Shear Strength and Microscopic Characterization of a Bamboo Bonding Interface with Phenol Formaldehyde Resins Modified with Larch Thanaka and Urea

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The aim of this study was to understand the microscopic characteristics of the bamboo bonding interface with phenol formaldehyde resin modified with larch thanaka and urea (PTUF) and its effect on the shear strength of two-ply bamboo laminated lumber. Bleached and carbonized bamboo strips were used, and two assembly patterns (outer-to-outer and inner-to-inner) were adopted to make two-ply bamboo laminated lumber with PTUF. The microstructure of the bonding interface and the bond-line thickness were investigated using a scanning electron microscope. The average depth and effective depth of PTUF on bamboo surfaces were evaluated by fluorescent microscopy characterization. The shear strength of two-ply bamboo laminated lumber was also examined. The results revealed a shallow depth of penetration of PTUF into the bamboo surface that was distributed primarily in the broken cell cavities formed during preparation, as well as between the cell walls. When the assembly pattern was inner-to-inner, the depth of penetration and bond-line thickness were higher, but the shear strength was lower than that of the outer-to-outer pattern. The carbonized bamboo laminated lumber provided a greater resin penetration and bond-line thickness, but lower shear strength, than the bleached bamboo laminated lumber.

Keywords: Phenol formaldehyde resin; Modification; Larch thanaka; Urea; Bamboo; Bonding interface; Scanning electron microscope; Fluorescent microscopy characterization; Shear strength

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INTRODUCTION

Bamboo laminated lumber is a newly engineered structural material that is primarily used in buildings, vehicles, ships, furniture, *etc.* Phenol formaldehyde (PF) has excellent shear strength and weatherability and is widely used in the bamboo industry. Many studies have investigated the use of modified PF resins because phenol is expensive and non-renewable. The common methods of PF resin modification include dosing with low-molecular weight PF, tannin, lignin, and urea (Tao *et al.* 2005; Li and Tang 2006; Tabarsa *et al.* 2011; Yong *et al.* 2014). Studies have shown that PF resins modified with tannin provide satisfactory results and are of a comparatively low cost. However, this kind of adhesive is rarely used in the bamboo industry. The current research on modified adhesives primarily focuses on how to improve curing speed and further lower the cost (Yu 2001). There have been a few studies on resin penetration into the bamboo surface, showing that the bond-line thickness and bond-line strength formed by adhesive penetration have a great influence on the microstructure, strain, and shear strength of bamboo composite materials (Guan *et al.* 2013, 2014). In addition, over penetration may lead to a weak bond, while a lack of penetration may lead to difficulties in meeting the requirements of chemical cementation and mechanical self-locking (Kamke and Johnson 1992). Thus, it is important to characterize the interaction between adhesives and the bamboo surface.

The primary aim of this study was to manufacture two-ply bleached and carbonized bamboo laminated lumber coated by PF resins modified with larch thanaka (*i.e.* larch bark powder, consisting rich tannin, an inexpensive material available locally in northern China) and urea using two assembly patterns (outer-to-outer and inner-to-inner). The term "carbonized" has come into common use when referring to hot aqueous treatments sufficient to darken the appearance of bamboo. The secondary aim of the study was to provide base data for further improvement and application of PTUF in the bamboo industry. The morphology of the adhesive bond-line on the bamboo surface was investigated using a scanning electron microscope (SEM), and the bond-line thickness was accordingly calculated. The average depth and effective depth of PTUF on the bamboo surface were evaluated using fluorescent microscopy characterization. The shear strength was also tested.

