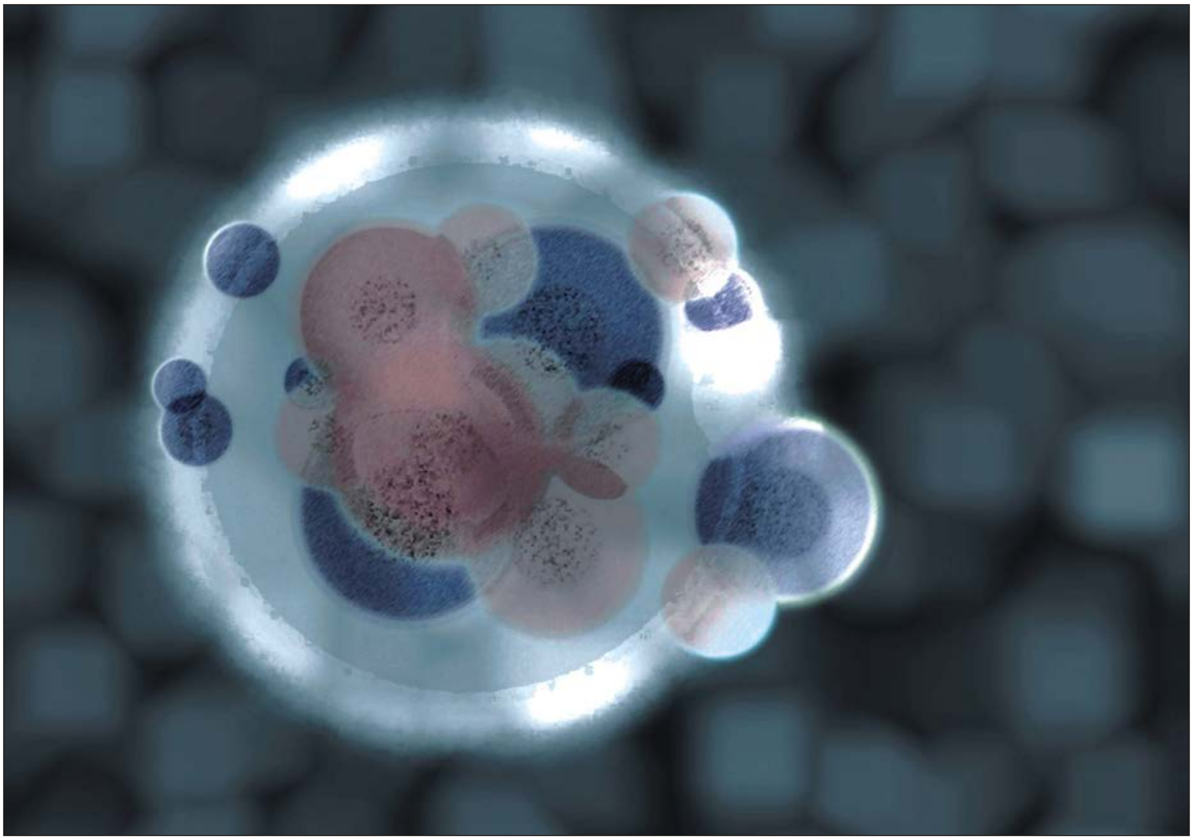

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Effects of Peroxide and Oxalic Acid Bleaching on the Colour and Gluing Properties of Some Tropical Bamboos

