

Original article

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Properties of a formaldehyde-free tannin adhesive and mechanical strength of oriented bamboo scrimber board bonded with it

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Abstract: In this study, oriented bamboo scrimber board (OBSB) was manufactured with a synthesized formaldehyde-free tannin adhesive. The chemical properties of the tannin adhesive were analyzed with ^{13}C nuclear magnetic resonance spectroscopy (^{13}C -NMR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). Results revealed that 70% aqueous acetone extractives of *Acacia confusa* bark (AcBAE) contained abundant phenolic compounds and condensed tannins comprising mainly B-type flavonoid bonds. Moreover, cross polarization magic angle spinning (CP/MAS) ^{13}C -NMR mapping of cured *Acacia confusa* bark tannin glue (AcBTanGlu) revealed that condensed tannin reacted with hexamethylenetetramine to form a polymer with a cross-link structure through a polymerization mechanism. According to the results obtained from gas chromatography-flame ionization detector (GC-FID) analysis, no formaldehyde was emitted from AcBTanGlu-glued OBSB. Thermogravimetric analysis indicated that AcBTanGlu significantly improved the thermal stability of AcBAE after the curing reaction. Comparison of the DRIFT spectra of bamboos before and after AcBTanGlu-glued treatment indicated AcBTanGlu did not impact the chemical functional properties of the bamboo. Compared to phenol formaldehyde (PF) and urea formaldehyde

(UF)-glued OBSBs, AcBTanGlu-glued OBSBs statistically had lower modulus of elasticity (MOE) and modulus of rupture (MOR). As for the nail withdraw resistance, AcBTanGlu-glued OBSBs are statistically comparable to PF-glued OBSBs and higher than UF-glued OBSBs.

Keywords: *Acacia confusa*; formaldehyde-free; mechanical strength; oriented bamboo scrimber board; tannin adhesive.

Abbreviations

^{13}C -NMR	^{13}C nuclear magnetic resonance spectroscopy
AcBAE	70% aqueous acetone extractives of <i>Acacia confusa</i> bark
AcBTanGlu	<i>Acacia</i> bark tannin glue
CP/MAS	cross polarization magic angle spinning
DRIFT	infrared Fourier transform spectroscopy
LBB	laminated bamboo board
MOE	modulus of elasticity
MOR	modulus of rupture
OBSB	oriented bamboo scrimber board

1 Introduction

In the design of green buildings, considerable attention is paid to the utilization of renewable and sustainable materials. Bamboo has the advantages of rapid growth, short renewal period, and excellent strength properties. Therefore, bamboo is not only an environmentally friendly fiber source, but also an alternative raw material for engineering and construction. However, the special shape of bamboo limits its application as a form of board. The innovation and development of laminated bamboo board (LBB) improves the utilization ratio and is in compliance with standardized processing of bamboo utilization. The strength of LBB is similar to that of bamboo; and the solid profile of LBB is more uniform than bamboo and it also has less variation in physical properties (Lee et al., 2012; Lee and Lan, 2006). However, the disadvantages of LBB are its

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standardized production methods produce lower strength board and higher costs.

On the other hand, the oriented bamboo scrimber board (OBSB) has been developed and widely used over the past 10 years (Chung and Wang, 2018a; 2018b; Sharma et al., 2015ab; Wang, 1989; Yu and Yu, 2013; Yu et al., 2015). Moreover, Chung and Wang (2018 ab) pointed out that the newly developed OBSB has excellent surface texture, hardness, bending strength, and longitudinal compressive strength properties. Therefore, it could be applied to manufacture indoor and outdoor floors, railings, furniture, and engineering materials.

Adhesive is a crucial factor for producing LBB and OBSB; different adhesives significantly influence the strength, dimensional stability, and durability of boards (Liu et al., 1992; 1993). Therefore, an appropriate adhesive is very important for producing LBB and OBSB. At present, formaldehyde is the cross-linking agent for most adhesives used in wood composite production. Although the cost of formaldehyde-containing adhesive is low and it is easy to process, free formaldehyde release causes damage to human health. Dalton (1950) was a pioneer, who applied tree bark tannin to synthesize wood adhesives with good gluing properties.

