicates. Standard deviations are given in parentheses. Values followed by a different letter within a column are statistically different at $P=0.05$ (ANOVA Single Factor and t-test).

	Water bath test		High humidity test		DFW cycle test	
	S (%)	ASE (%)	S (%)	ASE (%)	S (%)	ASE (%)
Control	13.5 ^X (1.6)		8.8 ^X (1)		12.8 ^X (2.3)	
160°C-3 h	8.9 ^Y (1.1)	33.9	6.0 ^Y (0.7)	31.7	8.0 ^Y (1.6)	37.8
180°C-3 h	8.2 ^Y (0.3)	39.1	5.4 ^Y (0.4)	38.7	8.0 ^Y (1.2)	37.5
210°C-3 h	6.2 ^Z (0.2)	54.1	4.1 ^Z (0.5)	53.2	5.2 ^Z (0.8)	59.8
Control	13.3 ^X (0.8)		4.7 ^X (1.6)		15.7 ^X (2.2)	
180°C-1 h	9.7 ^Y (0.9)	26.7	3.6 ^X (1.3)	22.4	8.8 ^Y (1.2)	43.9
180°C-3 h	8.2 ^Z (0.4)	38.2	2.7 ^Y (0.8)	42.9	7.7 ^Z (1.3)	50.8
180°C-6 h	8.2 ^Z (0.7)	38.4	2.5 ^Y (0.9)	45.9	7.5 ^Z (1.3)	52.2

Fungal resistance

Figure 2 shows the results of WL from laboratory pure culture decay trials against brown rot fungus *Oilgoporus placenta*. This fungus has been reported to cause a greater WL in heat-treated wood compared to other wood decaying fungi, namely *Coniophora putanea* and *Coriolus versicolor* (Welzbacher and Rapp 2002). The results show that the resistance of wood against this fungus was improved with the oil heat-treatment. The WL in untreated wood was 19.2% which was reduced to 13.2–17.6% for treated wood. However, no

Table 4 Tangential swelling (TS), radial swelling (RS) percentages and anti-swelling efficiency (ASE) of heat-treated wood specimens. Standard deviations are given in parentheses. Values followed by a different letter within a column are statistically different at $P=0.05$ (ANOVA Single Factor and t-test).

	TS (%)	ASE (TS) (%)	RS (%)	ASE (RS) (%)
Control	5.9 ^X (0.3)		3.7 ^X (0.1)	
160°C-3 h	4.9 ^Y (0.5)	18.6	3.1 ^Y (0.5)	12.7
180°C-3 h	4.7 ^Y (0.2)	27.4	3.0 ^Y (0.2)	22.7
210°C-3 h	3.4 ^Z (0.2)	41.9	2.3 ^Z (0.1)	39.9

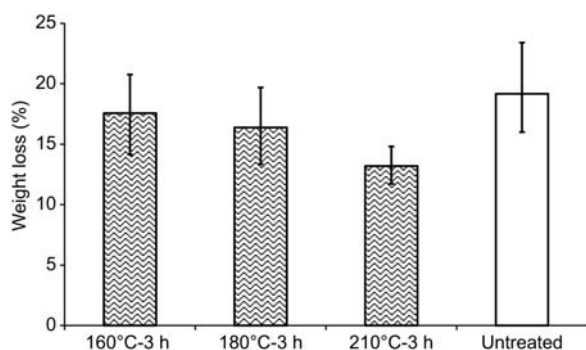


Figure 2 Mean percentage weight loss of heat-treated *Pinus radiata* wood in oil at 160°C, 180°C, and 210°C for 3 h in a pure laboratory decay trial against *Oilgoporus placenta* (number of specimens $n=8$).

significant difference ($P<0.5$ ANOVA single factor) in WL was found with the 160°C treatment. The specimens treated at 180°C and 210°C were improved moderately which matches the findings of others (Mazella et al. 2004; Paul et al. 2007). Based on the present study and studies of Kamdem et al. (2002) and Welzbacher and Rapp (2002), oil heat-treatment of *P. radiata* above 210°C could improve the durability of the species from non-resistant or perishable class to moderate resistant or resistant species depending on the fungus species and the treatment temperatures as defined in the Australian Standard and American Standard (AS5604 2003; ASTM-D2017 2005).