EXPERIMENTAL

Alkaline Phenolate Modification of Larch Thanaka

A reactor equipped with a mechanical stirrer (S312 Constant Speed Stirrer, Shanghai SENCO Technology Co., Ltd, China), a four-mouth flask, a reflux condenser, and a thermometer (GG17, Sichuan Shubo (Group) Co., Ltd, China) was assembled. The mass ratio of phenol to larch thanaka was 7:3, while water, sodium hydroxide (40% NaOH), sodium sulfite (Na_2SO_3), and calcium sulfite ($CaSO_3$) were added as activator agents at 48%, 34.25%, 2.13%, and 1.60% of the total mass of phenol and larch thanaka, respectively. Phenol, larch thanaka (red-brown powder), and these activator agents were put into the four-mouth flask and stirred well. The mixture was heated to 95 to 98 °C progressively for 2.5 h. An additional 25% water was then added and allowed to react for 10 to 20 min, and the temperature was decreased to 40 °C to complete the alkaline phenolate modification of larch thanaka (PT).

Synthesis of Phenol Formaldehyde Resins Modified with Larch Thanaka and Urea

The mass ratio of urea to PT was 1:2.5. In the first stage, PT, 83.3% formaldehyde (36% concentration) and 8.9% urea (92% concentration) were put into a four-mouth flask, stirred well, and heated to 88 to 90 °C for 40 min. In the second stage, the temperature of the reaction mixture was lowered to 83 °C; then, 83.3% formaldehyde (36% concentration) and 8.9% urea (92% concentration) were added to the solution. The temperature was controlled between 85 and 90 °C, and 6.7% NaOH solution (40% concentration) was added slowly after 30 min, then left to react for 70 min. In the third stage, the temperature was increased to 84 °C, and 35.6% formaldehyde (36% concentration) and 8.9% urea (92% concentration) were added again, followed by the addition of 6.7% NaOH (40% concentration) after 20 min. The temperature was raised to 85 to 90 °C, and the mixture was allowed to react until the measured value of Tu-4 cup viscosity was between 40 and 60 s. In the fourth stage, 16.7% urea (92% concentration) and 14.7% NaOH (40% concentration) were added, and the mixture was allowed to react for 15 to 20 min at a temperature of 80 to 85 °C, producing the phenol formaldehyde resin modified with larch thanaka and urea (PTUF). The basic properties of PTUF are shown in Table 1.

Table 1. Basic Properties of PTUF

Viscosity (25 °C, mPa·s)	pH	Solids Content (%)
195	12.1	42.25

Sample Preparation of Two-Ply Bamboo Laminated Lumber

Bleached and carbonized moso bamboo (*Phyllostachys pubescens*) strips (4 years old) were obtained from the Zhejiang Bamboo Factory, China. PTUF was used to glue two-ply bamboo panels parallel to each other, with each ply measuring 5 mm × 20 mm × 150 mm. Two assembly patterns were considered (outer-to-outer and inner-to-inner), as shown in Fig. 1. The specimens were all cured for 14 min in a Platen Vulcanizing Press (QLB-D 400×400×2, Shanghai First Rubber Machinery Works, China) at 1.2 MPa and an ambient temperature of 140 °C; the adhesive consumption was 140 g/m^2. After the curing process, the specimens were maintained in a constant temperature and constant humidity box (GDJS-100, Zhongya Test Equipment Co.,Ltd, China) at 65% RH and 20 °C until a constant weight was attained.

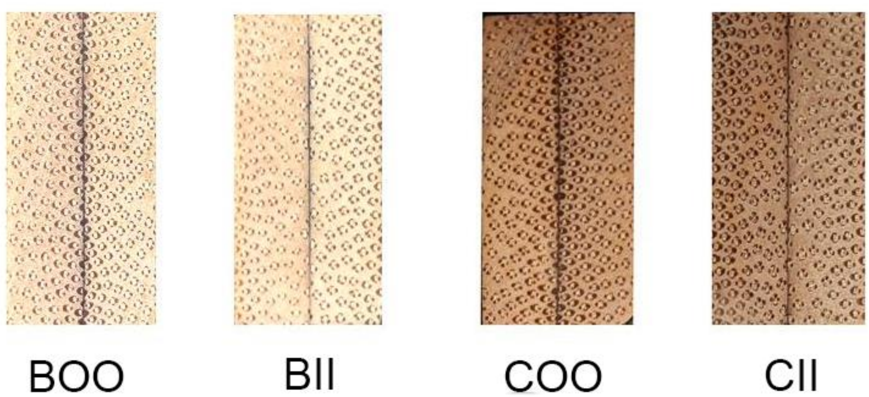

Fig. 1. Assembly patterns: (BOO) bleached bamboo, outer-to-outer; (BII) bleached bamboo, inner-to-inner; (COO) carbonized bamboo, outer-to-outer; (CII) carbonized bamboo, inner-to-inner

