Variation and Correlation of Heat-Treated Wood's Crystalline Structure and Impact Toughness

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This study aimed to investigate the changes in the fiber characteristics, relative crystallinity, and impact toughness of heat-treated *Eucalyptus urophylla* × *E. camaldulensis*. Samples were treated in a superheated steam kiln at 160, 180, 200, and 220 °C for 3 h. The crystallinity, length-width ratio of fibers, and impact toughness of the heat-treated and untreated wood were determined. The cellulose crystalline regions experienced no obvious change. However, the length-width ratio and the relative crystallinity of the fibers increased as the temperature increased. Results indicated a clear inverse trend in the impact toughness and relative crystallinity. Finally, the results could provide a new method for non-destructive testing of wood.

Keywords: Heat treatment; E. urophylla x E. camaldulensis; XRD; Length-to-width ratio; Aspect ratio; Impact toughness

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INTRODUCTION

Eucalyptus urophylla × *E. camaldulensis* is an excellent hybrid that is grown in the Guangxi Province of China. This *Eucalyptus* cross possesses many positive characteristics, such as rapid growth, straight trunk, straight texture, high quality, and high volume yielding rates. Therefore, it is an excellent industrial fiber timber and solid wood machining species. Consequently, because of its inherent value and research potential, it is widely planted in South China (Qin *et al*. 2012).

Eucalyptus can deform easily if it is used as solid wood, but high-temperature heat treatment is an effective way to solve this problem. Wood heat treatment is an excellent method of wood modification. Wood is treated at high temperature conditions in the absence of oxygen but the presence of water vapor. During the heat treatment process, the hemicellulose inside the wood is partially decomposed, and some extractives are simultaneously volatilized and react, forming new chemical bonds inside the wood. For these reasons, heat-treated wood possesses excellent characteristics, such as fine dimensional stability and durability (Cermak and Dejmal 2013; Feher *et al*. 2014; Tu *et al*. 2014), corrosion prevention, and pest control characteristics (Bourgois *et al*. 1991; Obataya and Tanaka 2000). However, the reduced impact toughness caused by heat-treatment is adverse to the use of wood (Unsal *et al*. 2003). Since the 1990s, researchers have focused their efforts on developing the treatment technology and physical mechanics properties of heat-treated wood and have obtained significant results (Kamden *et al*. 2002; Boonstram *et al*. 2007; Kol and Sefil 2011; Dundar *et al*. 2012; Zanuncio *et al*. 2014). According to Jiang *et al*. (2014), the modulus of elasticity (MOE) and modulus of rupture (MOR) are reduced after the heat treatment process, but the dimensional stability improves considerably. Tomak *et al.* (2014) showed that heat treatment seemed to protect wood

surfaces from becoming rougher when exposed to natural weathering factors. The reduction rate of the strength properties for heat-treated samples was relatively lower than that of control samples. Martinka *et al*. (2014) obtained results that the heat treatment of spruce wood causes a significant decrease in the maximum heat release rate, making heat-treated spruce wood safer than the untreated wood. Olarescu *et al*. (2014) reported a maximum dimensional stabilization of 66.4% and a hygroscopicity reduction of 33%. Therefore, heat-treated lime wood lamellas could be used for outdoor purposes. Akgül *et al*. (2007) also found changes in crystallinity related not only to the heating temperature, but also to time. The crystallinity of Scots pine (*Pinus sylvestris* L.) and Uludağ fir (*Abies nordmanniana* Stev. subsp. *bornmuelleriana* Mattf.) wood samples increased during heat treatment at 120, 150, and 180 °C for 6 and 10 h.

The aim of this paper was to assess the influence of heat treatment on the fiber morphology, relative crystallinity, and impact toughness of wood of a *Eucalyptus* cross. Furthermore, the relationships among impact toughness, fiber morphology, and crystallinity were evaluated and compared. To attain these research goals, wood samples were treated at 160, 180, 200, and 220 °C. A digital biological microscope system and an X-ray diffractometer (XRD) were used in this analysis.