Viscosity of the oil

Figure 3 is a comparison of the viscosities of unheated and heated oils both with and without wood during heating. These observations are relevant for re-use of the oil for further heat-treatment cycles. As visible, the oil viscosity increased moderately with the heating temperature which is mainly attributed to evaporation of volatile components and polymerization of the linseed oil at high temperatures (Mabery 1923; Powers 1950). The viscosity of heated oils was slightly higher in the presence of wood than that without

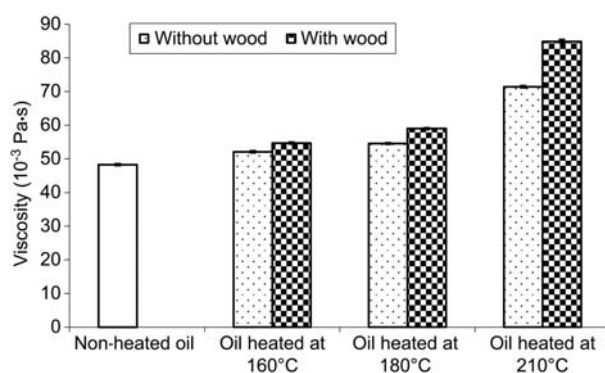


Figure 3 Mean viscosity (measured at $20.2\pm 0.1^\circ\text{C}$) of fresh oil and oil heated at 160°C, 180°C, and 210°C for 3 h with and without wood. Values are the mean of 10 replicates.

wood and this difference increased with the treatment temperature. This confirms that the release of wood extractives and wood degradation products contribute, to a certain extent, to the oil viscosity increment.

Factors influencing properties of oil heat-treated wood

The oil heat-treated *P. radiata* wood was darker in color, dimensionally more stable, and displayed a certain extent of improved fungal resistance. These changes can be due to: (a) change in wood chemistry at high temperatures; (b) the removal or migration of extractives and other compounds; and (c) oil uptake and the accumulation of oil on the wood surfaces.

Change in wood chemistry at high temperatures Oil heat-treatment resulted in changes in structure and proportions of the major chemical constituents of wood. The most significant changes occur in hemicelluloses as demonstrated by chemical analysis and FTIR spectroscopy. In a review by Rowell and Banks (1985), it is demonstrated that hygroscopicity of wood is a function of the content and structure of hemicelluloses, non-crystalline cellulose, surfaces of crystalline cellulose and, to a less degree, of lignin. Hemicelluloses play an essential role with this regard (Seborg et al. 1953; Hillis 1984; Evans 2003). Degradation of the hemicelluloses leads to a reduction of available free polar adsorption sites, mainly the hydroxyl groups are necessary for adsorption of water (Hillis 1984; Feist and Sell 1987). Denaturing (dehydroxylation) of polysaccharides hinder the fungi growth as they require adequate moisture in survival (Bowyer et al. 2003; Archer and Leebov 2006). Furthermore, at high temperatures above 210°C, the hemicelluloses are degraded to less hygroscopic substances, such as furfural polymers which are also toxic to fungal growth (Stamm 1964; Kamdem et al. 2002). Boonstra et al. (2007) also reported that heat-treatment of wood can induce chemical transformation of other wood constituents essential for fungal infection, such as minerals, vitamins, and low molecular mass carbohydrates.

It is an established knowledge (Kollmann and Fengel 1965) that the hemicelluloses degradation contributes essentially to the increased dimensional stability of heat treated wood. As the hemicellulose degradation becomes severer at high temperatures, the dimensional stability and fungal resistance of specimens treated at 210°C are better than those treated at 160°C and 180°C. The nature of color change is complex: all essential wood components including the extractives may contribute to it. The pH change (creation of acids) and heat promoted degradation and condensation reactions may contribute in various ways to the formation of chromophores (Bekhta and Niemz 2003).

