Effects of the Thickness of the Heat-Treated Wood Specimen on Water-Soluble Extractives and Mechanical Properties of Merbau Heartwood

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Merbau wood has a disadvantage in outdoor applications because its water-soluble extractives readily leach out and stain adjacent materials. This study examined the thickness of the heat-treated wood specimen on water-soluble extractives and some mechanical properties. The results show that heat treatment is efficient at removing the water-soluble extractives of merbau heartwood and overcoming the leaching problem. The absorbance of UV light decreased in intensity when the duration of heating was increased from 1 hour to 5 hours. The dominant absorbance peak increased from the surface layer to the core layer. The modulus of elasticity (MOE) and modulus of rupture (MOR) of heat-treated samples showed significant reductions when the heating duration exceeded a certain point. The total loss of mass during heat treatment and water extraction verified that heat treatment removes the water-soluble extractives efficiently.

Keywords: Heat treatment; Water-soluble extractives; Heartwood; Merbau; Bending strength

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INTRODUCTION

Merbau (*Intsia* spp.) is a highly valued species of tree, both in terms of its traditional cultural importance and its valuable commercial timber. The heartwood of merbau is extremely dense (641 to 961 kg/m^3), has low shrinkage movement over time, and exhibits insect repellent properties. It is widely used for the construction of houses, furniture, canoes, pavilions, stairs, parquet flooring, outdoor furniture, and weathering boards, and it is valuable for cultural artifacts such as kava bowls and weapons (Thaman *et al*. 2006). However, its extractives are water-soluble and readily leach to stain adjacent materials in some outdoor applications (Hillis and Yazaki 1973). The kraft pulping process is negatively affected by these water-soluble extractives, and their presence can delay the setting of or weaken concrete when used for formwork (Hillis and Yazaki 1973; Koch *et al.* 2006).

Heat treatment is often used to improve the dimensional stability and durability of wood, as well as to reduce wood's equilibrium moisture and the consequent swelling. The effects of heat treatment on the physical and chemical properties of wood, such as mass loss, wettability, wood color, and chemical transformations, have also been reviewed by Esteves and Pereira (2009). Wettability changes and mass loss during heat treatment of wood at different temperatures were investigated by Hakkou *et al.* (2005). Effects of heat treatment on some mechanical properties of Scots pine (*Pinus sylvestris*

L.) and redbud maple (*Acer trautvetteri* Medw.) under varying temperatures and durations have also been studied (Korkut *et al.* 2008a, 2008b, 2008c). Eucalyptus (*Eucalyptus saligna*) and pine woods (*Pinus caribaea*) showed a significant reduction in arabinose, manose, galactose, and xylose contents when subjected to increasing temperatures. There was a significant reduction in extractive content for *Eucalyptus*, but a slight increase in extractive content for the *Pinus* wood under a temperature of 180 °C (Brito *et al.* 2008). The effects of heat treatment on the behavior of extractives in softwood were studied by FTIR spectroscopic methods (Nuopponen *et al.* 2003). The influence of extractives on wood color and hygroscopicity in heat-treated wood were reported by González-Peña *et al.*(2004) and Sundqvist and Morén (2002). The changes on physical and mechanical properties of heat-treated wood with its possible reasons were intensively investigated (Yildiz *et al.* 2006; Yildiz and Gümüskaya 2007).

In a previous study, heat treatment was proved to be an efficient technique to solve the problem caused by water-soluble extractives in merbau heartwood (Hu *et al.* 2012). However, the modulus of rupture and modulus of elasticity of the heat-treated samples decreased by 29.6 and 12.9%, respectively. The present study was to investigate the thickness of the heat-treated wood specimen on water-soluble extractives and mechanical properties of merbau heartwood with the ultimate purpose to explore the possibility of solving leaching of water-soluble extractives without decreasing the mechanical strength by the control of heating duration.

EXPERIMENTAL

The gross density of the approximately 50-year-old merbau heartwood, which was imported from Papua New Guinea, was 800 kg/m^3. The moisture content was about 12.4% after the kiln-dried lumber with a thickness of 8.0 cm was conditioned for 6 months at 25 °C and 65% relative humidity. The heat treatment was conducted using an experimental oven in the presence of air. The samples were put in the oven when the air temperature inside the oven reached the target temperature.