EXPERIMENTAL

Materials

Samples were collected from 8-year-old *E. urophylla* ×*E. camaldulensis*, obtained from the Hezhou region of Guangxi Province. The average oven-dry densities of the samples were in the range of 0.63 to 0.72 g/cm^3. The moisture content of samples of *Eucalyptus* (with dimensions of 500 (L) mm × 120 (T) mm × 60 (R) mm) was adjusted from 80% to 10% *via* conventional drying methods.

Methods

Heat treatment

Samples were heat-treated in a conventional pressurized superheated steam kiln heat-treatment oven (capacity 30 m^3, maximum temperature 220 °C) at four temperature levels: 160, 180, 200, and 220 °C. For each heat treatment condition, the dried samples (with a moisture content of less than 5%) were placed in the oven. Then, the samples were kept at a dry-bulb temperature rising to the target temperature at a heating rate of 15 °C, with the wet-bulb temperature kept at 100 °C for the duration of the heating process. The target temperature was maintained for 3 h. The fan and the humidifier were turned off when the dry-bulb temperature dropped below 110 °C, and the sealed kiln was cooled. Heat treatment for the samples was completed when the dry-bulb temperature had decreased to 60 °C. Three replicates were used for each group of temperatures.

Analysis of heat-treated samples

Heat-treated samples were separated into wood fibers using potassium chlorate and nitrate. Fifty complete wood fibers were selected randomly from the samples and observed by the digital biological microscope system (Leica Corp. Germany). The dried samples were pressed into thin slices to determine their X-ray diffraction characteristics, using the XRD-6000 diffractometer (Shimadzu Corp. Japan), and the crystallinity was calculated.

The X-ray diffractometer was used with the following conditions: 2 mg of each sample was pressed into slices, the X-ray tube had a copper target, and the tube voltage was 40 kV. The scanning speed was 5°/min, and the scanning range was 10 to 50°. Calculation of the relative crystallinity was carried out using the Segal method, according to the intensity of the diffraction patterns (Li 2003; Yang *et al*. 2010a). The relative crystallinity was calculated using Eq. 1,

$$C_rI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (1)$$

where C_rI is the relative crystallinity (%), I_{002} is the maximum intensity of the (002) lattice diffraction angle (arbitrary units), and I_{am} is the scattering intensity of the non-crystalline background diffraction. When the 2θ angle is close to 18^o, I_{002} and I_{am} have the same units. The impact toughness was examined using a universal mechanical testing machine (Shimadzu Corp. Japan), in accordance with the GB/T 1936.1 (2009) and GB/T 1936.2 (2009) standards. Thirty replicates were recorded for each group.

RESULTS AND DISCUSSION

Fiber Characteristics of Heat-treated Wood

The fiber characteristics are presented in Table 1. The results showed that heat-treated *Eucalyptus* showed a higher length-width ratio of fibers in comparison to the untreated wood. Although both the length and width were decreased by heating, the width of fibers generally exhibited a greater relative decrease. The contents of the wood fiber cell lumen (such as starch, sugars, grease, tannins, and other substances) volatilized when the temperature increased. The reduced cavity material caused shrinkage in the wood fibers. The length of the wood fibers tended to increase as the temperature rose from 160 to 200 °C, because the hydroxyls of the wood molecular chain lost water through condensation at certain temperatures. Therefore, the arrangement of the micro fibrils was more orderly in treated wood than in untreated wood. The axial dimensions of the wood fiber increased during the rearrangement because the S_2 layer of the micro fibrils are parallel to the cell axis. The S_2 layer comprises 70% to 90% of the cell wall thickness (Li 2002).

Table 1. Fiber Characteristics of Wood Treated at Various Temperatures

Temperature (°C)	Length of Fibers (μm)	Width of Fibers (μm)	Length-width ratio of fibers (%)	Replicates	STDEV
160	993.32	20.32	48.87	50	9.31
180	1042.87	20.19	51.64	50	12.58
200	1097.06	15.72	69.77	50	17.45
220	1051.81	17.89	58.78	50	11.91
Untreated Wood	1058.26	22.21	47.63	50	10.43

However, from 200 to 220 °C, the length-width ratio of the fibers decreased as the heat-treatment temperature rose. The length of the wood fibers decreased for the same

reason: polysaccharides in the hemicellulose cracked at high temperature, and the arrangement of wood fibrils was destroyed.

