PROCESSING BAMBOO FOR STRUCTURAL COMPOSITES: INFLUENCE OF PRESERVATIVE TREATMENTS ON SURFACE AND INTERFACE PROPERTIES

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Abstract

Engineered bamboo is being increasingly explored for structural uses in the construction sector. To ensure durability, products such as laminated bamboo undergo essential preservation treatment steps during their manufacture. Recent studies have revealed that such treatments also affect the mechanical properties and structural behaviour of the material. In the present work, we examine the effects of caramelisation and bleaching, two commonly used treatment procedures in industry, on the surface and interfacial properties of laminated bamboo composites. By understanding the effects of processing methods on the surface and interfacial properties, the industrial manufacturing process can be optimised for structural applications.

Dynamic wettability studies through contact angle measurements and subsequent surface energy analysis revealed lower water contact angles, a greater degree of droplet spreading and liquid penetration, higher total surface energy and a slightly greater polarity ratio for bleached bamboo in comparison to caramelised bamboo. In addition, lap-joint shear tests established the significantly better adhesive bonding performance of bleached bamboo with all five surveyed commercial adhesives. Our observations were explained through the changes in chemical composition and structure of the bamboo material upon treatment.

1. Introduction

Bamboo is an outstanding natural composite: it is rapidly growing, low-cost and abundantly available, light yet stiffer and stronger than both timber and (chopped strand mat) glass fibre reinforced composites [1, 2]. However, in natural form – as a hollow cylinder – the structural applications are limited by form and shape. At the other extreme, it is possible to extract the structure-supporting sclerenchymatous fibre bundles from within the culm wall to be used as reinforcements in polymer composites [3, 4]. However, this approach is inefficient, as i) the extracted natural fibres form only a fraction (typically between 30-50% by weight) of the composite, and ii) residual bamboo material (which accounts for up to 70% by mass of the initial bamboo material) is formed as a waste by-product. An alternative approach is to produce laminated bamboo composites (Fig. 1), which exploit the inherent composite structure of bamboo, reduce polymer usage (to around 5-10% by weight of the composite) and maintain the longitudinal fibre direction. The typical process used in industry to produce such an engineered material is illustrated in Figure 1 [5, 6].

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An important step in the production of laminated bamboo (and in fact any raw or engineered bamboo product) is the preservative treatment for improved durability. Currently, two methods are utilised in laminated bamboo [7]: a) *bleaching* in a hydrogen peroxide bath at 70-80ºC (over 4 hours) resulting in a lighter yellow colour, or b) *caramelisation* using pressurised, wet steam at 120-130ºC (over 5-6 hours) yielding a darker brown colour. The processing methods appear to affect the mechanical and fracture behaviour of the laminated bamboo material [5]. For instance, bleached bamboo is found to be softer and more ductile, stiffer/stronger in tension but weaker in flexure and compression, and more prone to fibre pull-out, than caramelised bamboo.

Here, we examine the effects of treatment on the surface properties of bleached and caramelised bamboo, as well as the interfacial properties of the laminated composites. Insights from this study will enable a better understanding of differences in mechanical behaviour of the materials, as well as provide recommendations, following a scientific method, on processing and manufacturing.

