INFLUENCE OF DYEING TREATMENT ON THE PERFORMANCE OF BAMBOO-BASED FIBRE COMPOSITES

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HU YA, HE M, ZHU RX, ZHANG YH, YU YL & YU WJ. 2014. Influence of dyeing treatment on the performance of bamboo-based fibre composites. The objective of this study was to investigate the influence of basic dye on colour change, modulus of rupture (MOR), modulus of elasticity (MOE), shear strength (parallel loading), thickness swelling rate and water absorption rate of bamboo-based fibre composites from *Phyllostachys pubescens*. Oriented bamboo fibre mat was treated with Basic Brown G dye through three dyeing procedures, namely, in water at 20 °C, in water at 90 °C or in ethanol at 75 °C. Samples dyed in ethanol and water at 90 °C had higher exhaustion rates than those dyed in water at 20 °C. The colour change of oriented bamboo fibre mat dyed at 75 °C in ethanol was larger than that of samples dyed in water at both temperatures. Dyeing procedure slightly reduced the MOR, MOE and shear strength of bamboo-based fibre composites. Compared with samples dyed in water, samples dyed in ethanol had reduced shear strength and MOE. Thickness swelling rate and water absorption rate of bamboo-based fibre composites samples increased after dyeing treatments.

Keywords: Bamboo scrimber, colour difference, bamboo fibre mat, fibre composites

INTRODUCTION

Bamboo is commonly used in many tropical and subtropical regions of the world because of its fast growth rate, high mechanical strength, short rotation age, easy machinability and great potential as sustainable material. Since the 1980s, many bamboo-based materials have been developed such as bamboo plywood, particleboard, bamboo-laminated strand-board and bamboo scrimber. Production of these materials has been successfully developed in Asia. However, the sum value of all these kinds of bamboo products is not very high. Therefore, it is necessary to continue improving the utilisation ratio of bamboo (Zhang et al. 2013). Bamboo-based fibre composites manufacturing is a new technology for better utilisation of bamboo resources. This technology has several advantages such as it uses whole bamboo culms as manufacturing unit, it overcomes bonding problems for outer and inner bamboo culms and it improves bamboo utilisation ratio to more than 90%.

There are many potential indoor and outdoor applications of bamboo-based fibre composites. These include outdoor and indoor flooring, wood plank road, container flooring, garden landscaping, wind turbine blade, concrete board, horse stable boards and furniture (Qin et al. 2009, Yu et al. 2014). However, the application of composites in exterior environments has been greatly limited by their surface colour. Currently, only natural and carbonised colours are available in most bamboo markets, which can hardly satisfy the needs of consumers. Dyeing process is the most effective method for changing the colour of bamboo. Although dyeing of wood is common and results have shown good permeability, studies of dyeing technology and process for bamboo have yet to be reported.

Raw bamboo has dense outer layer and its inner layer has very different physical and mechanical properties compared with the main part of the bamboo and is difficult to penetrate deeply. Therefore, it is necessary to produce a novel component using mechanical treatment and moving the inner and outer layers, i.e. the green and yellow of bamboo. In previous work, we developed a rolling machine for manufacturing of oriented bamboo bundle mat. The rollers removed part of the waxy layer and the siliceous layer on the outer surface of bamboo culm. The outer most layer of bamboo tube were retained and cracked, fragmented or crushed in order to form dotted- or line-shaped cracks. Oriented bamboo bundle mat shows deep linear-shaped cracks that will help dye particles permeate into the bamboo easier (Yu et al. 2014).

This study aimed to explore new products of bamboo-based fibre composites using oriented bamboo fibre mat by treatment with Basic Brown G dye, which is a simple azo dye suitable for dyeing textile, waxes, varnishes and wood. The colour difference and the percentage of dye exhaustion of the oriented bamboo bundle mat, the amount of dye particles accumulating on the cell walls of raw bamboo culm and the distribution of dye particle aggregates in the bamboo cell structure were studied for the first time. Changes in board colour as well as physical and mechanical properties of the dyed bamboo-based fibre composites were also investigated. This study will offer a reference for research and production of bamboo-based fibre composites.