Acacia confusa is one of the most important plantation trees widely distributed in the low and medium altitude mountains of Taiwan. The bark extractives of *A. confusa*, containing abundant reactive phenolic compounds, could be reacted with resorcinol formaldehyde (RF) to form cold-set resin with good gluing effect (Lee and Liu, 1995ab; 1996). Pichelin and his coworkers (2006) manufactured structural beams using thick wood panels with formaldehyde-free tannin adhesive, in which polymerized condensed tannins with hexamethylenetetramine, and demonstrated a good adhesion property. From these findings, we speculated that condensed tannin extracted from the bark of *A. confusa* residue might possess the potential to synthesize a formaldehyde-free adhesive.

Since the formaldehyde-free adhesive tannin is an environmentally-friendly organic material. It has been used widely in leather, dyeing, biomedical, and adhesive industry (Hsieh and Chang, 2010; Lee and Lan, 2006). In this study, a formaldehyde-free adhesive was prepared by using *A. confusa* bark extractives. In addition to analyzing the chemical composition of extractives, the hardening mechanism, the releasing of formaldehyde, and thermal stability of tannin-based adhesives were also examined. Finally, the strength properties of OBSB glued by tannin-based adhesive were evaluated. Results obtained from this study contribute to the development of a formaldehyde-free OBSB, which would in turn provide ecological green building materials for a healthy living environment.

2 Materials and methods

2.1 Adhesives

Three kinds of adhesives were used for manufacturing OBSB. *A. confusa* bark tannin glue (AcBTanGlu) was synthesized in this study, of which the solid content was 72.3% and the curing temperature was 120 °C. The other two commercial adhesives were purchased from Wood Glue Co (Tainan, Taiwan), and were water-soluble urea formaldehyde (UF) resin with a solid content of 63.6% (curing temperature was 120 °C, pH 7.2, and gel time was 35 min), and phenol formaldehyde (PF) resin with a solid content of 58.1% (curing temperature was 140 °C, pH 8.5, and gel time was 45 min).

Tannin was collected from the bark of 55-year-old *A. confusa* at the Experimental Forest of National Taiwan University in Nantou County, Taiwan in September 2016. The bark was processed into particles of <2 mm in size. After air drying, the bark particles were extracted exhaustively by 70% aqueous acetone three times (3 × 7 days). Then, the extract was collected and filtered, concentrated, and lyophilized, to obtain AcBAE (yield = 227 g kg⁻¹). The method reported in Moubarik et al. (2010) was used to synthesize the AcBTanGlu with slight modification. Briefly, AcBAE was mixed with hexamethylenetetramine, (CH₂)₆N₄, with a molecular weight of 140.19 g mol⁻¹ (purchased from Hayashi Pure Chemical Ind.) in deionized water. The weight ratio of AcBAE/hexamethylenetetramine/deionized water is 28 : 2 : 70, respectively. AcBTanGlu was adjusted to pH 10 using NaOH solution and then uniformly sprayed on the bamboo strips with a solid content of 36.5%, followed by hot-pressing at 120 °C for 12 min to form an OBSB.

2.2 Sample preparation

Three-year-old makino bamboo (*Phyllostachys makinoi* Hayata) culms were harvested from the Experimental Forest of National Taiwan University in Nantou County, Taiwan in October 2016. All bamboo culms were cut into strips of 2 cm wide using a circular saw machine and nine bamboo samples ($n = 9$) were used in each test condition. In order to obtain better reagent penetration and chemical reaction post-treatment, it is necessary to remove the dirt and siliceous wax layers from bamboo surfaces. Thus, bamboo samples were pre-treated with an alkaline solution containing 2% potassium hydroxide (KOH) with 0.5% surfactant at 100 °C for 30 min and then oven-dried at 80 °C. After alkali pretreatment, bamboo culms were extruded into thin strips of 450 mm × 1.0–2.0 mm by mechanical processing (Chung and Wang, 2018 ab).

Further, for steam-heating treatment (SHT), bamboo strips were placed in a steam-heating furnace at 120 °C for 6 h. Then they were placed unidirectionally in an iron frame of 450 × 450 × 12.0 mm (length × width × thickness) to form a board at 1.00 g cm⁻³ density. AcBTanGlu, UF, and PF were applied at 10 wt% of oven dry raw materials. The strips were hot-pressed under curing temperature at 18 kgf cm⁻² for 12 min, followed by cooling for 10 min. All samples were conditioned in a controlled environment at 20 °C and relative humidity (RH) at 65% for 2 weeks. Figure 1 shows the processing of makino bamboo culms into an OBSB.

2.3 Determination of polyphenol content

The total phenolic content of AcBAE was measured according to the analytical method of Wu et al. (2005) with slight modification.