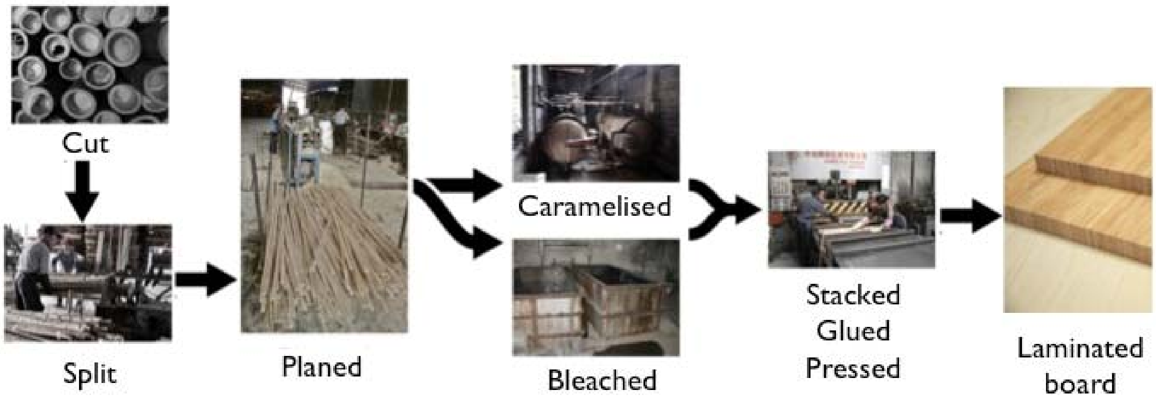

Figure 1. The process based on [7] involved in producing laminated bamboo is as follows: segmenting (transverse to culm axis), splitting (parallel to culm axis), and planing of bamboo culm, and thereafter treating (for improved durability) the material, followed by gluing, stacking and pressing to form a laminated material.

2. Methods

Bleached and caramelised Moso bamboo (*Phyllostachys pubescens*) were obtained as laminated sheet products from Moso International B.V. These were machined and planed to obtain strips of dimensions ~115 mm in length in the grain direction, ~20 mm wide, and ~5 mm thick.

To examine surface properties, dynamic contact angle measurements were made using the sessile drop technique on a FTA1000 instrument (First Ten Angstroms, USA), equipped with an AV-GC750 CCD camera (Allied Vision Technologies, Germany). Two different probing fluids were used: purified water (polar) and diiodomethane (non-polar). Droplet shape on the surface was photographed at regular time intervals (0.2 seconds) until they reached steady-state, $t = t_{eq}$ (up to 60 seconds for water and up to 10 seconds for diiodomethane). Evaluation of contact angles between the bamboo surface and the liquid-air interface was carried out using the FTA32 software (First Ten Angstroms, USA). Measurements were performed for at least twenty five droplets for each probing fluid and bamboo material combination. Surface free energy of the bamboo materials was thereafter determined through the OWRK (Owens, Wendt, Rabel and Kaelble) geometric mean method [8], based on the measured equilibrium contact angles and the surface properties for water and diiodomethane (from [8, 9]).

The interfacial properties of the bamboo materials were determined through single lap-joint shear tests, as per ASTM D31631 [10]. Strips of treated bamboo were bonded with the five different commercial adhesives: polyurethane (PU: Purbond, Henkel, Switzerland), polyvinyl acetate (PVA:

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Lumberjack wood adhesive, Everbuild, UK), soy-flour based adhesive (Soy: Soyad, Solenis, USA), resorcinol phenol formaldehyde (RPF: Polyproof, Polyvine, UK), and urea phenol formaldehyde (UPF: Cascamite, Polyvine, UK). Mechanical testing was conducted on an Instron universal test frame, equipped with a 150 kN load cell, at a displacement rate of 1.27 mm/min. The 'apparent' shear strength was determined from the failure load. Twenty specimens were tested for each sample type.

3. Results and discussion

Dynamic contact angle measurements on the untreated and treated bamboo surfaces were performed with water and diiodomethane as the probing fluids (Figure 2). While the contact angle for water exhibited an exponential decay, becoming fairly stable for $t > 20$ seconds, the contact angle for diiodomethane was stable throughout. The reducing contact angle in the case of water, a polar liquid, was due to a combination of spreading on the bamboo surface and absorption into the bamboo cellular structure. This is commonly observed on wood surfaces [11].
The initial and equilibrium contact angles at the water-caramelised bamboo interface were significantly higher than that at the water-bleached bamboo interface (Figure 2). Bleached bamboo therefore was more wettable and formed a more intimate contact with polar liquids. In addition, bleached bamboo exhibited better droplet spreading and liquid penetration. In contrast, with diiodomethane the equilibrium contact angle at the liquid-bamboo interface was comparable for both bleached and caramelised surfaces, implying comparable wettability with non-polar liquids, which was however substantially poorer than that for polar liquids.