Thirty specimens measuring 300 mm [longitudinal (L)] × 70 mm [radial (R)] × 70 mm [tangential (T)] were divided into five groups to be heated for varying durations of 1, 2, 3, 4, and 5 h at 170 °C, which was an optimum parameter for heat treatment of Merbau wood (Hu *et al.* 2012). The six samples from each group were equally divided into two subgroups.

One subgroup was used to study how deep-heat treatment into the wood could affect the sample. The heat-treated specimen was peeled every 2 mm and was considered one layer, as shown in Fig. 1. The peeled wood was then ground into wood flour and sized 40 to 60 mesh. Fifteen layers were obtained, starting from the very outside working toward the center. Three grams of wood floor from each layer were immersed in 200 mL of distilled water in a glass. Specimens were removed after standing for 48 hours. UV visible absorption spectra of the extracted solutions were measured by a UV spectrophotometer (Mapada V-1100D) within the wavelength region 320 to 600 nm (resolution: 10 nm).

The other subgroup was cut into smaller specimens measuring 300 mm (L) × 20 mm (R) × 20 mm (T) for a three-point static bending test according to ASTM D143-09 (ASTM 2009) to investigate the effects of heating duration on the mechanical properties.

The specimens were re-conditioned for a week at 25 °C and 65% relative humidity before the bending test. The treated wood was put on the tension surface.

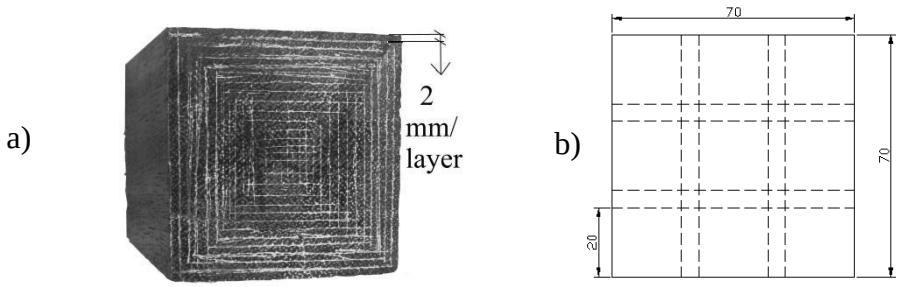

Fig. 1. Cross-sectional diagram of a) peeling and b) cutting plans

The mass loss during heat treatment and water extraction was also measured. Oven-dried wood flour was divided into five groups to be heated at 170 °C for durations of 1, 2, 3, 4, and 5 h. The wood flour's mass was measured before and after heat treatment. Heat-treated wood flour was immersed in 200 mL of distilled water for 48 hours. The measurement of the mass loss during water extraction was done according to the literature (Esteves *et al.* 2008). The total mass loss (M_t) can be expressed by Eq. 1 to 3 as follows,

$$M_t = M_h + M_w \quad (1)$$

$$M_h = (m - m_h)/m \quad (2)$$

$$M_w = (m_h - m_w)/m \quad (3)$$

where m is the oven-dried mass before heat treatment, m_h is the mass after heat treatment, and m_w is oven-dried mass after water extraction.

Three specimens measuring 320 mm (L) × 70 mm (R) × 300 mm (T) were heat treated at 170 °C for 4 h, which were optimum parameters for heat treatment of Merbau wood (Hu *et al.* 2012), to investigate the thickness of the heat-treated wood specimen on the mechanical properties along the radial or tangential direction toward the center. Each specimen was cut into 36 smaller specimens measuring 300 mm (L) × 20 mm (R) × 20 mm (T). These 36 smaller specimens were divided into three groups of top, center, and bottom (in the radial direction). Loads were applied on the longitudinal-tangential surface during the bending test. The heat-treated wood was put on the tension surface.

