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NOTE

Effects of heat treatment on water-soluble extractives and color changes of merbau heartwood

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Abstract Merbau is widely used for indoor finishing, outdoor constructions, and furniture. However, it has a disadvantage in some applications in that part of its extractives is water-soluble and can be readily leached out to stain adjacent materials. This study examined whether heat treatment could overcome the above-mentioned problem. Effects of the treatment temperature and time on water-soluble extractives and color changes of merbau heartwood were studied. CIELAB ΔL^*, Δa^*,Δb^*, and ΔE^* parameters and absorbance spectra were used to evaluate color change and water-soluble extractive solutions, respectively. The results show that heat treatment is an efficient technique to overcome the problem caused by water-soluble extractives of merbau heartwood. Surface color of the treated samples tends to become darker and color of the extractive solution becomes fading to transparent when the treatment temperature and time increased. The absorbance of UV light decreases in intensity and the dominant absorption peak appears around 350 nm when the treatment temperature and time increase. The optimized parameters of treatment temperature and time are 170 °C and 4 h. Modulus of rupture and modulus of elasticity of the heat treated samples under the optimized parameters decrease by 29.6 and 12.9 %, respectively, compared with those of the untreated samples.

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Introduction

Merbau (*Intsia* spp.) is undoubtedly one of the most highly valued trees in the western Pacific and Indo-Malaysian region, both in terms of its traditional cultural importance and its value for commercial timber. Its durability, favorable physical and mechanical properties, ease of machining, and attractive dark red-brown color are especially favored for use in house construction, furniture, canoe making, pavilions, stairs, parquet flooring, outdoor furniture, weathering boards, and woodcarving of valuable cultural artifacts such as kava bowls and weapons [1]. The heartwood of merbau is extremely dense (641–961 kg/m^3), has low shrinkage movement over time, and good insect repellent property. However, it has a disadvantage in some applications in that part of its extractives is water soluble and can be readily leached out to stain adjacent materials [2]. In addition, during kraft pulping, the process is negatively affected by these water-soluble extractives. When used for formwork, the presence of water-soluble extractives could delay the setting of or weaken concrete [2]. The influence of extractives on the photo-discoloration and photo-degradation of wood was reported [3, 4].

Robinetin is the main polyphenol of the heartwood of merbau, together with smaller amounts of tri- and tetra-hydroxystilbenes, dihydroxymyricetin, myricetin and naringenin on chemical isolation [2]. Merbau also contains large amounts of water-soluble polymers, including leucocyanidin. The high water solubility of these polymers is responsible for some disadvantageous properties. Abenzenoid or terpenoid nature or aluminium succinate was

identified in the deposits of heartshakes in merbau [5, 6]. The topochemical distribution of polyphenols in the vessel of merbau heartwood was investigated using cellular UV microspectrophotometry and transmission electron microscopy [7]. It was reported that satisfactory stabilization of small samples was achieved by painting the surface with a formaldehyde solution (40 %) after drying with ammonia (27 %). Subsequent heating (above 100 °C) for a short period (1–2 min) rendered the components in the surface layers insoluble in water and evaporated the solvents, although the color of the wood was darkened [2].

Some researchers have reported how the heat treatment affects the physical and chemical properties of wood [8–10]. The purpose of the present study was to investigate the use of a heat treatment process to solve the problem caused by water-soluble extractives in merbau heartwood.

Materials and methods

The gross density of the about fifty-year old merbau heartwood, which was imported from Papua New Guinea, was 0.80 g/cm^3 and the moisture content was about 12.4 % after the kiln dried lumber with thickness of 8.0 cm was conditioned for 6 months at 25 °C and 65 % relative humidity. The thermal analysis was conducted using the ground merbau heartwood powder on simultaneous thermogravimetry–differential scanning calorimetry (STA) (STA 449C, Netzsch) to determine the reasonable temperature ranges of the heat treatment. The size of the powder was less than 150 μm filtered by a grit # 80 mesh. The powder was oven dried at 103 ± 2 °C for 2 h before conducting the thermal analysis. The heating rate was 10 °C/min and temperature range was in 25–300 °C. The longitudinal-radial surface of each specimen measuring 60 mm [longitudinal(L)] × 60 mm [radial(R)] × 20 mm [tangential(T)] was sanded using 380 grit sanding papers. The heat treatment was conducted using an experimental oven in the presence of air. Color changes on wood surfaces due to heat treatment were analyzed using a color measuring system (Hunter-lab-Ultrascan XE model). CIELAB L^*, a^*, and b^* parameters were measured at three locations on the sanded surface of each specimen and the average value was calculated. CIELAB ΔL^*, Δa^*, Δb^*, and ΔE^* parameters were calculated as follows:

$$\Delta L^* = L_t^* - L_i^* \quad (1)$$

$$\Delta a^* = a_t^* - a_i^* \quad (2)$$

$$\Delta b^* = b_t^* - b_i^* \quad (3)$$

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad (4)$$

where L_i^*, a_i^*, and b_i^* are parameters measured before heat treatment; L_t^*, a_t^* and b_t^* are parameters measured after heat treatment; ΔL^*, Δa^*, Δb^*, and ΔE^* represent changes in lightness, red/green chromaticity, yellow/blue chromaticity, and overall color, respectively.