Sample Sections and Scanning Electron Microscope Observation

A cross section with 20 μm × 5 mm × 5 mm was created from each sample with an ultramicrotome (TU-213, Yamato Kohki Industrial Co., Ltd, Japan), equipped with a sapphire knife, at room temperature after the specimens had been softened by 2-week soaking in water at room temperature. The cross sections were then dehydrated with graded ethanol (30%, 50%, 75%, 95%, and 100%). After desiccation, fixing, and gold spraying (E-1010, Hitachi Ion Sputter Jeol, Japan), the cross sections were observed under an SEM (Quanta 200, FEI, USA) at 20 kV to evaluate the morphology of the adhesive bond-line in the bamboo matrix. The images were recorded digitally, and the bond-line thickness was studied and analyzed with ImageJ software (1.42q, National Institutes of Health, USA).

Sample Sections and Fluorescent Microscopic Observation

Cross sections were made with the same experimental method used for SEM imaging. After the mixture was dehydrated with graded ethanol, 0.5% of the fluorescent dye toluidine blue-O was added, dropwise, over 30 min. Each sample was then washed twice with distilled water, and glycerin blended with ethanol was added. The mixture was covered, and fluorescent microscopic observations were made (BX51, Olympus Corporation, Japan). The 50 images taken were recorded digitally, and the penetration into the bamboo surface, by measuring parameters such as depth and color, was studied and analyzed using ImageJ software.

Shear Strength Testing

Shear strength was measured to determine the bonding strength of the PTUF on the bamboo surface (CMT4304, MTS Systems (China) Co., Ltd, China). Specimens were manufactured experimentally in accordance with DIN EN 302-1 (CEN, 2004), with a total length of 150 mm, a width of 20 mm, and a thickness of 10 mm. Making shear strength test rabbet of 2.5 mm width in the bonded sections across the grain so that an overlap of width 10 mm was defined in the middle section centered in the groove in test pieces on thick glue lines.

RESULTS AND DISCUSSION

Microstructure of the Bonding Interface

Figure 2 shows the presence of an intact bonding interface in the cross sections of the four kinds of bamboo laminated lumber. The bond-line thickness was relatively small. As the coarse arrow shows, it was difficult for the adhesive to penetrate into the bamboo block, instead distributing in the broken cell cavities formed during sample preparation, as well as between the cell walls on the surface. As there is no transverse tissue in bamboo (Yong *et al*. 2014), the only permeability channel along the radial direction is the pit of the cell wall. It was difficult for high-molecular weight PTUF to penetrate adjacent cells through cell wall pits, so PTUF was mainly distributed in the bond-line. Cells near the adhesive interface were deformed and even crushed under heat and pressure, while cells far away from the adhesive interface maintained their basic forms, as the thin arrow shows in Fig. 2.

Figure 3 shows the morphology of the bonding interface between the parenchyma cells, demonstrating a clear boundary between the matrix and the adhesive in the bleached bamboo laminated lumber. The adhesive interface was flat and smooth; although the parenchyma cells near the interface deformed under heat and pressure, the cell walls maintained their basic morphology. However, in the carbonized laminated lumber, the boundary between the bamboo surfaces and the adhesive was indistinct. In this case, the deformation of the parenchyma cells near the interface was more severe than that of the bleached bamboo laminated lumber, to such an extent that some of the cells were even crushed. This effect occurred because the major components of the cell walls were degraded during carbonization; the densities and relative amounts of cellulose and hemicellulose decreased under high temperature. In addition, hyperthermia caused surface hardening and matrix brittleness. The surface cells of carbonized bamboo strips are crushed more easily than those of bleached bamboo strips (Shao *et al.* 2003).