RESULTS AND DISCUSSION

Absorbance visible spectra of extractive solutions from different peeled layers at 170 °C for 4 hours are shown in Fig. 2. Absorption bands within 320 to 600 nm decreased in intensity from the first layer (the very outside surface) to the 15th layer (the core) along the radial or tangential direction. Additionally, the color of the extracted solution gradually faded from the first layer to the 15th layer, due to the removal of color derivatives from the extractives. The water-soluble extractives evaporated or chemically

reacted during heat treatment. The dominant absorption peak decreased from about 2.8 to 1.2 at 350 nm. The extractives may be polyphenols and terpene alcohols, according to the relationship between the structure of the compounds and absorption at the UV region. It would be necessary to use techniques such as FTIR and LC-MS for further chemical analysis. The results indicated that the removal of water-soluble extractives was different at the different layers along the thickness of the heat-treated wood specimen. Similar spectra were observed for the other treatment durations.

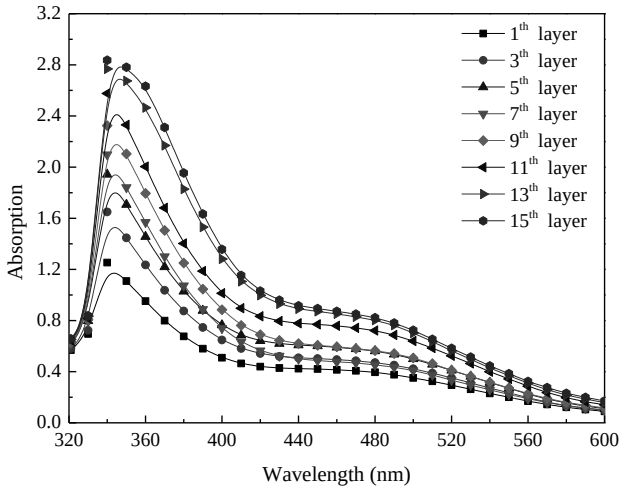

Fig. 2. Absorbance spectra of extractive solutions from different peeled layers at 170 °C for 4 h

The dominant absorption peak of extractive solutions from different layers at 170 °C under varying heating durations is shown in Fig. 3. The dominant absorption peak decreased when the duration of heating increased. However, there was no difference between the absorption of the extracted solutions treated for 4 or 5 hours. The dominant absorption peak of the first layer was the smallest. The peaks increased from the first layer (the very outside layer) to the 15 layer (the center layer) in the radial direction. The layers from depths 6 mm, 6 mm, 10 mm, 12 mm, and 12 mm exhibited dominant absorption peaks that were smaller than that of the untreated sample after heating durations of 1, 2, 3, 4, and 5 h, respectively. The reduction in extractive contents occurs, with heating up to a certain temperature and duration, due to the isolated effect of degradation and volatilization of extractives originally present in the wood. The degradation of extractives is related to oxidation reactions, accelerated by the effect of rising temperatures and durations (Moura *et al*. 2012). The dominant absorption peaks were almost the same for the very inner layers after varying durations of heating. Additionally, the dominant absorption peaks of the inner layers were even higher than that of the untreated sample, due to the accumulation of water-soluble extractives inside the inner layers during heat treatment. Low molecular weight substances are assumed to emerge, supposedly extracted during heat treatment and extraction (Moura *et al*. 2012). It is thus assumed that a share of the substances extracted from the inner layer is not constituted by the original extractives of the wood in natural form, which was thermally degraded and still remained inside.

It was found in a previous study that the heating temperature and duration had a negative effect on the mechanical properties of merbau heartwood during heat treatment (Hu *et al*. 2012). To reduce this negative effect, it was suggested to treat the surface layer only through the adoption of appropriate treatment time to form a protective layer instead

of treating the whole piece through to the inner core. The results obtained here verify the feasibility for obtaining such a protective layer through heat treatment.