Crystalline Characteristics of Heat-treated Wood

The diffraction intensity curves of heat-treated wood at the 002 crystal plane angle are given in Fig. 1. Visual analysis of Fig. 1 suggests that the distance between the crystal layers remains unchanged. The peak position of the 002 crystal plane diffraction for the heat-treated wood is located at approximately 22.3°, which coincides with that of untreated wood.

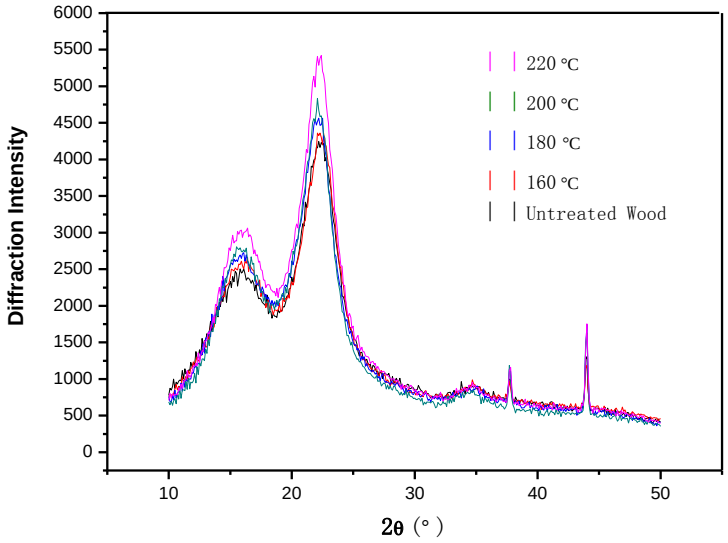

Fig. 1. Diffraction intensity curves of wood treated at various temperatures

Table 2 shows that the cellulose crystalline structure of the wood cell wall was altered after thermal treatment. Furthermore, the crystallinity of the wood fibers was increased as a result of heat treatment. However, there were different changes at different temperature stages. The relative crystallinity increased slightly when the temperature was 160 °C because the microfibrils in the amorphous regions became more orderly and closer to the crystallization regions. At this temperature, the cellulose molecular chains lose water and generate ether bonds when the poly condensation reaction occurs in the hydroxyl region of the cellulose molecular chains in the amorphous regions.

Table 2. Crystalline Characteristics of Wood Treated at Various Temperatures

Temperature (°C)	002 Crystal Plane Angle (°)	I_{002}	I_{am}	Relative Crystallinity (%)
160	22.1	4362	1880	56.9
180	22.2	4566	1990	56.4
200	22.1	4834	1906	60.6
220	22.4	5422	2114	61.0
Untreated Wood	22.2	4244	1832	56.8

The crystallinity decreased slightly when the heat-treatment temperature was 180 °C. This phenomenon can be attributed to the plasticization of lignin, which makes it become soft. Meanwhile, the lignin macromolecules become fragmented at this temperature. Hydrophilic groups were simultaneously created in the wood, which increased the amorphous regions of the fibers. The relative crystallinity increased again at 200 and 220 °C because the acidic xylan and glucomannans in the hemicellulose split at 200 °C, and split materials can polymerize and crystallize again under the action of heat (Yang *et al*. 2010b).

Analysis of the Impact Toughness of Heat-treated Wood

The impact toughness of untreated and heat-treated *Eucalyptus* at various temperatures is given in Table 3. The impact toughness decreased with increasing temperature. Compared with untreated wood (impact toughness of 84.86 kJ/m^2), the impact toughness of heat-treated *Eucalyptus* was decreased by 30.16%, 33.14%, 55.29%, and 63.77% as the temperature rose from 160 to 220 °C. The decrease in the impact toughness was because of the decline of porosity and diminution of molecular chain flexibility with the increase in crystallinity of wood (He 1993). These results are consistent with the results given in Table 2. Meanwhile, the softening and degradation of hemicellulose and lignin are important reasons for the reduction in impact toughness during heat treatment.