Dynamic contact angle measurements on bamboo in literature, although sparse, are comparable to our measurements. In their wettability study, Chen et al. [12] observed that the initial and equilibrium contact angles at the water-untreated bamboo interface was at 60-70° and <5°, respectively. Li [13] found that urea formaldehyde resin (a relatively polar liquid) and untreated bamboo (in the middle section) had an initial and equilibrium contact angle of 60° and 35°, respectively, although this can vary substantially with different sections (e.g. epidermis and inner-most surface).

Based on the equilibrium contact angles of water and diiodomethane with the different bamboo surfaces, total surface energy and its polar and dispersive components were determined. These are presented in Table 1. Bleached bamboo possessed a statistically significant higher total surface energy (of 74.0 ± 0.2 mJ/m^2) than caramelised bamboo (70.7 ± 1.3 mJ/m^2). The polarity (ratio of polar component to total surface energy) ranged between 0.46-0.56 for the bamboo surfaces. Specifically, the treatments had a minor influence on the balance of polarity of the substrate, with bleached bamboo having a relatively larger polar component of surface energy, but caramelised bamboo having a relatively larger dispersive component. The surface energy of bamboo (not its fibres) is not well-reported in literature: Zhang et al. [14] calculate it to be of the order of 40-50 mJ/m2, much lower than our measurements.

Figure 3 presents measurements and variation of apparent shear strengths for the various adhesive/bamboo surface interfaces. For all adhesives, bleached bamboo interfaces displayed significantly ($p < 0.005$) higher mean shear strengths than caramelised bamboo interfaces. Notably, the different surfaces exhibited lowest and highest shear strengths with different adhesives: the mean shear strength for bleached bamboo ranged from 6.6 MPa (for Soy) to 8.5 MPa (for RPF), while the mean shear strength of caramelised bamboo ranged from 2.8 MPa (for PVA) to 5.1 MPa (for PU). These observations reveal that the differences in surface chemistry between bleached and caramelised bamboo not only leads to lower adhesive bonding strengths for caramelised bamboo, but also affects their affinity and bonding performance with different adhesives.

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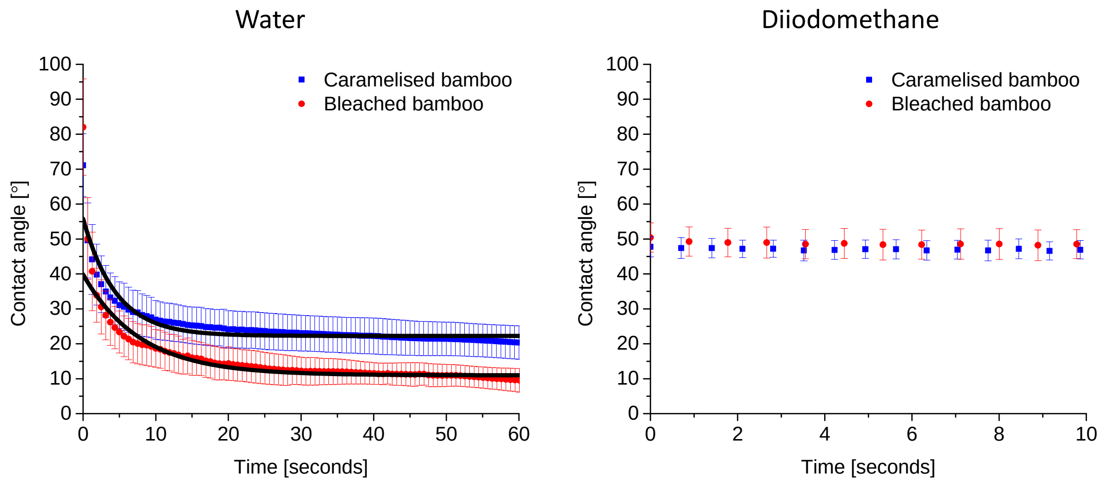

Figure 2. The evolution of contact angle with time for a droplet of water (left) and diiodomethane (right) over the two bamboo surfaces. Error bars indicate ± one standard deviation (n = 25).