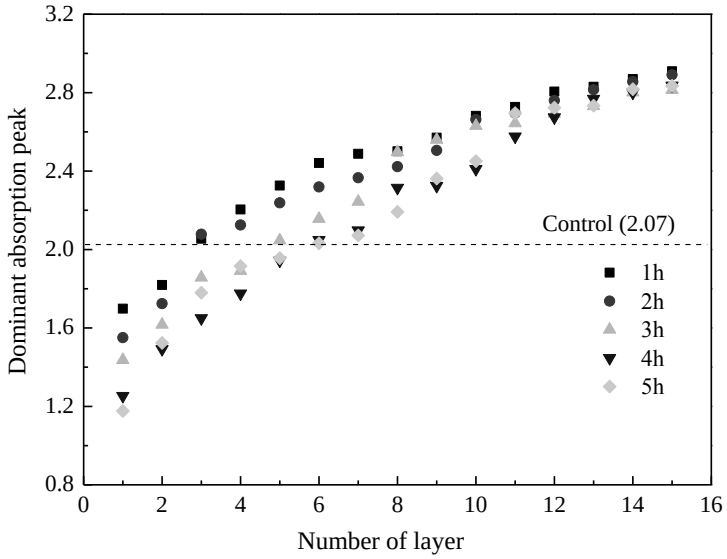

Fig. 3. Dominant absorption peaks of extractive solutions from different layers at 170 °C after varying heating durations

The effects of heating duration on the modulus of rupture and modulus of elasticity of heat-treated samples measuring 300 mm (L) × 70 mm (R) × 70 mm (T) treated at 170 °C are shown in Table 1. F-test results of ANOVA statistical analysis using SPSS 19.0 showed that the effects of heating duration on MOR and MOE were significant. MOE and MOR generally decreased with an increase of heating duration. MOE and MOR decreased 3.7% and 3.9%, 6.1% and 9.7%, 6.3% and 8.6%, 9.8% and 20.4%, and 18.2% and 35.6%, respectively, compared with MOE and MOR of the untreated sample when the heating durations were 1, 2, 3, 4, and 5 h, respectively. The ANOVA post hoc multiple comparisons of MOEs indicated that there was no significant difference between MOEs of the untreated sample and those of the treated sample when the heating duration was less than 3 h. However, there was a significant reduction in MOE when the heating duration exceeded 3 h. The ANOVA post hoc multiple comparisons of MORs indicated that there was a significant reduction in MOR when the heating duration was 2, 3, 4, or 5 h. Yildiz *et al.* (2006) reported that the mechanical strength values of heat-treated spruce wood decreased with increasing exposure durations and temperatures because of changes of chemical structure of wood components, especially the degradation of hemicelluloses. The content of hemicellulose decreases with increased heating durations and temperatures as a result of the degradation and volatilization of hemicelluloses (Yildiz *et al.* 2006; Yildiz and Gümüskaya 2007; Moura *et al*. 2012). These changes were mainly attributed to degradation and volatilization of carbohydrates (pentoses and hexoses) that compose hemicelluloses (Kotilainen 2000). Changes in, or loss of, hemicelluloses play key roles in the strength and stability of wood heated at high temperatures (Hillis 1984; Gunduz *et al.* 2009). So the strength losses of merbau heartwood heat treated at 170 °C are mainly caused by the degradation of

hemicelluloses. According to the data in Table 1, it is clear that an increasing duration of heating had a negative impact on MOE and MOR. With respect to the reduction of mechanical properties and the efficiency of heating treatment, it is recommended that the heating duration be kept less than 4 h.

Table 1. Statistical Analysis of the Effects of Heating Duration on MOR and MOE

Heating duration (h)	Moisture content	MOE (MPa)				MOR (MPa)			
		Mean	SD	F-test	Sig.	Mean	SD	F-test	Sig.
Untreated	13.4%	14015 (/)	1155		/	146 (/)	10.3		/
1	8.1%	13492 (3.7%)	671		0.872	140 (3.9%)	12.4		0.201
2	7.8%	13161 (6.1%)	1022	F = 7.9	0.529	131 (9.7%)	13.7	F = 27.6	0.007
3	8.0%	13133 (6.3%)	1107	P = 0.000	0.418	133 (8.6%)	11.5	P = 0.000	0.013
4	6.9%	12636 (9.8%)	1118		0.031	116 (20.4%)	14.5		0.000
5	6.2%	11466 (18.2%)	1580		0.004	94 (35.6%)	10.3		0.000

SD is standard deviation. The comparisons of MOE and MOR at varying heating durations were computed based on the LSD and Tamhane methods, respectively, according to the ANOVA test results (F-test) using SPSS 19.0. The significance (Sig.) is compared with the value of the untreated sample. N=27.