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Abstract: The effects of bleaching on the colour and gluing properties of *Gigantochloa scortechinii, Dendrocalamus asper* and *Bambusa vulgaris* bamboos were studied. The bamboo strips were bleached with sodium hydroxide (NaOH, 1% w/v) followed by hydrogen peroxide (H_2O_2, 12.5% w/v) and in a mixture of oxalic acid ($(COOH)_2$. $2H_20$, 1% w/v) and NaOH (0.5%, w/v). The bleaching was carried out by cold soaking. The colour changes (ΔE) and whitish value (W) of the strips before and after bleaching process were examined using colour meter and Munsel soil colour chart. The unbleached and bleached strips were glued parallel to each other using phenol formaldehyde adhesive to produce three-ply laminates. The gluing properties were evaluated based on their shear strength and wood failure percentage. The tests were carried out in dry and cyclic boiling conditions (CBR) in accordance with BS 6566: Part 8: 1986. Regardless of species, strips that were soaked in NaOH followed by in H_2O_2 solution had better colour properties than soaking in NaOH + ($(COOH)_2$. $2H_2O$). *B. vulgaris* had the highest ΔE (10.8 – 24.5%) whilst the *G. scortechinii* had the highest W (64.6– 67.3%) when bleached with these two processes. Bleaching with oxalic acid did not increase the W of *D. asper* even though the ΔE was 19.98%. The bleaching agents to some extent, reduced the gluing properties of the laminates. The unbleached *G. scortechinii* had dry shear strength of 4.60 Nmm^{-2} and CBR shear strength of 3.47 Nmm^{-2} whilst *D. asper* had 4.40 and 2.11 Nmm^{-2}, respectively. Nonetheless, the glue bond quality of the bamboo laminates still meets the minimum standard requirement.

Key words: Bamboo, bleaching, gluing, laminate, shear strength

INTRODUCTION

Bamboo is well known for its versatile use and has been getting attention as a substitution material for wood. Owing to some of the advantages like fast growing, environmental friendly plants, unique appearance and tough, this material can be converted into engineered products such as composites, laminated boards and plywood. Due to the nature of the plants, the utilization of bamboo culm can only be done through lamination. These laminated products have been commercialised in China and Japan. In Malaysia bamboo is still being intensively used in the cottage industry like poultry cage, vegetable basket, incense stick and joss paper, skewer and chopstick and handicraft.

Gigantochloa scortechinii, the most common bamboo found in Malaysia has a potential in the production of plywood[1]. The product had superior glue bond quality and higher strength properties than commercial plywood from merawan (*Hopea* spp.). However, the aesthetic value of laminated bamboo products is still low due to colour variation of the raw materials. The natural colour of bamboo strips vary from culm to culm and from species to species and to some extend may vary between internode and node portions in a single culm. Hence, to achieve a certain degree of homogeneity in colour, bamboo strips have to be bleached before they can be glued into laminates. Selection of correct bleaching agents and processes is very crucial in order to increase the aesthetic value of the laminated bamboo products while maintaining the glue bond quality and strength properties

Bleaching of bamboo strips or sliver with sodium hypochlorite, hydrogen peroxide and oxalic acid using either cold or hot soaking, boiling and steaming processes have been reported by Zaidon *et al.*[2], Ganapathy *et al.*[3]. Zaidon *et al.*[2] found that boiling in 6% w/v H_2O_2 for 30 min or soaking in 2% (w/v) NaOCl for 16 hrs was an effective bleaching system for some Malaysian bamboos, but the surface of the bamboo strips deteriorated quite significantly.

Most of the bleaching agents available in the market such as peroxides and oxalic acid are sold as two parts[4]. The component normally to be used with is sodium

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hydroxide. This combination will normally produce a strong oxidising reaction which is most effective in removing the natural colour in wood.

This paper reports the colour and glue bond properties of three tropical bamboo strips after bleaching with either peroxide or oxalic acid bleaches.

MATERIALS AND METHODS

This experiment was conducted in November 2002 to August 2003 at Faculty of Forestry, University Putra, Malaysia. When and where experiment was conducted mention here time period and year. Three common bamboo species found in Malaysia were selected in this study. They were *Dendrocalamus asper* (Buluh betong), *Gigantochloa scortechinii* (Buluh semantan) and *Bambusa vulgaris* (Buluh gading). They were extracted from Hulu Langat Forest Reserve, Selangor. The bamboo culms were cut just above the ground level up to 6 m long and were transported to the laboratory for further processing. The culms were further cut into 1 m long using radial arm saw before splitting into strips of 20 mm width, using sizing and splitting machine. The epidermis of the splits were removed by planning using a single face-planning machine and finally dressed into strips of dimensions 420 mm (length) x 20 mm (width) x 4 mm (thickness).

Colour evaluation of the surface of the strips was carried out before and after bleaching and calculated using a fixed colour system L*, a* and b*, in which the indices were measured using colour meter[5]. Evaluation was made based on the colour changes value (ΔE) and the whitish value (W) of the bamboo strips. The higher the ΔE, the more the changes of colour in the treated strips and the higher the W, the whiter the colour of the strips.