Migration or removal of extractives and other compounds The heat-degraded compounds with low molecular weights tend to migrate towards the surfaces along with extractives (Theander et al. 1993; Sundqvist and Morén 2002). The oil viscosity increment confirms indirectly the removal of materials from wood (Mabery 1923; Powers

1950). But the color change is not restricted to the wood surface.

The color of the oil heat-treated specimens was found to be homogenous without any resin patches. In previous studies on thermally treated birch wood (175–200°C for 1–10 h in steam) non-homogenous distribution of color was observed (Johansson and Morén 2006). Obviously, during the heat-treatment in air or steam, migration of extractives towards the surface leads to the formation of unsightly resin spots in wood (Mayes and Oksanen 2002). The oil as a heating medium provides an oxygen-free environment and uniform heat transfer from oil to wood compared to air or steam as heating medium (Sailer et al. 2000a), thus the color is more uniform.

Oil uptake and the accumulation of oil on the wood surface From the results presented in Figure 1, it is visible that the greatest net weight gain (14%) was for wood treated at 160°C for 1 h, which can be attributed to the greatest oil uptake under this condition. However, the actual oil uptake at higher temperatures should be greater than the measured values considering the weight loss due to wood degradation and removal of extractives. The wood loss was more severe for wood treated at 210°C for 6 h and the net weight loss of wood treated under this condition was about 1.8%.

Linseed oil is hydrophobic (ASTM-D234-82 1998; Chem-watch 2007) and non-swelling as its molecule size is too large to penetrate in the cell wall (Rosenqvist 2000; Olsson et al. 2001; Hill 2006). Thus, the absorbed oil in the treated wood remains in the cell lumens. On this basis, contribution of the absorbed oil to the wood dimensional stability is expected to be limited. Therefore, specimens treated at 160°C with the highest oil uptake exhibited more volumetric swelling (Table 3) and less fungal resistance (Figure 2) than specimens treated at 210°C. Obviously, chemical changes at higher temperatures are more influential for dimensional stability and fungal resistance than the oil uptake alone. On the other hand, hydrophobic oils in the lumens block the water uptake of the walls and contribute indirectly to quality improvements (Wang and Cooper 2005). Furthermore, being a drying oil, the linseed oil forms a stable film on the outer and inner surfaces so that the barrier to water absorption is long-standing.

Conclusions

P. radiata wood was heat-treated in a linseed oil bath over a range of temperatures and times. Wet chemical analysis and FTIR analysis confirmed that the wood heat-treatment resulted in degradation of hemicelluloses (up to 70%). The treated wood was less hygroscopic and more dimensionally stable. The anti swelling efficiency (ASE) of the treated wood was found to range from 31% to 60%, depending on the treatment temperature and time. The ASE in the tangential direction was greater than in the radial direction; however, the differences between the two directions decreased with higher treatment temperatures. The resistance of the

treated wood against the brown rot fungus *Oilgoporus placenta* was also improved moderately by up to 30% (at 210°C). The degradation of hemicelluloses contributes largely to improvement in dimensional stability and fungal resistance of the treated wood. The color of the treated specimens became uniformly darker without patches. Oil heat-treatment of *P. radiata* wood can be an effective way to improve its dimensional stability and its color quality.

Acknowledgements

The authors wish to thank Ms. Diahanna O'Callahan of the Scion, Rotorua, New Zealand, for conducting the laboratory decay trials and Mahbulul Hassan of the AgResearch Ltd, Lincoln, New Zealand, for his help in the chemical analysis of the oil heat-treated wood. Postgraduate Scholarship from New Zealand Aid (NZAID) is acknowledged by the senior author.

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Received September 2, 2010. Accepted June 6, 2011.