In brief, 0.5 mL of AcBAE was mixed with 0.5 mL of 1 N Folin-Ciocalteu reagent. After being left to stand for 5 min, 1 mL of 20% Na_2CO_3 was added. Then the mixture was left to stand for another 10 min. The mixed solution was centrifuged at 1200g for 8 min to separate the solution and the precipitates. Finally, absorbance of the upper-layer clear liquid was determined at 730 nm using a microplate analyzer (Molecular Devices Spectra Max 190). In addition, 0.5 mL of AcBAE was replaced by gallic acid solution to establish a calibration curve. The total phenolic content was calculated from the calibration curve with results expressed as gallic acid equivalent (GAE) per gram dry weight. Each test was done in triplicate.

The total flavonoid content of AcBAE was analyzed according to the method reported in Hsieh and Chang (2010). Briefly, 150 μL of AcBAE was mixed with 150 μL of 2 wt% AlCl_3 aqueous solution, followed by 30-min standing at room temperature. Then, the absorbance was measured at 420 nm using a microplate analyzer (Molecular Devices Spectra Max 190). In addition, 150 μL of AcBAE was replaced by quercetin solution for drawing the calibration curve. The total flavonoid content was calculated from the calibration curve with results expressed as quercetin equivalent (QE) per gram dry weight. Each test was performed in triplicate.

The total condensed tannin content in AcBAE was determined according to the method reported in Sun et al. (1998). In brief, 0.5 mL of AcBAE was reacted with 1.25 mL of 1% Vanillin/MeOH solution and 1.25 mL of 10% H_2SO_4 /MeOH solvent at 30 °C for 15 min. The absorbance was measured at 500 nm using a microplate analyzer (Molecular Devices Spectra Max 190). In addition, 0.5 mL of AcBAE was replaced by catechin solution for drawing the calibration curve. The total condensed tannin content was calculated from the calibration curve with results expressed as catechin equivalent (CE) per gram dry weight. Each test was performed in triplicate.

2.4 Chemical composition analysis and thermal behavior

To identify the compounds of the AcBAE, 3 g of AcBAE was dissolved in hexadeuterodimethyl sulfoxide ($\text{DMSO-}d_6$) and the absorption positions of ^{13}C under the magnetic field were examined using nuclear magnetic resonance spectroscopy (NMR 300 MHz, Magnet system 400/54 ascend, Bruker BioSpin AG). AcBTanGlu-glued OBSBs were ground into the 60–80 mesh powder, and the spectrum of each sample in the range of 4000–400 cm^{-1} was analyzed with 64 scans at the resolution of 4 cm^{-1} using infrared Fourier transform spectroscopy (DRIFT, Bio-Rad FTS-40) equipped with a diffuse reflectance accessory (Spectra Tech Co.). The spectrum of each sample was corrected with the spectrum of background, which collected with the reflector made

by potassium bromide powder. Then, the diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) spectrum of AcBTanGlu-glued OBSBs powder was compared with that of bamboo powder to determine the changes in chemical composition. To examine the solid state of extractives before and after hardening, powders of AcBAE and cured AcBTanGlu were analyzed using cross polarization magic angle spinning (CP/MAS) NMR Spectrometer (NMR) (Bruker Avance III 400 NMR Spectrometer).

Volatile organic compounds (VOCs) emitted from formaldehyde (4 μL of 37% formaldehyde, $w\ w^{-1}$, $d = 1.083$) and AcBTanGlu-glued OBSBs (5 × 5 × 2 cm) were analyzed by an ITQ Series GC mass system, equipped with a DB-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness; J & W Scientific). The samples were allowed to stand for 1 h inside different sealed 250-mL beakers. The temperature program was as follows: 50 °C for 2 min, then increased by 3 °C min^{-1} to 200 °C and held for 1 min, finally at 10 °C min^{-1} to 250 °C and held for 3 min. The other parameters were as follows: injection temperature, 250 °C; ion source temperature, 280 °C; EI, 70 eV; carrier gas, He at 1 mL min^{-1} ; injection volume, 1 μL ; spilt ratio, 1:10; and mass range, m/z 45–425. Identification of the major VOCs emitted were confirmed by co-injection with and comparison against standards of the Wiley Registry 7.0 the National Institute of Standards and Technology V2.0. In addition, Kovats index (Adams, 2007) was also used for compound identification.