The colour changes (ΔE) and whitish value (W) of the bamboo strips can be calculated using following equations:

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

$$W = 100 - [(100- L^*)^2 + a^{*2} + b^{*2}]^{1/2}$$

L* = Fairest value (The higher the value it become more white)

a* = Chromaticness index (The higher the value it become more red)

b* = Chromaticness index (The higher the value it become more yellow)

ΔE = Colour changes value

W = Whitish value

Munsel Soil Colour Chart was used to determine the colour of the unbleached and bleached strips.

Bleaching process: Bleaching agents used were hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH) and oxalic acid ($(COOH)_2 . 2H_2O$). They were diluted with water. The bleaching was carried out by cold soaking the strips into I) 1% (w/v) NaOH for 3 h followed by soaking in 12.5% (w/v) H_2O_2 for 8 h and ii) mixture of 1% (w/v) oxalic acid and 0.5% NaOH (w/v) for 16 h[3]. After bleaching, the bamboo strips were washed with distilled water and left to dry in the laboratory. The pH of these solutions was determined using a pH meter.

Gluing of bamboo strips: Gluing study was carried out on 150 mm long x 20 mm wide x 4 mm thick strips. Phenol formaldehyde (PF) adhesive used to bond the strips. The adhesive formulations were slightly modified from the original formulation which was specifically made for plywood[1,6]. Preliminary study showed that bleaching process were slightly increased the wettability of the bamboo strips. Hence, a modified adhesive formulation with acceptable high viscosity to control over penetration of adhesive into the strips have been used. Table 1 shows the properties of modified adhesive formulations used in this study. Three layers bamboo strips were glued parallel to the grain. The bonding properties were examined each for unbleached and bleached laminates for each species.

Table 1: Phenol formaldehyde adhesive formulation for bonding bamboo strips

Material	Measurement (Weight/parts)
Phenol formaldehyde resin	70.4% (100 parts)
Industrial wheat flour	8.5% (12 parts)
Calcium carbonate ($CaCo_3$)	17.6% (25 parts)
Water	3.5% (5 parts)
Total	100% (142 parts)
Viscosity	20 poise

Source: Zaidon[1], Anonymous[6]

The glue spread was 230 g m^{-2} for a single glue line. The assemblies were cold pressed at 10 kg cm^{-2} for 5 min and hot pressed at 140°C for 7 min and with a specific pressure of 14 kg cm^{-2}. The laminates were then conditioned at 20°C and 65% (EMC = 12%). A shear test was conducted on 20x150x12 mm sheared area in accordance with BS 6566: Part 8[7]. The tests include dry condition (DT) test and cyclic boiling resistance (CBR). For CBR test, specimens were first submerged in boiling water for 4 h±5 m. They were then dried in a ventilated at 60±3°C for 20 h. Subsequently, the dried specimens were again submerged in boiling water for another for 4 h±15 m. Finally the specimens were cooled in water kept at 15±5°C for 3 days prior to testing. Ten specimens from each laminate group were tested either in dry or wet conditions. Upon completion of the test, the specimens were examined for the estimated percentage of wood failure along the glue line. The wood failure of individual specimens was recorded to an accuracy of 10% and the average shear strength and wood failure were compared with the standard requirement.

An analysis of variance (ANOVA) was used to detect any shear strength changes between the bleached laminated bamboos compared to the unbleached laminated bamboos . The means were separated using least square difference (LSD).

RESULTS AND DISCUSSION

Colour properties of bamboo strips after bleaching: The mean colour changes and whitish values of three species of bamboo strips after undergone bleaching are shown in Table 2. The pH of each bleaching solution is also presented in the table. Higher ΔE was obtained on strips bleached with hydrogen peroxide than strips bleached with oxalic acid. Among the three species, regardless of bleaching systems, *B. vulgaris* strips had the highest ΔE, i.e., 24.48% for H_2O_2-bleached strips and 10.77% for $((COOH)_2.H_2O)$-bleached strips. For *G. scortechinii* and *D. asper*, the ΔE value after bleaching with hydrogen peroxide were similar (19.75–19.98%), however, *D. asper* had significant lower ΔE value (2.68%) than *G. scortechinii* (4.29%) when bleached with oxalic acid.