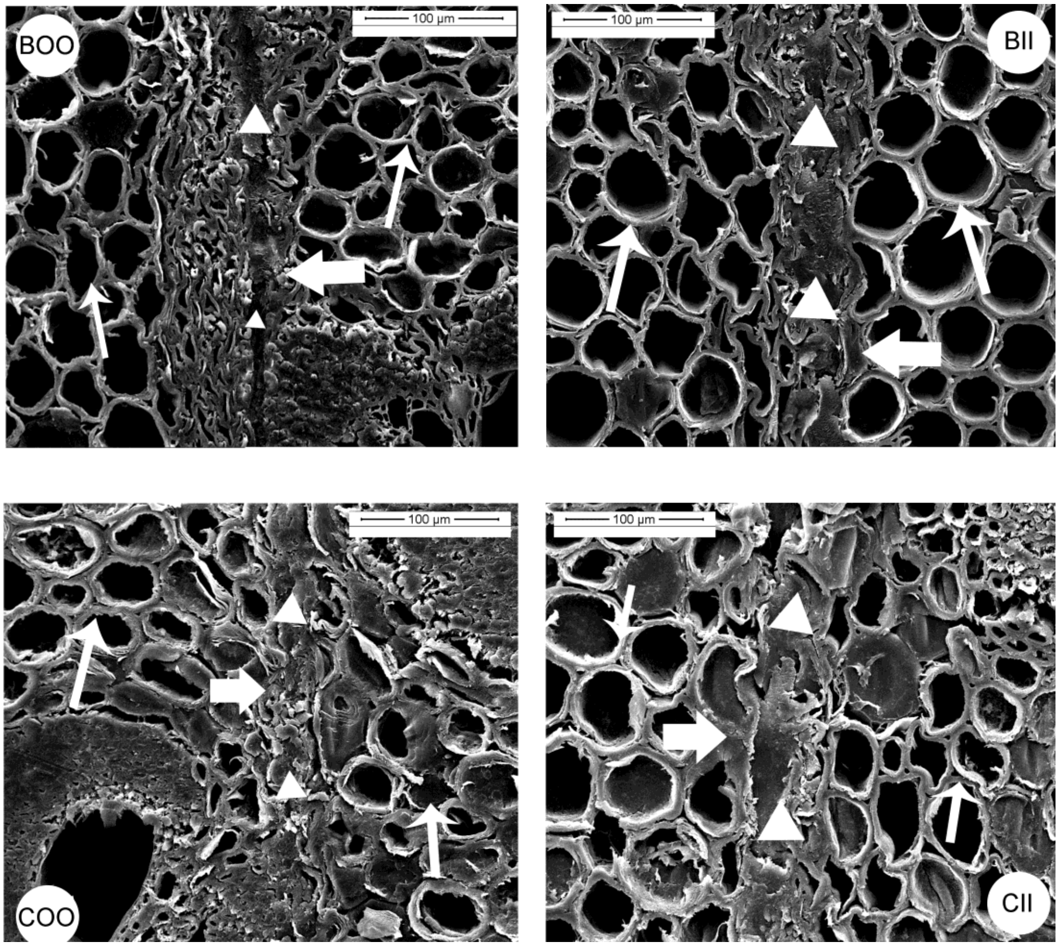

Fig. 2. SEM images of the bonding interface of the four kinds of bamboo laminated lumber. The triangles, coarse arrows, and thin arrows indicate the pure PF bond-line, the adhesive between cell walls, and the parenchyma cells without adhesive, respectively.