MATERIALS AND METHODS

Sampling and raw material

Commercial low-molecular weight phenol formaldehyde used in this study had the following parameters: solid contents 45.59%, viscosity 36 cP, pH 10 to 11 and water miscibility 7 to 8. Bamboo *(Phyllostachys pubescens)* culms were obtained from the bamboo forest in Xuancheng, southeast Anhui, China. The bamboos were 4 to 5 years old and had diameters of 80–100 mm and wall thickness values of 7–12 mm. Raw bamboo culms were cross-cut into 2-m long segments. Using bamboo culm splitter, each segment was split right down the middle into two or three parts. Each part was then pressed to form oriented bamboo bundle mat using methods described by Yu et al. (2014) (Figure 1c). The oriented bamboo bundle mat was dried in a drying house (70 ºC) until moisture content reached 10%.

Bamboo mat was dyed in a water bath. In many preliminary experiments, we observed that oriented bamboo bundle mat dyed in water at 90 °C and in ethanol at 75 °C had good colour and penetration depth. Therefore, in this study, we used three methods to dye the oriented bamboo bundle mat, namely, in water at 20 °C and 90 °C and in ethanol at 75 °C. Dye solutions were made by mixing Basic Brown G dye at concentration 8% (based on weight of bamboo) with surface active agent alkylphenol polyoxyethylene(10) ether (3 g L^{-1}), acetic acid (3 g L^{-1}) and sodium acetate (1 g L^{-1}) for 12 hours. The pH value was controlled at 5 to 6. After treatment, the oriented bamboo bundle mat was dried to reach equilibrium water content. The mat was then immersed into phenol formaldehyde adhesive for 5 min. The target resin content of the bundle mat was controlled at 15% (ratio of resin dry weight to bamboo bundle dry weight).

The bundle mat was then dried to achieve a moisture content of 12%. The dried oriented bamboo bundle mat was reconstituted in a hot-pressing mold (300 mm × 170 mm × 20 mm) at 140 °C for 25 min. Thickness of the composite was set at 20 mm and target of density was 1.1 g cm^{-3}. Figure 1 shows the flow chart for making bamboo-based fibre composites.

Evaluation of properties

The rolling machine caused the surface of the oriented bamboo bundle mat to be rough (Figure 1c). Therefore, we chose raw bamboo culm as the object of microscopic investigation and evaluation. Three raw bamboo sections of approximately 15 mm were collected for anatomical investigation. These sections were taken from the culms and macerated at 75 °C for 72 hours. One was macerated with Basic Brown G mixture, i.e. in ethanol, acetic acid and surface active agent, while the second was macerated with Basic Brown G in water, acetic acid and surface active agent and the third, with only water as the untreated control.

Transverse and radial sections (15- to 25-μm thick) were cut from each bamboo section on a sliding microtome and mounted in synthetic resin. Evaluation was performed using light