Thermal stability of both AcBAE and cured AcBTanGlu powder were examined using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851e) with oxygen at a flow rate of 70 mL min^{-1} as filling gas. The initial temperature was held at 100 °C for 3 min, and then heated at 10 °C min^{-1} to 600 °C. The thermal stability of samples was evaluated using the TGA/DTG curves plotted during the heating procedure.

2.5 Measurement of mechanical strength

The mechanical strength of AcBTanGlu-glued OBSB samples was measured according to the American Society Testing and Materials (ASTM) method standard D-1037 (2006). The static bending test was conducted using a universal-type testing machine (Shimadzu UH-10 A, Tokyo, Japan) by the center-loading method for samples. A concentrated bending load was applied at the center of the sample with a span 15 times the thickness of the sample. Both modulus of elasticity (MOE) and rupture (MOR) were calculated from load-deflection curves.

The Chinese National Standards (CNS) method standard 2215 (1999) for testing nail withdrawal resistance of particleboards was performed in this study. Briefly, the AcBTanGlu-glued OBSB samples (100 × 50.0 × 12.0 mm; length × width × thickness) were placed in a controlled environment with 65% relative humidity for 3 weeks. Wood

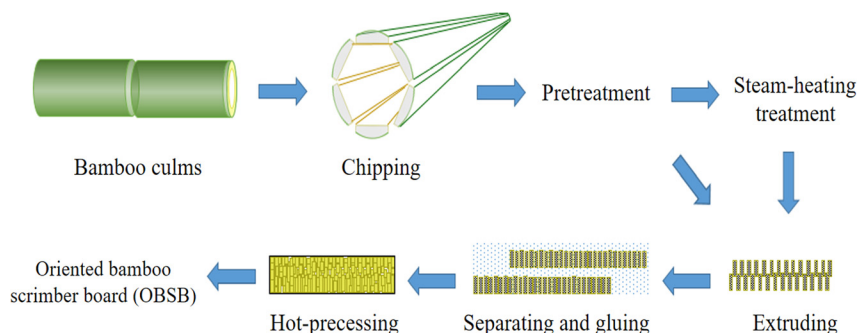


Figure 1: Manufacturing process of OBSB.

screws (2.7 × 16.0 mm; diameter × length) were drilled vertically into the samples to a depth of 11.0 mm and then pulled up vertically at 2.0 mm min⁻¹. The maximum pull loading was measured, and the average of three measurements was taken as the nail withdrawal resistance.

All multiple comparisons of physical, chemical and mechanical properties were subjected to Tukey's test and analysis of variance. Significant differences were determined using the Duncan's multiple range test. All analyses were performed by the software Statistical Analysis System (SAS Institute, NC, USA) 8.0.

3 Results and discussion

3.1 Chemical properties of AcBAE

Chemical analysis of AcBAE revealed that the total phenolic content was 758 ± 12 mg (GAE g⁻¹ of crude), and the total condensed tannin content was 739 ± 15 mg (CE g⁻¹ of crude). Flavonoids were not detected, indicating that AcBAE is rich in phenolic compounds and condensed tannins. Our finding is consistent with the results obtained by Wei et al. (2010) that the bark of *A. confusa* is high in total phenolics and extractable condensed tannins. Figure 2 shows the ¹³C-NMR spectrum of AcBAE. Peaks are seen at δ157–153 ppm (C5, C7 and C9), δ146–143 ppm (C3' and C4'), δ136 ppm (C10), δ132–130 ppm (C1'), and δ127–109 ppm (C6, C8, C2', C5' and C6), revealing the typical signals of condensed tanning (Figure 3). A previous study indicated that when C6 and C8 on the A-ring form interflavonoid bonds with C4 on the C-ring in the unit structure of condensed tannins, the signals will shift from δ98–96 ppm (C6) and δ96–95 ppm (C8) to a lower magnetic field of δ111–107 ppm (C4) (Newman et al., 1987; Pizzi and Stephanou, 1994; Thompson and Pizzi, 1995).

As shown in Figure 2, unbonded C6 and C8 signals observed at δ98–95 ppm were very weak. In contrast, stronger signals were observed at δ111–107 ppm for C4-C6/C4-C8 condensed flavonoid (condensed tanning) bonds, demonstrating that AcBAE contained high amounts of condensed tannins. Moreover, signals observed at δ88–71 and δ69 ppm were the signals of C2 and C3 with -OH substituents on the alkyl group of condensed tannins. In addition, the signal shown at δ43 ppm was C4 on the extension unit of condensed tannins while those at δ30 and δ32 ppm are also the signals of C4 but on the terminal unit. According to the results of Wei et al. (2010), all the flavonoid units of condensed tannins extracted from *A. confusa* are linked by B-type bonds, a finding that agrees well with observations in both the extension and terminal units of condensed tannins (Figure 3).