Figure 4 shows the bond-line thickness of the four kinds of bamboo laminated lumber, indicating that, when the same materials are used, the average bond-line thickness of the inner-to-inner glued bamboo laminated lumber was greater than that of the outer-to-outer glued lumber, with the average thickness increment from 1.2 μm (BOO to BII) to 1.4 μm (COO to CII). The fiber close to the outer surface was treated more intensively than the fiber close to the inner surface, resulting in increased density (Yu *et al.* 2006). Therefore, the outer surface of the bamboo became harder than the inner surface, producing more severe interfacial squeezing under heat and pressure when the outer-to-outer assembly pattern was used. When the assembly patterns were the same, the average bond-line thickness of the carbonized bamboo laminated lumber was greater than that of the bleached bamboo laminated lumber, with the average thickness increment from 2.5 μm (BOO to COO) to 2.7 μm (BII to CII). The density of the bamboo strips decreased during carbonization, resulting in less interfacial squeezing than in the bleached bamboo strips. However, from the microscopic images, it can be seen that the crushed parenchyma cells near the interface of the carbonized bamboo surface led to greater penetration of the adhesive. Therefore, the bond-line thickness of the carbonized bamboo laminated lumber was greater than that of the bleached bamboo.

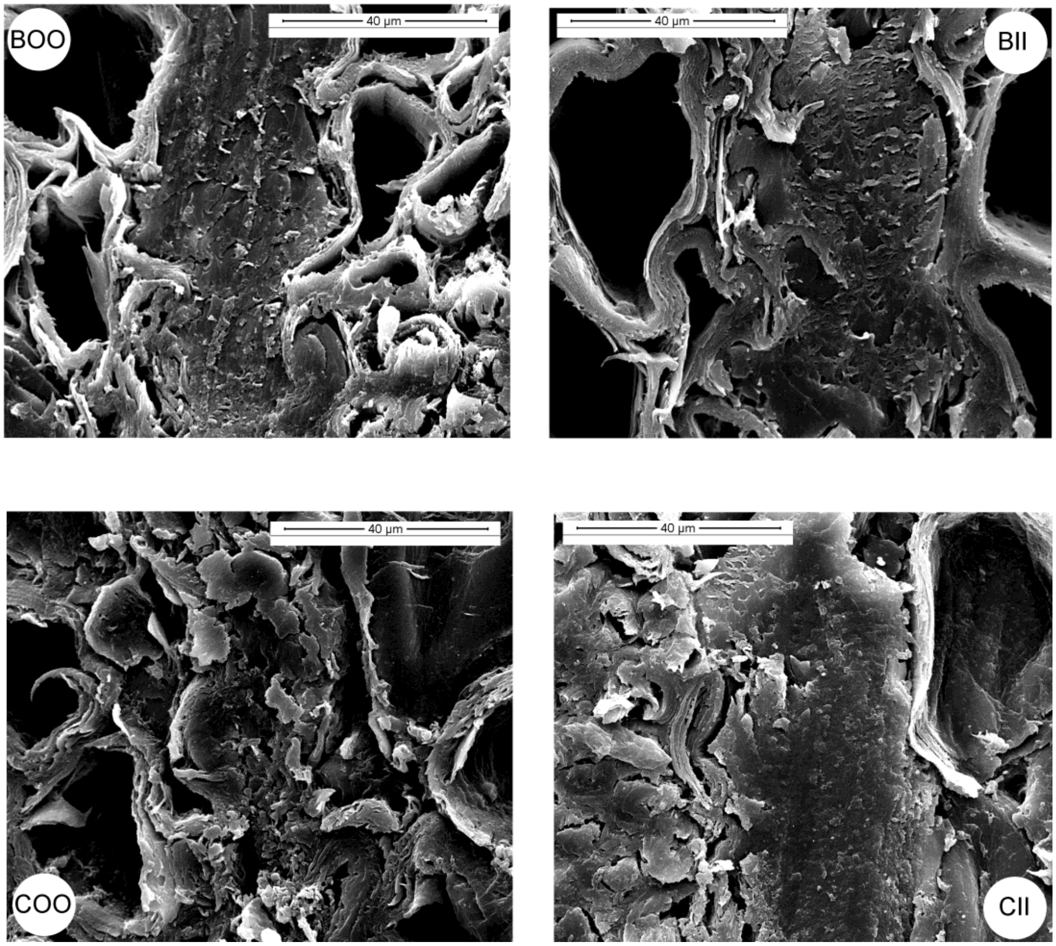

Fig. 3. Morphology of the bonding interface between parenchyma cells of the four kinds of bamboo laminated lumber