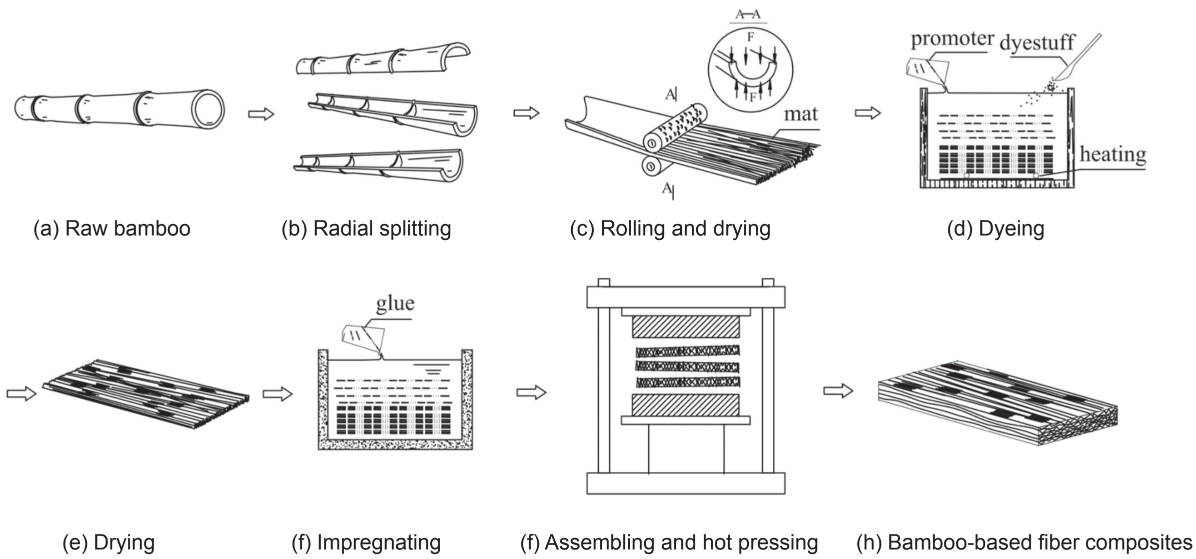

Figure 1 Flow chart for making bamboo-based fibre composites

microscope, and images were taken using DP2-BSW software. A digital camera was installed and adapted on the microscope. All microscopic investigation and evaluation were conducted on transverse and tangential sections (Kim et al. 2008, Wahab et al. 2012). The surface of samples was also sputter-coated with gold and analysed under scanning electron microscope at working distance of 25 mm, voltage 10 kV and probe current 6×10^{-10} A.

Dyeing of oriented bamboo bundle mat was done using exhaustive dyeing procedure. The absorbance of the dyes at their maximum wavelengths was evaluated using ultraviolet spectrophotometer. Unfixed dye from samples was extracted with hot water and measured in the same way. Exhaustion rate of the dye was calculated as in equation 1.

$$\text{Exhaustion } (\%) = (A_0 - A)/A_0 \times 100 \quad (1)$$

where A_0 and A = absorbance of the dye solution before and after exhaustion respectively (Kim & Sun 2002). Colour measurements of bamboo samples were made using chroma meter with D_{65} light source, 8-mm aperture size and 10° normal observer. Six measurements per specimen were carried out using a pattern that minimised structural influence of the bamboo. Colour evaluation was performed using the system where L*, a* and b* components were based on nonlinear transformation of primary colorimetric values in the XYZ colour spaces. The X, Y and Z values were calculated from the absorbance spectra. L* axis represented the colour lightness of an object, varying from 0 (black) to 100 (white), and a* and b* axes were the chromaticity coordinates (a* for green, +a* for red, b* for blue and +b* for yellow). Colour differences were calculated using equation 2:

$$\triangle E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (2)$$

where $\triangle L^*$, $\triangle a^*$ and $\triangle b^*$ = differences of L*a*b* components between dyed oriented bamboo bundle mat and initial values. The resulting $\triangle E^*$ values indicated the extent of the occurring change in colours (Park et al. 2008, Miklečić et al. 2012).

Modulus of rupture (MOR), modulus of elasticity (MOE) and shear strength (parallel loading) were compared for dye-treated and untreated composites samples, based on China standards (Anonymous 2003, 2006). Nine samples were prepared for each measurement of MOR, MOE and shear strength and the results were averaged. Samples were cut from the composites according to requirements of the standards. Thickness swelling and water absorption of samples were determined to 0.001-mm accuracy at marked positions before and after immersion in boiling water for 4 hours and drying in oven at 63 °C for 20 hours before being immersed again in boiling water for 4 hours.

RESULTS AND DISCUSSION

The bamboo anatomical structure is illustrated in Figures 2 and 3 for comparison. A great increase in colour was observed in the transverse and radial sections of the bamboo (Figure 2). Since parenchymatous cells were crushed during hot pressing, we paid more attention to the colour change on the cell wall of the vascular bundle of bamboo. Vascular bundle of bamboo in the transverse section was nearly completely red. The fibres had stronger red–brown colour than the parenchymatous cells of the bamboo (Figures 2a–c). Bamboo treated in ethanol was less red–brown than that treated in water. This result showed that the method of dyeing using ethanol could improve colour strength of bamboo.