Table 1. Surface energy of untreated and treated bamboo surfaces.

Bamboo surface	Total surface energy [mJ/m^2]	Polar component [mJ/m^2]	Dispersive component [mJ/m^2]	Polarity (polar/total)
Caramelised	70.7 ± 1.3	34.6 ± 2.8	36.1 ± 1.5	0.46-0.52
Bleached	74.0 ± 0.2	38.5 ± 2.7	35.5 ± 2.9	0.48-0.56

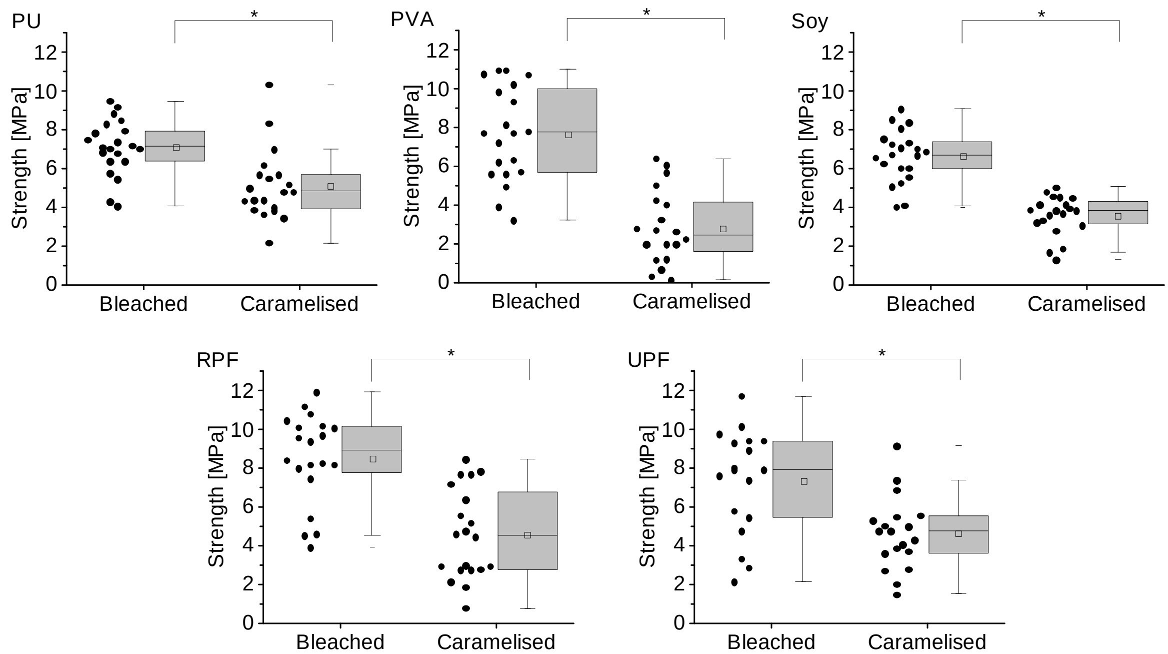

Figure 3. Apparent shear strengths for various adhesive/bamboo surface interfaces. Data points (dots) are graphically described through box-and-whisker plots (mean – unfilled square, inter-quartile range and median – box, maximum and minimum – whiskers).

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Our measurements and observations reveal that bleached bamboo exhibited lower water contact angles, and a greater degree of spreading and penetration than caramelised bamboo. The surface energy analysis revealed that bleached bamboo possessed a significantly higher total surface energy (of 74.0 ± 0.2 mJ/m2) and a slightly greater polarity than caramelised bamboo (70.7 ± 1.3 mJ/m2). Good wetting requires the surface energy of liquid to be less than that of the solid substrate. For reference, polymer adhesives, including the ones employed in this study, tend to have surface energies in the range of 20-40 mJ/m2 [8, 15]. As good wetting behaviour is a prerequisite for good adhesive bonding performance, all these wetting analysis results suggest that, in general, bleached bamboo should bond better with polymer adhesives than would caramelised bamboo. Indeed, our results from lap shear testing validate this hypothesis, with all bleached bamboo-adhesive interfaces yielding higher apparent shear strengths.