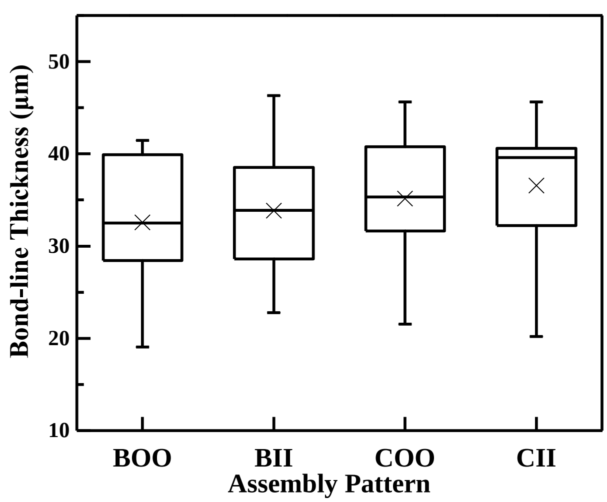

Fig. 4. Bond-line thickness of the four kinds of bamboo laminated lumber

Fluorescent Characterization of Bamboo Bonding Interface

The quantitative index of adhesive penetration into the matrix includes effective penetration (EP) and average penetration (AP). EP refers to the area of penetration (μm^2)

divided by the length of the glue-line (μm), and AP refers to the average value of the five farthest penetration distances (μm). These values were calculated using ImageJ software from bitmaps of the bamboo bonding interface according to Eqs. 1 and 2,

$$EP = \sum_{i=1}^{n} A_i \Big/ X_0 \tag{1}$$

$$AP = \sum_{i=1}^{5} (y_i) \Big/ 5 \tag{2}$$

where n represents the resin spot numbers, A_i is the "i"th area of penetration (μm^2), x_0 denotes the length of the glue-line (μm), and y_i is the farthest penetration distance (μm). To differentiate between the adhesive and the matrix, the bleached and carbonized bamboo cross sections were observed under infrared light and ultraviolet light, respectively. The results are shown in Figs. 5 and 6.