Furthermore, the ¹³C-NMR spectrum of AcBAE (Figure 2) also showed the signals of the alkoxy group at

δ55–58 ppm and that of methylene at δ21 ppm. Tung et al. (2009) isolated and identified various compounds from AcBAE including 3,4-dihydroxy-*trans*-cinnamic acid ethyl ester, 3,4-dihydroxy-*trans*-cinnamic acid pentyl ester, 3,4-dihydroxybenzoic acid butyl ester, 3,4-dihydroxybenzoic acid ethyl ester, 4-hydroxybenzoic acid ethyl ester, 4-hydroxy-3-methoxybenzoic acid, 3-hydroxy-4-methoxybenzoic acid, 4-hydroxy-3,5-dimethoxybenzoic acid ethyl ester, and 4-hydroxy-3,5-dimethoxybenzoic acid, all of which showed characteristic signals of alkoxy and methylene groups, as well as 1-isobutoxy-4-(4-isobutoxybenzyl) benzene with characteristic signals of methylene. Hence, it is speculated that alkoxy and methylene are the characteristic signals of other phenolics besides condensed tanning in AcBAE.

The DFIFT-IR spectrum (Figure 4) also showed the characteristic signals of carbonyl and carboxylic groups at 1680–1820 cm⁻¹ presented. These signals should be mainly contributed by other phenolic compounds such as 3,4-dihydroxy-*trans*-cinnamic acid and hydroxybenzoic acid presented in AcBAE. The above analysis showing that B-type condensed tannin was the main component of AcBAE was further supported by the DRIFT spectrum (Figure 4). A broad absorption peak was seen at 3700–3000 cm⁻¹, which was the stretching signal of the -OH functional group in the condensed tannin; and absorption peaks at 1450, 1524, and 1626 cm⁻¹ are the benzene rings in condensed tannins. According to the results of Hsiao et al. (2017), the peaks at 1450 and 1524 cm⁻¹ are deformation vibration signals belonging to the flavanol units in condensed tannin; moreover, the peak at 1626 cm⁻¹ is the interflavonoid bond at the A-ring of flavanol units in condensed tannin. Kim and Kim (2003) pointed out that the stronger the signal intensity at 1626 cm⁻¹, the more interflavonoid bonds were formed. The current observations demonstrated that AcBAE comprised mainly of B-type condensed tannins made up of C4-C8/C4-C6 interflavonoid bonds.

It is interesting that the chemical composition of the 1% sodium hydroxide extractive from *A. confusa* bark collected by Lee and Lan (2006) seems different with the 70% aqueous acetone extractive from *A. confusa* bark. According to the DRIFT results from Lee and Lan (2006), the characteristic signals of carbohydrates were obvious and the characteristic signals of B-type condensed tannins were rare. Moreover, Antwi-Boasiako and Animapauh (2012) compared the influences of extraction yields and tannin qualities of extractives from the barks of three tropical hardwoods by water and 1% sodium hydroxide solution, showing that although there is higher extraction yield with 1% sodium hydroxide solution extraction, the tannin quality was more poor. These results indicating that

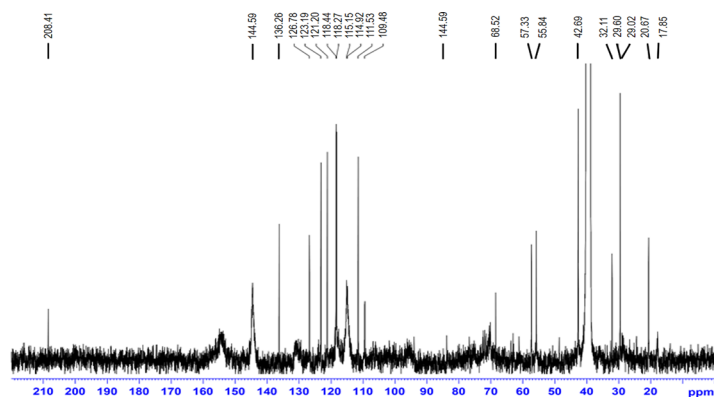


Figure 2: ^{13}C -NMR spectrum of AcBAE (300 MHz, in $\text{DMSO-}d_6$).