Table 3. Impact Toughness of Wood Treated at Various Temperatures

Temperature (°C)	Impact Toughness (kJ/m^2)
160	79.082
180	54.51
200	36.45
220	29.55
Untreated Wood	84.86

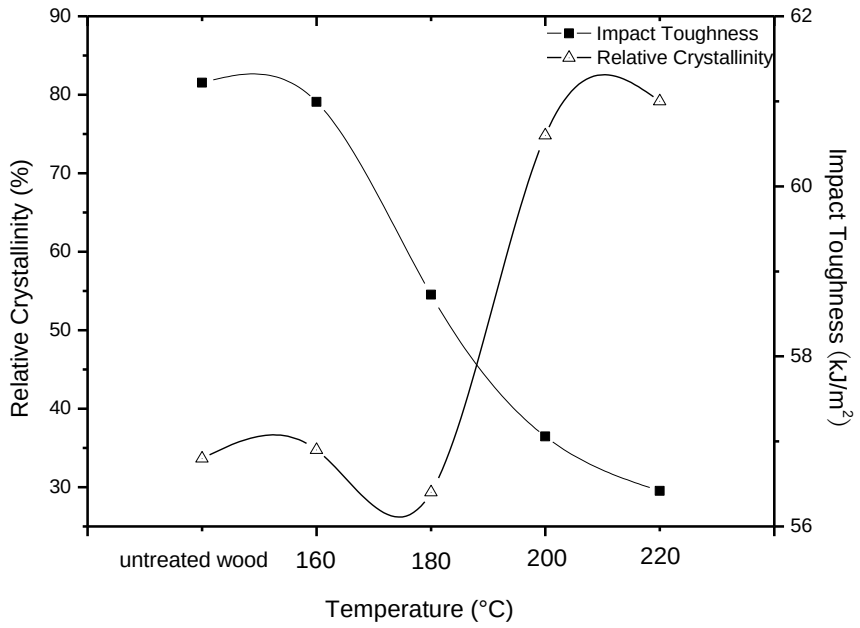

Fig. 2. Relative crystallinity and impact toughness of wood treated at various temperatures

Figure 2 shows that the relative crystallinity and impact toughness were well correlated through a series of temperature changes. In general, the impact toughness gradually decreased and the relative crystallinity increased as the temperature increased. Therefore, the impact toughness of the heat-treatment wood can be predicted through the relative crystallinity, suggesting a method for the non-destructive testing of heat-treated wood.

CONCLUSIONS

1. Heat treatment of *Eucalyptus urophylla*×*E. camaldulensis* at temperatures ranging from 160 to 220 °C had obvious effects on the fiber morphology and the relative crystallinity. The length-width ratio of the fibers increased after heat-treatment, and an increasing trend appeared with the rise of the heat-treated temperature from 160 to 200 °C.
2. Heat treatment had no clear effect on the diffraction pattern of the cellulose crystalline region, and the diffraction peak position of the 002 planes stayed at approximately 22.3°. However, the cellulose relative crystallinity showed a gradual increase with heat treatment.
3. The impact toughness of the *Eucalyptus* was reduced as the heat-treated temperature increased, presenting an inverse trend with respect to the relative crystallinity. Therefore, the relative crystallinity can be used to predict the impact toughness of heat-treated wood.

ACKNOWLEDGMENTS

This study was supported by the Science and Technology Development Program Project of Guangxi Province (Grant No. 2013BA15) and the Department of Education Nursery Project of Guangdong Province (Grant No. 2013LYM_00030003).

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Article submitted: November 12, 2014; Peer review completed: January 7, 2015; Revised version received: January 10, 2015; Accepted: January 11, 2015; Published: January 20, 2015.