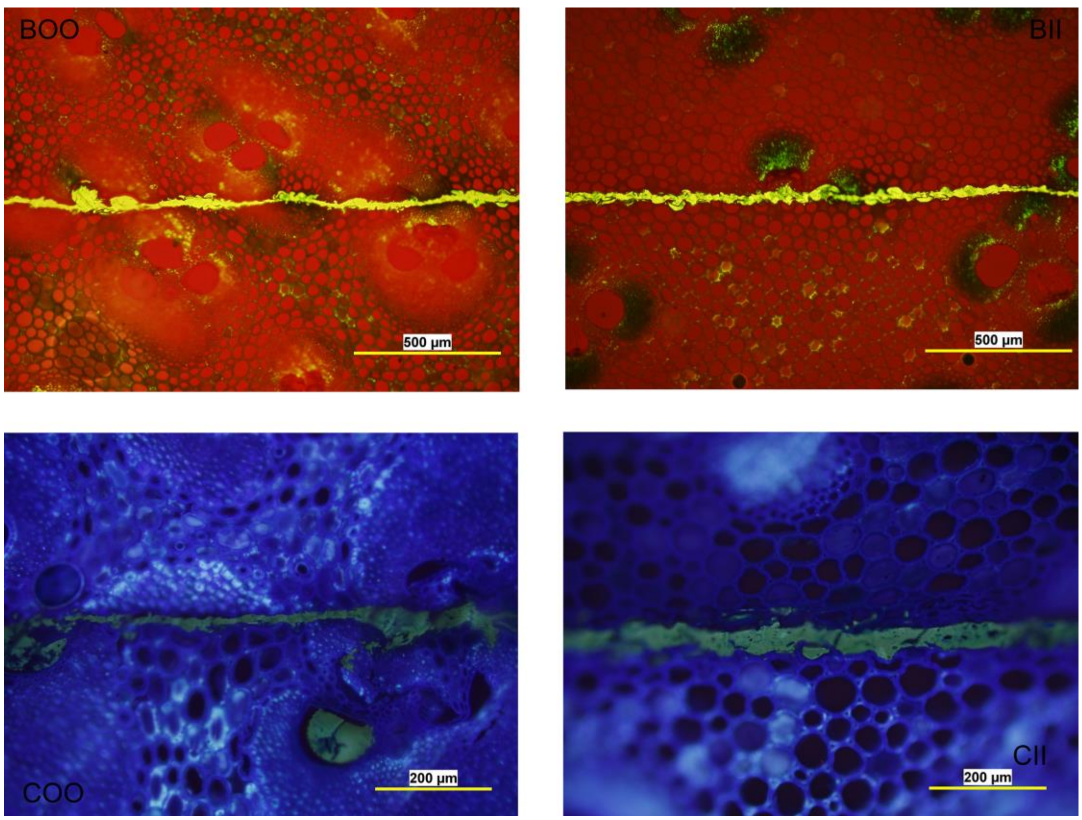

Fig. 5. Fluorescent photomicrographs of the four kinds of bamboo laminated lumber

Figure 5 depicts fluorescent photomicrographs of the bonding interface of bamboo parenchyma cells, showing that the adhesive was primarily distributed in the broken cell cavities formed during preparation, as well as between the cell walls. Furthermore, the bond-line thickness of the inner-to-inner glued bamboo laminated lumber was greater than that of the outer-to-outer glued lumber. These findings substantiate those of the SEM images.

Table 2 shows the AP and EP of PTUF in the bamboo bonding interface. The effective penetration depth was relatively small, ranging from 33.8 μm to 39.2 μm.

Table 2. Average Penetration and Effective Penetration of PTUF in the Bamboo Bonding Interface

Assembly Pattern	EP			AP		
	Average Value (μm)	Standard Deviation (μm)	Variable Coefficient (%)	Average Value (μm)	Standard Deviation (μm)	Variable Coefficient (%)
BOO	33.8	3.4	10.1	35.2	1.7	4.8
BII	34.1	1.9	5.8	37.6	3.2	8.5
COO	38.5	3.4	8.8	41.8	8.4	20.1
CII	39.2	3.9	9.9	45.9	5.3	11.5

In previous bamboo bonding interface studies, the effective penetration depth of phenol formaldehyde adhesives produced with low-molecular weight (LMW) PF was 59.68 μm to 83.23 μm (Guan *et al.* 2014), which was greater than was found in this research. This difference indicates that the PTUF penetration was not as good as that of pure PF mixed with LMW PF. One explanation could be that the larch thanaka was partially liquefied, leaving large molecules of cellulose and hemicellulose in the adhesive, which affected the penetration of PTUF into the bamboo. When the same materials were used, the penetration depth of the inner-to-inner glued bamboo laminated lumber was greater than that of the outer-to-outer glued lumber, with the effective penetration depth increment from 0.3 μm (BOO to BII) to 0.7 μm (COO to CII) and the average penetration depth increment from 2.4 μm (BOO to BII) to 4.1 μm (COO to CII), as the density of the outer layer was higher than that of the inner layer (Tan *et al.* 2011). As shown in Fig. 1, the outer fiber was treated more intensively than the inner fiber, generating a higher outer density and resulting in a penetration depth that was less than that of the inner fiber. When comparing the same assembly patterns, the penetration depth of the carbonized bamboo laminated lumber was higher than that of the bleached bamboo laminated lumber, with the effective penetration depth increment from 4.7 μm (BOO to COO) to 5.1 μm (BII to CII) and the average penetration depth increment from 6.6 μm (BOO to COO) to 8.3 μm (BII to CII). Surface free energy increased during the heat treatment (Ma *et al.* 2010), indicating that the contact angle of the carbonized bamboo strip was lower than that of the bleached bamboo strip. This orientation benefited the adhesive penetration on the bamboo surface to some extent. Furthermore, the SEM images show that the surface cells of the carbonized bamboo were crushed under heat and pressure, resulting in more penetration and differences in penetration depth.