To study the effect of the thickness of the heat-treated wood specimen with full sizes on MOE and MOR, specimens measuring 320 mm (L) × 70 mm (R) × 300 mm (T) were heated at 170 °C for 4 hours. The mechanical properties of the different layers are shown in Table 2.

Table 2. Mechanical Properties of Different Layers Heated at 170 °C for 4 Hours

Layer	Moisture content	MOE (MPa)		MOR (MPa)	
		Mean	SD (COV)	Mean	SD (COV)
Untreated	13.4%	14015	1155 (8.2%)	145.5	10.3 (7.1%)
Top	5.5%	13722	784 (5.7%)	146.8	15.1 (10.3%)
Center	8.6%	13026	703 (5.4%)	128.2	11.2 (8.7%)
Bottom	6.7%	14021	536 (3.8%)	140.0	12.7 (9.1%)

The MOE and MOR of samples did not show any significant reduction after heat treatment. The MOE and MOR of the center layers were slightly less than the MOE and MOR of the top and bottom layers. The reasons were thought to be low moisture content and the strength reinforcement in heat-treated wood at the top and bottom layers. The strengths of heat-treated wood can benefit due to its lower equilibrium moisture content

as well as higher crystallinity of cellulose with heating temperature below 200 °C (Finnish ThermoWood Association 2003; Yildiz and Gümüskaya 2007).

Mass loss is one of the most important indications of quality for the heat-treated sample (Esteves and Pereira 2009). Extractives, especially volatile extractives, degrade or evaporate during heat treatment. Weak mass loss is attributed to the presence of volatile extractives in heat treatment with a temperature below 200 °C (Hakkou *et al.* 2005). The total mass loss (M_t) consists of the mass lost during heat treatment (M_h) and the mass lost during water extraction (M_w). Mass loss during heat treatment and water extraction is shown in Fig. 4. The results indicate that mass loss during heat treatment increases with an increase of heating duration, while mass loss during water extraction decreases. The total mass loss showed a slight increase with an increase of heating duration. This fact verifies that water-soluble extractives of merbau heartwood can be removed by heat treatment, which can reduce or eliminate the problem of water-soluble extractives leaching out and staining adjacent materials when used in outdoor applications.

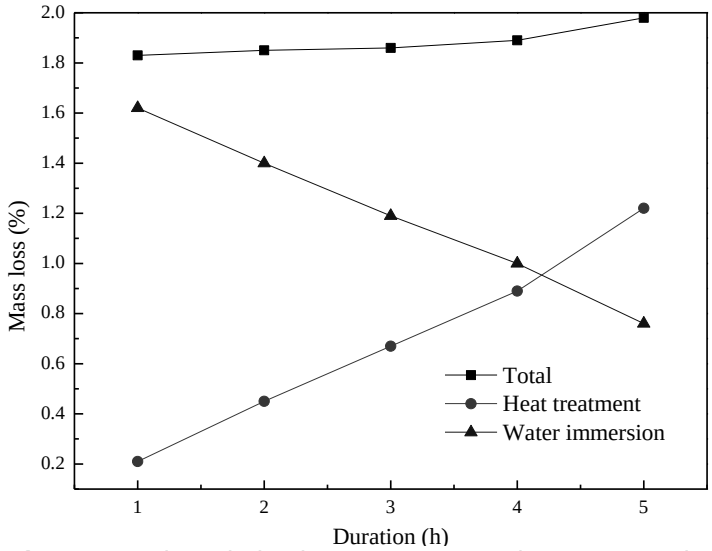

Fig. 4. Mass loss during heat treatment and water extraction

CONCLUSIONS

1. Heat treatment is an efficient technique for removing the water-soluble extractives of merbau heartwood and reducing or solving the problem of staining adjacent materials caused by the leaching of water-soluble extractives when such wood is used in outdoor applications.
2. MOE and MOR of heat-treated samples showed a significant reduction compared with MOE and MOR of the untreated samples when the heating duration exceeded a certain limitation. However, the MOE and MOR of heat-treated samples with larger dimensions did not show any significant reduction, due to their low moisture content and the strength reinforcement in heat-treated wood at top and bottom layers.

3. The total mass loss and UV-spectra also verify that heat treatment is an efficient way to remove the water-soluble extractives of merbau heartwood.

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