Hydrogen peroxide bleaching system also increased the brightness of the bamboo strips more than oxalic acid as reflected by the increment of whitish values (W) after bleaching. The W of *G. scortechinii* strips increased from 61.7% before bleaching to 67.3% after bleaching with hydrogen peroxide. For *D. asper*, the W was increased from 61.2 to 64.9% and *B. vulgaris* from 59.7 to 64.6%. When determined using Munsel Soil chart, all the H_2O_2-bleached strips changed into pale yellow colour (Table 2). These results are in good agreement with those found by Zaidon *et al.*[2] in the previous study. The authors also found that the strips can be changed into white colour only if they were boiled in hydrogen peroxide solution for at least 30 m.

When bleached using oxalic acid only the whitish values of *G. scortechinii* (from 61.7 to 64.6%) and *B. vulgaris* (59.7 to 62.6%) increased whilst the W for *D. asper* decreased (from 61.2 to 59.8%). The decrement of W for *D. asper* implied that the bleaching agent had somehow reduced the brightness of the strips. Munsel soil chart showed that the original colour of this bamboo changed from Light brownish grey to light yellow brown.

The above results showed that hydrogen peroxide bleaching system had better oxidizing properties than oxalic acid in removing the natural colour of the bamboo strips. This is shown by the pH values of the bleaches which were 4.73 for hydrogen peroxide solution and 6.06 for oxalic acid solution. Among the three bamboo species, *G. scortechinii* was the easiest bamboo to be bleached by these two systems followed by *B. vulgaris* and *D. asper*. The degree of difficulty in bleaching the strips was probably due to the degree of lignin and other coloured materials such as tannin contents in the bamboos.

Effect of bleaching on glue bond quality of bamboo strips: Shear strength and wood failure percentage values of a laminate would indicate the glue bond quality of bonded product. Theoretically, when both the shear strength and wood failure percentage are high, a good bonding has occurred. If one of them is high and the other is low, it indicates that either the bamboo strips is of low strength or the adhesive bond is poor.

Shear strength and wood failure percentage results of bleached and unbleached laminated bamboos are summarised in Table 3. Means followed by the same letter are not significantly different ($p<0.05$) using least significant difference (LSD) test. In this study only *G. scortechinii* and *D. asper* strips were evaluated. They were chosen based on the best and worst effect of colour properties given by the bleaching systems. As a whole, both bleaching systems significantly reduced the shear strength of the bamboo laminates when tested either in dry or wet conditions. Regardless of bleaching systems, *G. scortechinii* laminates had superior glue bond quality than *D. asper*. The unbleached *G. scortechinii* had dry shear strength of 4.60 Nmm^{-2} and CBR shear strength of 3.47 Nmm^{-2} as compared to 4.40 and 2.11 Nmm^{-2}, respectively for *D. asper*. However, the dry and CBR wood failure percentages for both species were 100%.

Between the bleaching systems, the peroxide-bleached laminates had lower dry and wet shear strength than oxalic acid-bleached laminates, but the difference was not significant. The dry and wet shear values for the former were respectively 4.04 and 2.01 for *G. scortechinii* and 3.50 and 1.81 Nmm^{-2} for *D. asper*, whilst for the latter, the values were 3.83 and 1.77 Nmm^{-2} and 1.58 to 3.03 Nmm^{-2}. The results of wood failure percentage shows that majority of the hydrogen peroxide-bleached strips failed 100% in the wood but oxalic acid-bleached strips failed 88 to 95% in the wood for *G. scortechinii* and 73 to 87% for *D. asper*.

The higher wood failure percentage and lower shear values found in the bleached laminates when compared to the unbleached laminates implied that the bleaching system to some extent had significantly reduced the strength properties of the bamboo. The solutions used may have oxidised some polysaccharides and lignins subsequent responsible for the depolymerisation of the

Table 2: Mean colour changes (ΔE, %) and whitish values (W) of bamboo strips before and after bleaching with peroxide and oxalic acid bleaches