Shear Strength of Bamboo Laminated Lumber

Clear differences in shear strength were observed in the specimens glued by PTUF. As depicted in Fig. 6, when the materials were the same, the shear strength of the outer-to-outer glued bamboo laminated lumber was higher than that of the inner-to-inner glued lumber. The cohesive strength of the adhesive itself and the interfacial strength between the adhesive and the matrix were higher than the cohesive strength of the matrix, resulting in interfacial damage to the matrix. Thus, an increase in bamboo density near the interface led to an increase in the shear strength of the bamboo laminated lumber. When assembly patterns were the same, the shear strength of the bleached bamboo laminated lumber was higher than that of the carbonized bamboo laminated lumber. On the basis of the fluorescent photomicrographs shown in Fig. 5, it can be said that the penetration depth of PTUF into the carbonized bamboo was greater than that of the bleached bamboo. However, there was no direct link between the penetration depth and shear strength; the elements that influence shear strength include materials, density, moisture content, and surface characteristics (Wang and Cheng 2006). Bamboo density and mechanical properties increased during the bleaching treatment and decreased during the carbonization treatment (Shao *et al.* 2003). However, the SEM images indicated that bleached bamboo parenchyma cells near the interface were deformed under heat and pressure, but the cell walls maintained their basic morphology. Some of the carbonized bamboo parenchyma cells were also crushed. Thus, it is possible that the difference in intensity between the bleaching and carbonization treatments influenced the bonding shear strength of the bamboo laminated lumber.

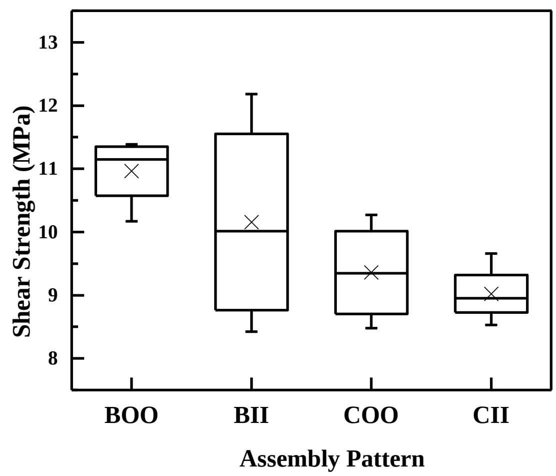

Fig. 6. Shear strength of the four kinds of bamboo laminated lumber

CONCLUSIONS

1. The adhesive could not penetrate properly into the bamboo surface; it was mostly distributed in the broken cell cavities formed during preparation, as well as between the cell walls. It was observed that the average bond-line thicknesses of the inner-to-inner glued bamboo laminated lumber was higher than that of the outer-to-outer glued bamboo laminated lumber, with the average thickness increment from 1.2 μm (BOO to BII) to 1.4 μm (COO to CII). The average bond-line thickness of the carbonized bamboo laminated lumber was higher than that of the bleached bamboo laminated lumber, with the average thickness increment from 2.5 μm (BOO to COO) to 2.7 μm (BII to CII).
2. The penetration of PTUF into the bamboo surface was relatively small. The penetration depth of the inner-to-inner glued bamboo laminated lumber was higher than that of the outer-to-outer glued bamboo laminated lumber, with the effective penetration depth increment from 0.3 μm (BOO to BII) to 0.7 μm (COO to CII) and the average penetration depth increment from 2.4 μm (BOO to BII) to 4.1 μm (COO to CII). The penetration depth of the carbonized bamboo laminated lumber was higher than that of the bleached bamboo laminated lumber, with the effective penetration depth increment from 4.7 μm (BOO to COO) to 5.1 μm (BII to CII) and

the average penetration depth increment from 6.6 μm (BOO to COO) to 8.3 μm (BII to CII).

3. The shear strength of the outer-to-outer glued laminated lumber was higher than that of the inner to inner glued bamboo laminated lumber and the bleached bamboo laminated lumber was higher than that of the carbonized bamboo laminated lumber.

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