Untreated raw bamboo culm sample had relatively smooth surface (Figure 3c). Basic dye accumulated on the surface of fibre cell as fine spherical particles (Figures 3a and b). Particle size was not larger than 1 μm (Figures 3b and d) while pit diameters in cells were approximately 3–10 μm (Figure 3d). These results indicated that there were favourable factors that caused the decrease of water-soluble basic dye particles from the bamboo pit into the cell walls.

Exhaustion rate and colour lightness of oriented bamboo bundle mat are illustrated in Figure 4. Increasing dyeing time resulted in increased exhaustion rate of samples dyed in ethanol at 75 °C and those dyed in water at 90 °C (Figure 4a). When surface tension of ethanol decreased, dye entered the interior of the bamboo easily. The increase in temperature, which had exacerbated the collision frequency among molecules was also helpful in improving exhaustion rate. The effects of dyeing on colour changes in oriented bamboo bundle mat samples are shown in Figure 4(b). Distinct colour changes were observed in samples after dye treatment. When bamboo was dyed in ethanol, its surface colour changed rapidly from light to dark, as indicated by the decreasing values of lightness (L*) during the first 2 hours, after which the rate of change slowed down.

The a* and b* values of oriented bamboo bundle mat are illustrated in Figure 5. The increasing a* value of samples indicated the tendency of red, while the decreasing b* value, the tendency to turn blue (Tenorio et al. 2012). Values for green and blue shifts were positive (Figure 5), which indicated that the colour of treated bamboo was becoming redder than the untreated bamboo. When samples were dyed in ethanol solution at 75 °C, a* and b* values changed more rapidly than samples in the other two treatments.

The colour difference and surface colour of bamboo-based fibre composites are shown in Figure 6. The value of $\triangle E^*$ increased with increased temperature and duration of treatment (Figure 6a). Values of $\triangle E$ * for samples dyed in ethanol were higher than samples treated in water. Colour change was greatest after treatment for 12 hours in ethanol. Samples treated in ethanol and water at 90 °C had more violent collision among molecules than samples treated in water at 20 °C (Guo et al. 2011). Decomposition of hemicelluloses and chemical changes of extractives are also accountable for changes in colour of bamboo (Martina et al. 2012, Nguyen et al. 2012). This is also observed in this study (Figure 6b).

Mechanical properties of bamboo-based fibre composites can be seen from Figure 7. Composite samples of bamboo dyed at 20 °C in water showed better performance in MOR compared with those dyed at 75 °C in ethanol and at 90 °C in water. MOE value decreased in samples dyed in ethanol at 75 °C. Loss in MOR corresponds to changes in cell wall components such as decomposition of hemicelluloses or demethoxylation of lignin during dyeing treatment (Qin & Yu 2009). This also explained why the MOE and MOR showed decreased values after heat treatment. Pair-wise comparison showed that there was no significant difference between water-dyed and untreated samples, which indicated that MOR and MOE values were not influenced by dye treatment. However, dye treatment with ethanol had more negative effects on mechanical strength of bamboo-based fibre composites than when using water.

Composite samples of bamboo dyed in water at 20 and 90 °C had better shear strength than those dyed in ethanol at 75 °C. However, untreated samples had the highest shear strength value but the difference was only significant for samples dyed in ethanol (Duncan test, $p > 0.05$), not in water.