The heating temperatures were 100, 140, 170, and 200 °C when the heating time was kept at 4 h to study the effects of the heating temperature. The heating times were 1, 2, 3, 4 and 5 h when the heating temperature was kept at 170 °C to study the effects of heating time. Each of the treated and untreated specimens was immersed in 800 mL of distilled water within a glass. Specimens were removed after standing for 48 h. UV visible absorption spectra of the extracted solutions were measured by a UV spectrophotometer (Mapada V-1100D) within the wave length region from 320 to 600 nm (resolution: 5 nm).

Specimens measuring 50 mm (R) × 50 mm (T) × 760 mm (L) were tested using a three-point bending arrangement to study the effects of heat treatment on mechanical properties according to ASTM D143-09 [11]. A total of thirty specimens were tested. Half of these were treated at 170 °C for 4 h before bending tests, and the remaining 15 was untreated as a control group. The three-point bending test was carried out on a Shimadzu testing machine (AG-1 type).

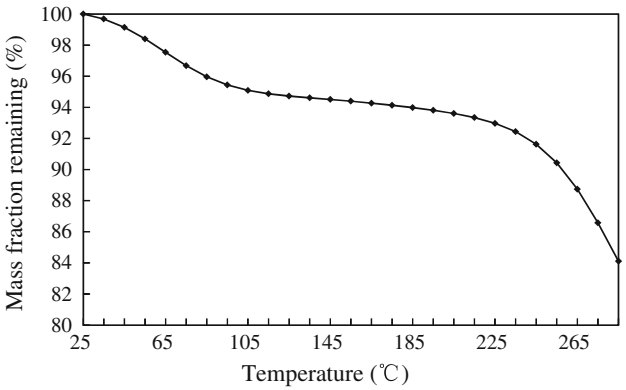

Fig. 1 Mass loss–temperature curves for merbau heartwood powder by heating at 10 °C/min increase from room temperature

Table 1 Effect of different heating temperatures on heartwood color

Heat treatment conditions		ΔL^*	Δa^*	Δb^*	ΔE^*
Heating temperature (°C)	Heating time elapsed (h)				
Control	0.0	0.0	0.0	0.0	0.0
100	4	−13.5	1.2	−5.6	17.5
140	4	−16.8	2.3	−9.9	22.1
170	4	−32.5	−21.7	−12.6	41.1
200	4	−34.7	−40.8	−18.7	55.1

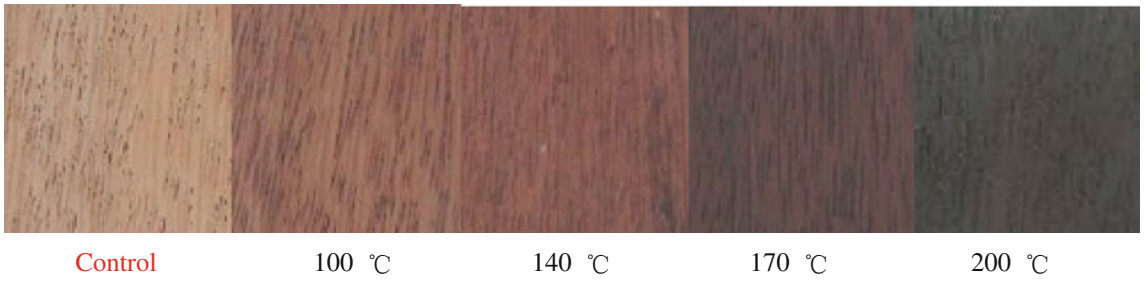

Fig. 2 Color changes under different heating temperatures for 4 h

Results and discussion

Figure 1 shows the thermogravimetry curve of merbau heartwood. The mass loss is about 5.0 % when the heating temperature is lower than 100 °C. The mass loss was due to the evaporation of water although the ground Merbau heartwood powder was oven dried before conducting the thermal analysis. Traces of the mass loss can be observed when the heating temperature is between 100 and 200 °C. Merbau heartwood remains thermally stable in this temperature range. The mass loss rate increases fast when the heating temperature exceeds 200 °C due to the thermal decomposition occurring in the hemi-cellulose and cellulose [12]. A conclusion can be drawn that the heat treatment should be conducted below 200 °C, considering the thermal degradation of the merbau heartwood.