How do our findings on the surface wetting properties and adhesive bonding properties of the differently treated bamboo together tie-up with the (changes in) chemical composition and structure of bamboo?

Preservative treatments aim to chemically decompose the starch or physically limit access to it [16]. However, invariably, treatments also alter other chemical constituents and the physical structure of bamboo.

The effects of caramelisation (or pressurised steaming) on chemical composition of bamboo have been reported in a number of studies [17-20], albeit for a wide range of processing conditions. All studies report a notable reduction in the holocellulose content. Specifically, hemicellulose content drops substantially (by up to 50% [17, 18]), with the cellulose content remaining unchanged or decreasing, depending on bamboo species and temperature. Lignin and extractives content consequently increases (in relative terms). More detailed analyses on steamed hardwoods, which have similar chemical composition to grasses like bamboo, have revealed that the principal changes are from (partial) degradation of glucuronic acid unit of xylan (pentosans/hemicellulose hydrolyse to form pentoses), and decomposition of the aromatic skeleton (C=O linkage) in lignin [21, 22]. Some studies also suggest a small increase in cellulose crystallinity due to such thermal treatments [14, 18]. These effects lead to higher contact angles with polar liquids (i.e. poorer wetting), lower polarity ratio, lower surface energy and lower spreading rates. There is, however, no substantial effect on structure implying that liquid penetration is not affected. Consequently, although mechanical interlocking between the bamboo substrate and adhesive may be unaffected, the worsened chemical interactions governed by energy states and wetting kinetics lead to poor bonding performance for caramelised bamboo.

Unlike caramelisation, which is a hygro-thermal treatment, bleaching is a chemical treatment at lower temperatures [7]. With increasing severity (pH and temperature), the peroxide bleaching process oxidises the chromophores in lignin (discolouration without delignification), the aromatic rings of polyphenols and lignin (and therefore decomposing lignin) and even hydroxyl groups in polysaccharides resulting in shorter cellulose chains and reduced crystallinity for example [23-25]. The density of bleached bamboo at 644 kg/m3, despite the relatively higher moisture content, is lower than that of caramelised bamboo at 686 ± 34 kg/m3 [5]. This indicates a marginally (ca. 3%) higher porosity content in bleached bamboo. The better bonding performance of belached bamboo is explained as follows. Decomposition of hydrophobic lignin increases the polarity ratio, reduces contact angles, improves spreading rate and results in a higher surface energy (than caramelised bamboo) and more favourable chemical interactions, but also the chemical treatment may be increasing surface roughness, permeability and porosity (by breaking down material, including pit membranes [26]) and therefore facilitating penetration of the adhesive and mechanical interlocking.

4. Conclusions

Engineered bamboo composites have shown much promise as a structural material for infrastructure applications, in many cases as alternatives to engineered timber. Yet, the industrial processing, testing

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and targeted use of engineered bamboo is still largely based on engineered timber. To optimise industrial manufacturing and material performance of laminated bamboo, it is imperative to understand processing-property relations specific to bamboo.

Our study finds that preservative treatments have significant effects on the wetting behaviour and adhesive bonding performance of the laminated bamboo material. Specifically, bleached bamboo exhibits better wettability, higher surface energy and better liquid penetration than caramelised bamboo. This translates to higher adhesive bonding strengths for bleached materials for all commercial adhesives tested here. Changes in chemical composition and structure upon hygro-thermal (caramelisation) and chemical treatment (bleaching) produce these changes in surface and interface properties.

We are currently working on a complete chemical composition and structure analysis of the untreated and treated bamboos to examine this further. Such studies will help build a complete picture of how processing induces chemical and physical changes in the bamboo material, which controls the various structural properties of the engineered bamboo composite, including surface, interface, and mechanical performance. This will then enable building predictive models to enable complex and reliable designing with engineered bamboo. Routinely implementing Weibull probabilistic failure analysis, as we have done in this study for bonding strength, is critical for reliability engineering.

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