Acidic condition at elevated temperature can degrade wood via hydrolysis and affect its

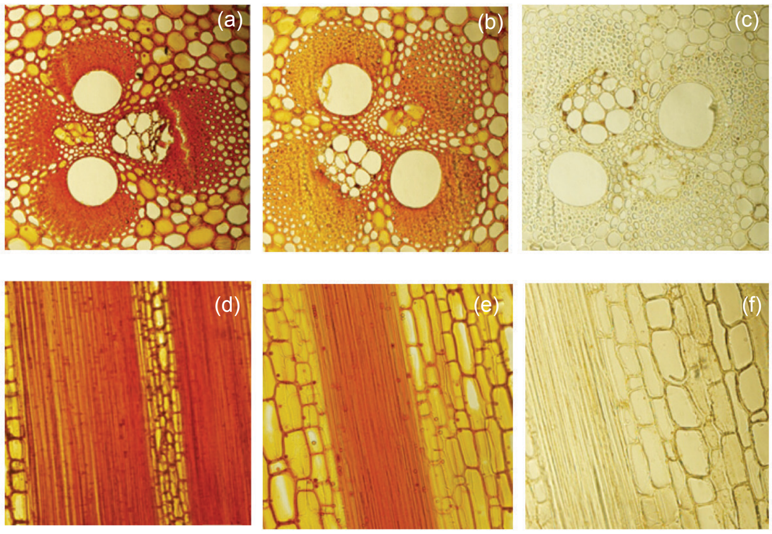

Figure 2 Light micrographs of bamboo anatomical structure: (a) raw bamboo culm dye-treated in ethanol, transverse section, (b) raw bamboo culm dye-treated in water, transverse section, (c) untreated raw bamboo culm, transverse section, (d) raw bamboo culm dye-treated in ethanol, radial section, (e) raw bamboo culm dye-treated in water, radial section and (f) untreated raw bamboo culm, radial section

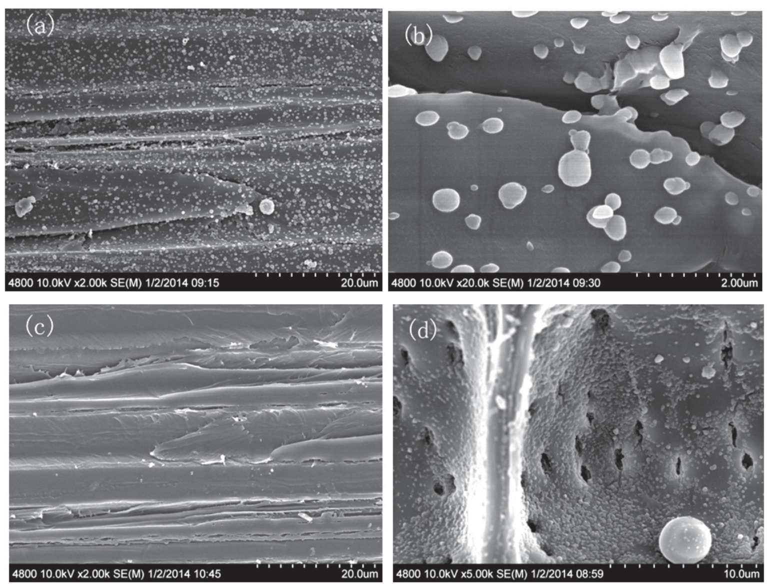

Figure 3 Scanning electron microscope images of raw bamboo culm in radial section untreated and after dye-treatment: (a) raw bamboo fibre after dye treatment, (b) dye particle attach to bamboo fibre cell, (c) raw bamboo fibre untreated and (d) distribution of dye particle around bamboo pit