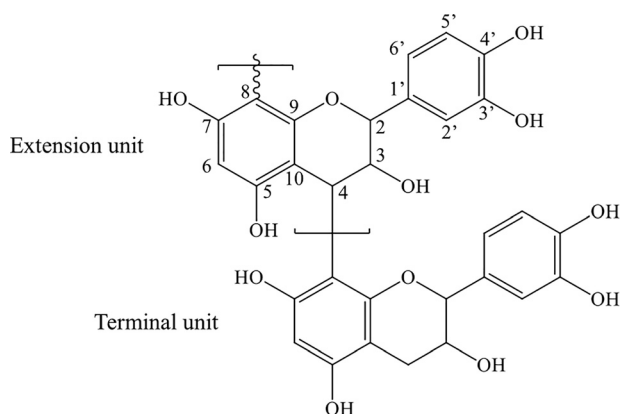


Figure 3: C4-C8 interflavonoid B-type bond of condensed tannins.

as for the purpose to the collection of raw condensed tannin, water or aqueous acetone may be the suitable extraction solutions which better than 1% sodium hydroxide solution.

3.2 Curing mechanism of AcBTanGlu

Figure 5 shows the CP/MAS ^{13}C -NMR spectrum of AcBAE. The signals of C5, C7 and C9 are at $\delta 155$ ppm; C3' and C4' at $\delta 145$ ppm; C10 at $\delta 137$; C1' at $\delta 131$ ppm; C2', C5' and C6' at

$\delta 128$ – 110 ppm; unbonded C6 and C8 at $\delta 98$ and $\delta 92$ ppm, respectively; and C4-C8/C4-C6 interflavonoid bonds at $\delta 110$ – 102 ppm. Compared with those shown in ^{13}C -NMR spectrum of AcBAE (Figure 2), the signals in the CP/MAS ^{13}C -NMR spectrum (Figure 5) are stronger and more obvious. Such a discrepancy may be attributed to the different state of the sample being analyzed. For ^{13}C -NMR analysis, AcBAE samples were dissolved in $\text{DMSO-}d_6$.

Interaction with the solvent expands fully each molecular chain of condensed tannin. However, the larger number of $-\text{OH}$ groups present in each molecular chain generate intermolecular hydrogen bonds, which shorten the molecular distance, thus it might form a steric effect. This effect made it difficult for unbonded C6 and C8 to display ^{13}C -NMR signals. On the contrary, during CP/MAS ^{13}C -NMR analysis, the AcBAE sample was in a solid state with molecular chains aggregated or even distorted due to intermolecular hydrogen bonding, thus exposing unbonded C6 and C8. Therefore, in the absence of a steric effect, ^{13}C -NMR signals could be generated.

Furthermore, the signals at $\delta 76$ and $\delta 72$ ppm represent the C2 and C3 of the alkyl group with $-\text{OH}$ substituents, respectively (Figure 5). C4 on the extended unit structure of condensed tannin were shown at $\delta 37$ and $\delta 44$ ppm; and C4 on the terminal unit structure was shown at $\delta 29$ ppm.

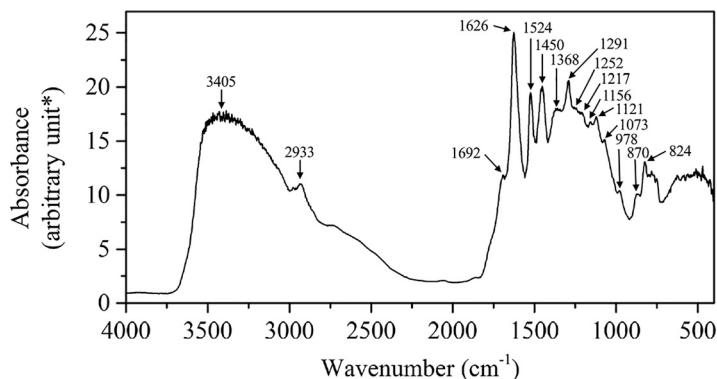


Figure 4: DRIFT spectrum of AcBAE.