CIELAB ΔL^*, Δa^*,Δb^*, and ΔE^*parameters under different heating temperatures are shown in Table 1. The overall color change ΔE^*increases monotonously from 0, 17.5 to 55.1 when the heating temperature increases from room temperature 100 to 200 °C. The lightness decreases monotonously from 0, −13.5 to −34.7 and the overall color becomes darker when the heating temperature increases. The yellow/blue chromaticity decreases monotonously from 0, −5.6 to −18.7. The red/green chromaticity first increases from 0, 1.2 to 2.3 when the heating temperature increases from room temperature 100 to 140 °C. It decreases from −21.7 to −41.8 when the heating temperature continues to increase from 170 to 200 °C. Experimental results show that the surface color first becomes red then green when the heating temperature increases. Surface color changes are shown in Fig. 2. It can be observed that the surface color becomes dark brown and uniform after heat treatment. Overall color changes do not lead to a decline in value when the heating temperature is below 200 °C.

UV visible absorption spectra of the extracted solutions under different heating temperatures are shown in Fig. 3. Absorption bands within 320–600 nm decrease in intensity when the heating temperature increases. The reason is due to the removal of color derivatives from the extractives. It was reported that the heartwood sample of merbau from Papua New Guinea contained 29.0 % methanol extractives and 15.3 % water-soluble extractives [3]. The absorption is almost close to zero when the heating temperature is 200 °C and the extracted solution is nearly transparent. The results indicate that the water-soluble extractives have evaporated or chemically reacted during heat treatment. UV absorbance spectra of the deposits attached to the

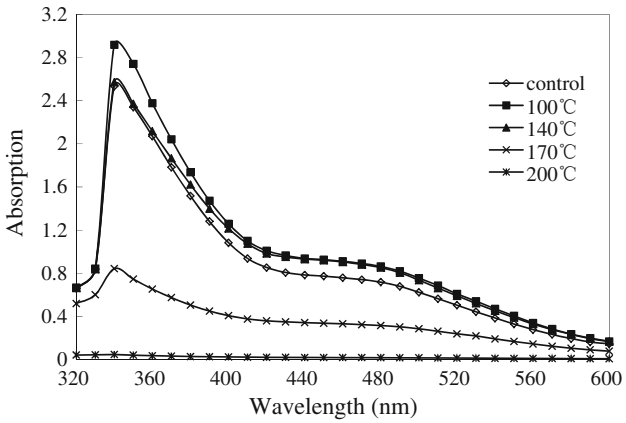

Fig. 3 Absorbance spectra of extractive solutions under different heating temperatures for 4 h

Table 2 Effect of different heating exposure time on heartwood color under 170 °C

Heat treatment conditions		ΔL^*	Δa^*	Δb^*	ΔE^*
Heating temperature (°C)	Heating time elapsed (h)				
Control		0.0	0.0	0.00	0.0
170	1	−18.1	6.7	−9.0	21.3
	2	−22.5	2.3	−10.6	25.0
	3	−23.4	−15.2	−9.4	29.5
	4	−32.5	−21.7	−12.6	41.1
	5	−31.1	−24.1	−14.1	41.8

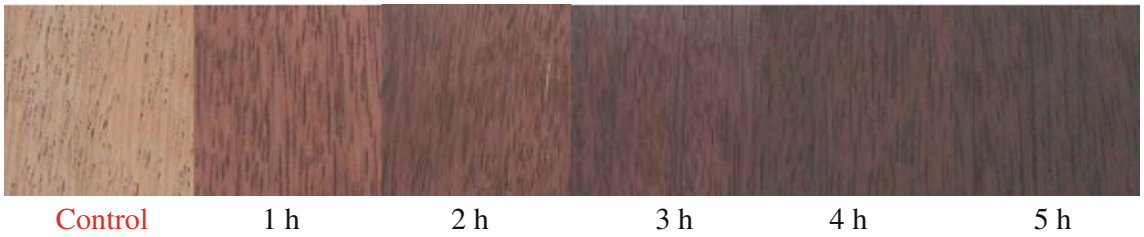

Fig. 4 Surface colors under different heating times elapsed at 170 °C

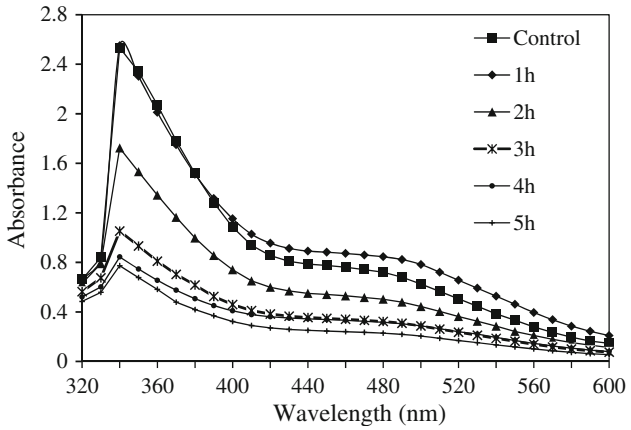

Fig. 5 Absorbance spectra of extractive solutions under different heating times elapsed at 170 °C