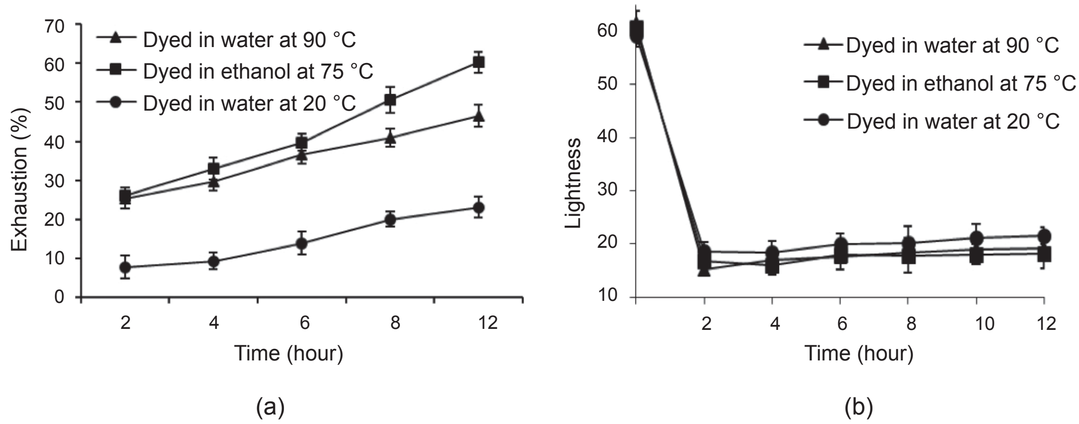

Figure 4 (a) Exhaustion rate of oriented bamboo bundle mat and (b) colour lightness of oriented bamboo bundle mat

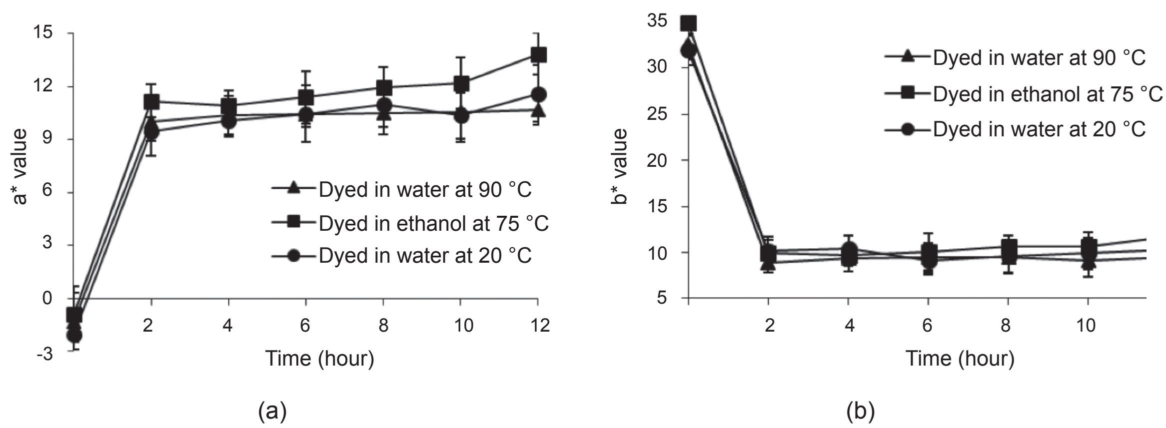

Figure 5 (a) a* (green) value of oriented bamboo bundle mat and (b) b* (blue) value of oriented bamboo bundle mat