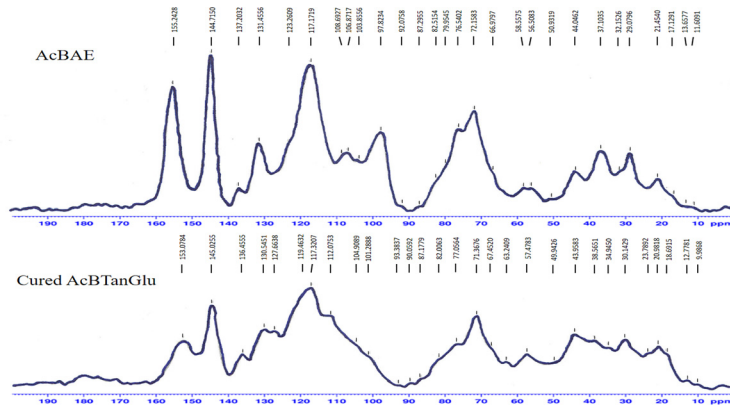


Figure 5: CP/MAS ^{13}C -NMR spectrum of AcBAE and cured AcBTanGlu.

Moreover, the signal intensity of unbonded C6 is stronger than that of C4, indicating that the condensed tannin in AcBAE comprised mainly C4-C8 flavonoids. A comparison before and after the curing reaction of CP/MAS ^{13}C -NMR spectra (Figure 5) showed that the signal intensity at 844 ppm in AcBTanGlu was enhanced after hardening. Pichelin et al. (2006) demonstrated that hexamethylenetetramine reacted with condensed tannins decomposed into $\text{CH}_2=\text{N}-\text{CH}_2^+$ (amino-imino methylene bases) after heating displaying signals at 845–38 ppm.

In addition, $\text{CH}_2=\text{N}-\text{CH}_2^+$ further reacted with C6 at the A-ring as well as C2' and C5' at the B-ring to form tri-benzylamine or dibenzylamine bonds (Pichelin et al. 1999; 2006), showing signals near 858, 851, and 845 ppm (Pizzi and Tekely, 1995). Hence, our findings of signals at 857, 850, and 844 ppm in the CP/MAS ^{13}C -NMR spectrum of cured AcBTanGlu, and the signal of C6 at 898 ppm on the

A-ring as well as C2' and C5' at 819 and 817 ppm at the B-ring of condensed tannins shifting to lower magnetic fields, are in good agreement with previously reported results (Pizzi and Tekely, 1995; Pichelin et al. 1999; 2006). In other words, condensed tannin of AcBAE could react with hexamethylenetetramine to form a polymer compound of cross-link structure through the polymerization mechanism as shown in Figure 6.

3.3 VOC analysis

Figure 7 shows the gas chromatography-flame ionization detector spectra of VOC emitted from a formaldehyde-glued OBSB sample. Peak one in Figure 7A was formaldehyde; however, this peak did not show in AcBTanGlu-glued OBSB samples (Figure 7B and C). It revealed that

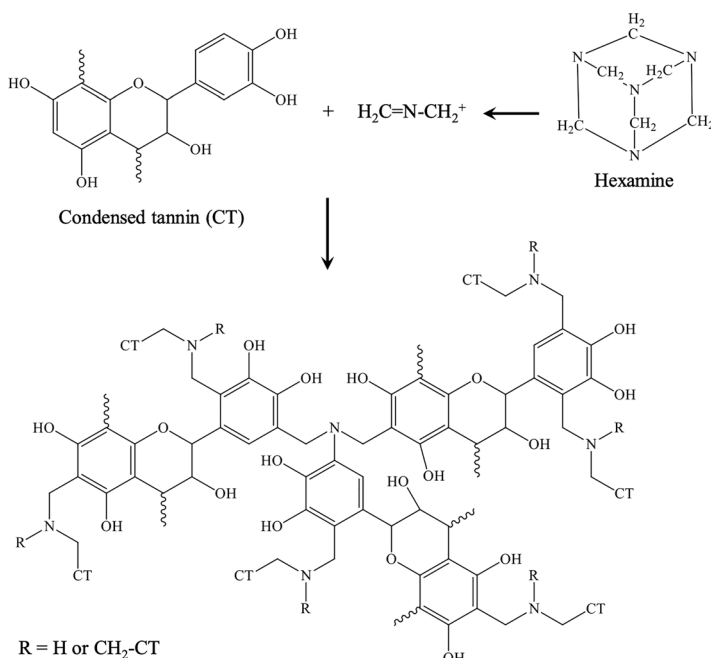


Figure 6: Reaction mechanism of condensed tannins with hexamethylenetetramine of AcBAE.

AcBTanGlu-glued OBSB samples did not emit formaldehyde in their VOCs. Besides, the peak two in B and C was a non-toxic compound, *i. e.* acetic acid compound. It might be generated from lignocellulose material during hot-pressing procedure.