vessel walls of merbau are characterized by a distinct peak at a wavelength of 368 nm representing the UV absorbance of pure robinetin ($C_{15}H_{10}O_7$) by means of cellular UV microspectrophotometry [7]. It can be observed that the dominant absorbance peak locates at wavelength approximately 350 nm. It is only obvious that extractives may be polyphenols and terpene alcohols according to the relationship between the structure of the compounds and absorption at the UV region [7]. However, it is necessary to use some efficient techniques such as LC–MS and FTIR to do more chemical analysis.

The optimum heating temperature is 170 °C considering the information of the absorbance spectra, overall color changes, and thermogravimetry. CIELAB ΔL^*, Δa^*, Δb^*, and ΔE^*parameters under different heating times are shown in Table 2. The overall color change ΔE^*increases monotonously from 0, 21.3 to 41.1 when the heating time increases from control, 1–4 h. The lightness decreases monotonously from 0, −18.1 to −32.5 and the overall color becomes darker when the heating time increases. It is interesting to note that the yellow/blue chromaticity first increases from 0 to 6.7 and then decreases to −21.7. The red/green chromaticity decreases from 0, −9.0 to −12.6. Surface color changes under different heating times are shown in Fig. 4. It can be observed that the surface color becomes dark brown when the heating time increases. However, there is no big difference between the surface color of 4-h treated sample and that of the 5-h treated sample. The overall color changes do not lead to a decline in value within the range of the heating time studied.

UV–visible absorption spectra of the extracted solutions under different heating times are shown in Fig. 5. Absorption bands within 320–600 nm decrease in intensity when the heating time increases. The dominant absorption peak decreases from about 2.6 to 0.6. Meanwhile, the color of the extracted solution is gradually fading when the heating time increases from 1 to 4 h. The results indicate that the water-soluble extractives have gradually evaporated or chemically reacted with the increase of the heating time. However, there is no big difference between the absorptions of the extracted solutions of 4-h and 5-h treated samples.

Mechanical properties of untreated and treated samples are shown in Table 3. Heat treatment was conducted on samples at 170 °C for 4 h. The average modulus of rupture (MOR) of the untreated and treated samples is 137.3 and 96.7 MPa, respectively. The modulus of elasticity (MOE) of the untreated and treated samples is 13.2 and 11.5 GPa, respectively. The MOR and MOE of the treated samples decrease by 29.6 and 12.9 % compared with those of the untreated samples. The differences of the MOR and MOE values between the treated samples and control are statistically significant based on the two-tailed t test on paired samples. It is obvious that the heat treatment degrades the mechanical properties of merbau heartwood.

The heat treatment is an efficient way to solve the staining problem caused by the water-soluble extractives of merbau heartwood. However, the mechanical properties will decrease after heat treatment. This degradation is expected to be minor because only thin surface layer would be heat treated to solve the problem caused by the water-soluble extractives. The next phase of the research will include chemical analysis on the water-soluble extractives containing within merbau heartwood in an attempt to understand the mechanism behind this degradation.

Table 3 Mechanical properties of untreated and treated samples

	Moisture content (%)	Number of replication	*df*	MOR (MPa)				MOE (MPa)			
				Mean	Standard deviation	*t* statistic	Sig. (2-tailed)	Mean	Standard deviation	*t* statistic	Sig. (2-tailed)
Control	12.0	15		137.3	26.5			13191	1155		
Heat treated	8.0	15	14	96.7	14.0	4.36	0.02	11493	1201	2.54	0.03

t statistics and Sig. values were generated from a two-tailed *t* test on two paired samples using SPSS 19.0

Conclusions

Heat treatment is an efficient technique to remove the water-soluble extractives of merbau heartwood with the ultimate aim of solving the problem of staining adjacent materials when the water-soluble extractives leach out. The main results and findings are as follows:

1. Surface color of treated samples tends to become darker and the color of the extractive solutions becomes fading to transparent when the heating temperature and heating time increase.
2. The absorbance of the UV light decreases in intensity and the dominant peak appears around 350 nm when the heating temperature and heating time increase.
3. Heat treatment is an efficient technique to overcome the problem due to its water-soluble extractives. The optimized parameters of heating temperature and time are 170 °C and 4 h, respectively.
4. MOR and MOE of the heat-treated samples under the optimized parameters decreases by 29.6 and 12.9 %, respectively, compared with those of the untreated samples.

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