	Unbleached		NaOH followed by H_2O_2, pH (4.73)		Mixture of NaOH and Oxalic acid, pH (6.06)	
Species	ΔE, %	W,%	ΔE, %	W,%	ΔE, %	W,%
G. scortechinii	-	61.7	19.75	67.3	4.29	64.6
		(2.72)	(2.49)	(1.98)	(1.32)	(1.25)
	Pale yellow light grey		Pale yellow		Yellow light brown	
D. asper	-	61.2	19.98	64.9	2.68	59.8
		(1.82)	(2.79)	(1.90)	(0.75)	(1.38)
	Light brownish grey		Pale yellow		Light yellow brown	
B. vulgaris	-	59.7	24.48	64.6	10.77	62.6
		(1.06)	(7.02)	(2.66)	(7.17)	(1.50)
	Light yellowish brown Pale yellow		Yellow light grey			

No. of samples, 10. Colour of the strips was determined using Munsel Soil Chart

Table 3: Mean shear strength and wood failure percentage of bleached and unbleached laminated bamboo strips as compared to British Standard (Anonymous, 1986)

	Average shear strength, τ (N mm^{-2})		Average wood failure, %	
Treatments	DT	CBR	DT	CBR
G. scortechinii				
Unbleached	4.60^{a}	3.47^{a}	100	100
	(1.10)	(0.29)		
Peroxide-bleached laminates	4.04^{b}	2.01^{b}	100	100
	(0.73)	(0.52)		
Oxalic acid-bleached laminates	3.83^{b}	1.77^{b}	88	95
	(1.05)	(0.42)		
D. asper				
Unbleached	4.40^{a}	2.11^{a}	100	100
	(0.99)	(0.43)		
H_2O_2–bleached strips	3.50^{b}	1.81^{ab}	88	100
	(0.55)	(0.47)		
$(COOH)_2.H_2O$-bleached strips	3.03^{b}	1.58^{b}	73	87
	(0.72)	(0.55)		
BS Standard	$0.35 < \tau < 0.7$		> 75	
	$0.70 < \tau < 1.7$		> 50	
	$1.70 < \tau < 2.5$		> 25	
	$2.50 < \tau$		> 15	

Note: [1]Means with different letters across rows differ significantly at $P < 0.05$ using LSD and values in parentheses are Standard Deviation

cellulose chains. The higher reduction of shear strength for oxalic acid-bleached laminates compared to those peroxide-bleached laminates could probably due to the extend of soaking period. Even though, the ($(COOH)_2$. H_2O) solution was less acidic (pH 6.06) than H_2O_2 solution (pH 6.06) (Table 2), but the soaking period in the former was 100% longer than in the latter, i.e., 16 h in the oxalic acid as compared to 8 h in hydrogen peroxide. An investigation on the effect of these bleaching systems on strength and chemical properties of bamboo are currently being conducted.

Even though the bleaching systems significantly reduced the shear strength of the bamboo laminates, the glue bond quality still meets the minimum standard requirement (Table 3). This shows that bamboo materials which had been bleached with peroxide and oxalic acid can be manufactured into both interior and exterior grade laminated products.

The study shows that the colour properties *D. asper, G. scortechinii* and *B. vulgaris* strips are affected by the bleaching systems used. Peroxide solution changed the colour of the strips more than oxalic acid solution. *B. vulgaris* had the highest colour changes value compared to the other species when bleached with these two systems. As regards brightness, *G. scortechinii* had the highest whitish value followed by *B. vulgaris* and *D. asper* when bleached with either peroxide or oxalic acid bleaches. Bleaching with oxalic acid did not increase the whitish value of *D. asper* even though there was a change in colour changes value. All strips changed into pale yellow colour when bleached with hydrogen peroxide. However, with oxalic acid, *G. scortechinii* changed into yellow light brown, *D. asper* into light yellow brown and *B. vulgaris* changed into yellow light grey.

Both H_2O_2 and ($(COOH)_2$. $2H_20$) solutions reduced the shear strength of the bamboo laminates when tested either in dry or wet conditions. Between the two species, regardless of bleaching processes, *G. scortechinii* had superior glue bond quality than *D. asper*. Between the bleaching systems, the shear strength for oxalic acid-bleached laminates was lower than hydrogen peroxide-bleached laminates, however, the difference was not significant. The higher wood failure percentage and lower shear values found in the bleached laminates when compared to those unbleached laminates implied that the treatments, to some extent had significantly reduced the strength properties of the bamboo. However, the glue bond quality met the minimum standard requirement for plywood.

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