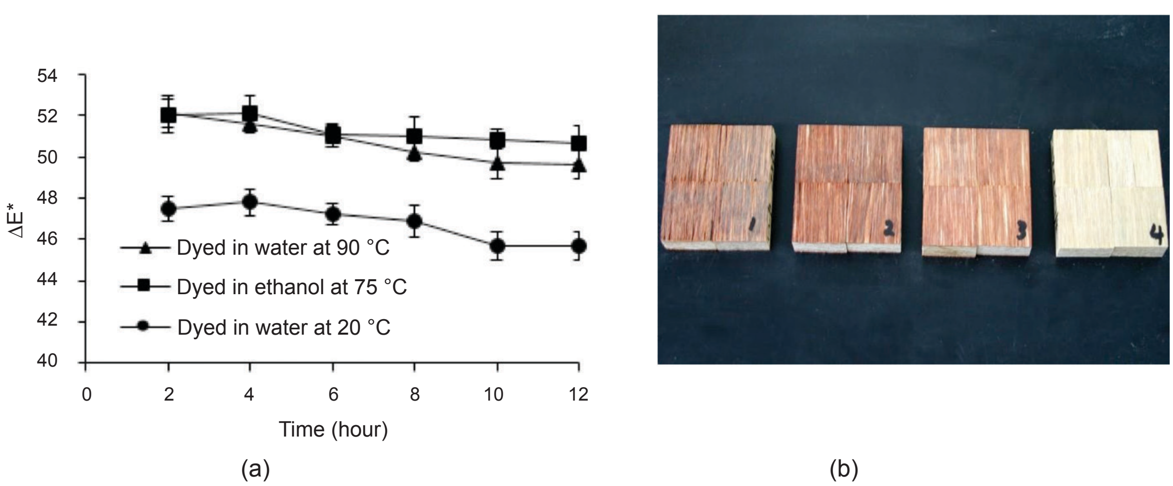

Figure 6 (a) Colour difference of bamboo-based fibre composites and (b) colour difference and surface colour of bamboo-based fibre composites: 1 = dyed in ethanol at 75 °C, 2 = dyed in water at 90 °C, 3 = dyed in water at 20 °C and 4 = untreated composites

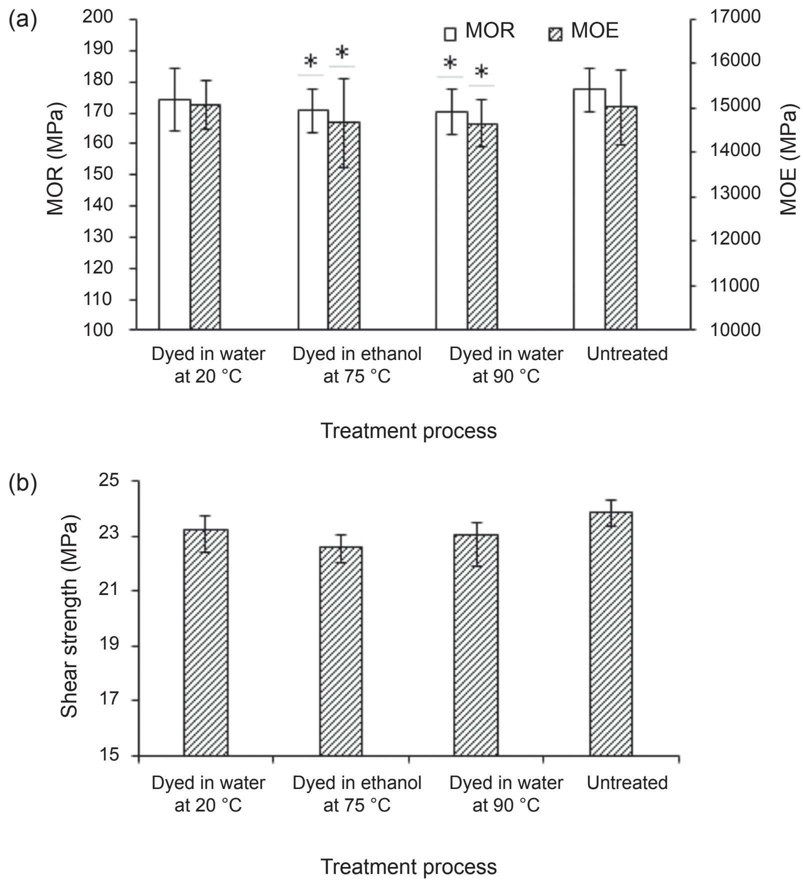

Figure 7 (a) Modulus of rupture (MOR) and modulus of elasticity (MOE) of bamboo-based fibre composites and (b) shear strength of bamboo-based fibre composites; * = different from untreated values at p = 0.05 according to the Duncan's test

properties (Tjeerdsma & Militz 2005, Mohebby et al. 2008). The pH value was lower during dyeing because of the use of acetic acid. Bamboo-based fibre composites were made using phenolic resin adhesive, which was alkaline. The increase in acidity influenced curing of adhesive. In addition, the increase in acid had adverse effect on adhesive curing and, thus, resulted in reduction in shear strength.

Thickness swelling of treated samples after 28 hours was higher than that of untreated samples (Figure 8). The same trend also occurred for thickness swelling measured after 4 hours in the oven. Thickness swelling of reconstituted bamboo lumber was 2.6% after being immersed in water for 24 hours (Ye et al. 1996), which was higher than control specimens in this study. Oriented bamboo bundle mat was effectively softened by dye treatment. This process improved permeation effect which effectively made gluing more effective during hot pressing for making fibre composites. The change in resin content of oriented bamboo bundle mat led to the differences in dimensional stability. This is shown in water absorption values of samples (Figure 8b). Dye-treated bamboo-based fibre composites samples demonstrated higher water absorption than untreated samples after 4 and 28 hours treatment.

CONCLUSIONS

We investigated the changes in board colour, water resistance as well as physical and mechanical properties in the dyed bamboo-based fibre composites from *P. pubescens*. Colour of oriented bamboo bundle mat turned into reddish brown during dyeing treatment. Dye treatment changed

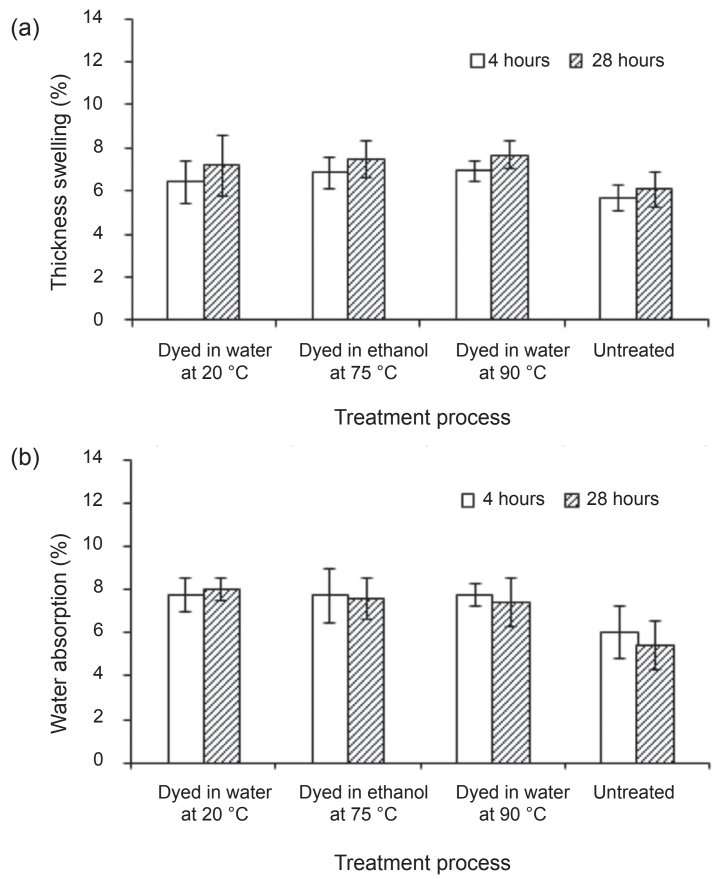

Figure 8 (a) Thickness swelling and (b) water absorption of bamboo-based fibre composites after 4 and 28 hours

the colour of oriented bamboo bundle mat from cream to light red brown with decreased value of colour lightness. The total colour change of samples dyed in ethanol at 75 °C was higher than samples dyed in water at 20 and 90 °C. In ethanol, colour change was greatest after treatment for 12 hours. MOR, MOE and shear strength values of untreated bamboo-based fibre composites samples were higher than treated samples. Dyed samples demonstrated lower dimensional stability than untreated samples. Dyeing in ethanol had more negative effects on mechanical strength of bamboo-based fibre composites than using water, which showed higher sensitivity of the composites towards treatment involving ethanol. Strength properties decreased with dye treatment. In summary, dyed bamboo-based fibre composites was successfully produced in this study. Composites had good physical, mechanical and colour properties. This product will increase the diversity of bamboo and its market potential.

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