3.4 Thermal stability

Thermogravimetric analysis results of AcBAE and cured AcBTanGlu showed 10% weight loss at a temperature of 268 °C (T_{10}) in AcBAE and 273 °C in cured AcBTanGlu (Figure 8 and Table 1). The increase of T_{10} for cured AcBTanGlu could be attributed to an increase in reticulated polymers after curing. Zhang et al. (2016) also pointed out that the thermal stability of novolac-type resin is proportional to the ratio of reticulated polymer structure.

As shown in Figure 8, the first stage of thermal decomposition of AcBAE began at 186 °C, followed by the second stage at 256 °C, the temperature at which thermal decomposition was most rapid. Finally, the third-stage thermal decomposition temperature was at 526 °C, and the residual weight at 600 °C was rest only 10 wt%. In other words, thermal decomposition of cured AcBTanGlu began at 272 °C, followed by slower thermal deposition at 272–600 °C, and the residual weight at 600 °C remained high at 65 wt%. Taken together, these results observed in cured AcBTanGlu indicated significant improvement in the thermal stability of AcBAE after the curing reaction.

3.5 Changes in chemical composition of AcBTanGlu-glued OBSB

The DRIFT-IR spectra of AcBTanGlu-glued OBSB and untreated bamboo samples were very similar (Figure 9). Further deciphering the absorption signals in the range of

4000–400 cm^{-1} revealed no significant differences in the main reaction signals, that were the lignin characteristic absorption peaks at 1513 and 1603 cm^{-1} ; 1464 cm^{-1} was lignin and carbohydrate; 1329 cm^{-1} was CH cellulose, and 1734 cm^{-1} was for non-conjugated C=O in hemicellulose (Chang et al. 2002). To summarize, the results indicated that bonding with AcBTanGlu had no significant influence on the chemical functional properties of bamboo.

3.6 Mechanical strength

Table 2 summarizes the MOE, MOR, and nail withdrawal resistance testing results of OBSBs glued with the three types of adhesives. The standard deviations of the average density of the three OBSB samples are between 0.01 and 0.04, indicating no significant difference ($P > 0.05$) among them. The MOE of OBSB samples were in the order of PF- (20.7 GPa) > UF- (19.6 GPa) > AcBTanGlu-glued (17.2 GPa) ($P < 0.05$). Similarly, their modulus of rupture were also in the order of PF- (210.5 MPa) > UF- (196.5 MPa) > AcBTanGlu-glued (172.5 MPa) ($P < 0.05$). For both MOE and MOR, the differences among the three OBSB samples were significant ($P < 0.05$). Furthermore, the nail withdrawal resistance of OBSB samples were in the order of AcBTanGlu-glued (160.0 kgf) \geq PF- (158.6 kgf) > UF- (152.4 kgf) with AcBTanGlu-glued and PF- revealing the same higher

Table 1: Thermogravimetric analysis of AcBAE and cured AcBTanGlu.

Samples	T_{10}^* (°C)	Thermal stability in air		Residual yield at 600 °C (wt%)
		1st DTG peak (°C)	2nd DTG peak (°C)	
AcBAE	268	256	526	10
AcBTanGlu	273	272		65

* Temperature at 10% weight loss.

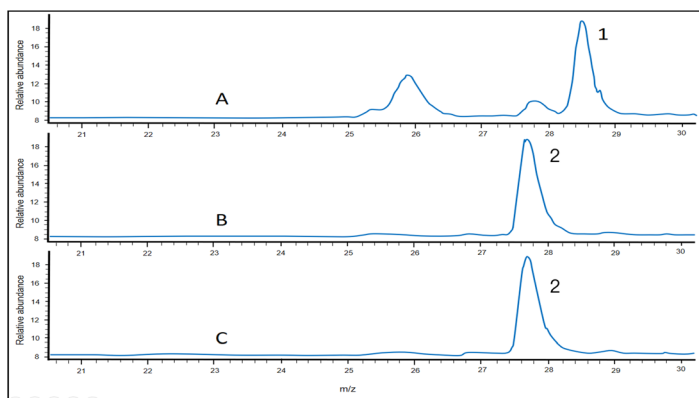


Figure 7: GC-MS spectra of formaldehyde and AcBTanGlu-glued OBSB (A) Formaldehyde used, (B) one piece and (C) two pieces of AcBTanGlu-glued OBSB samples (Peak 1: formaldehyde; Peak 2: acetic acid).

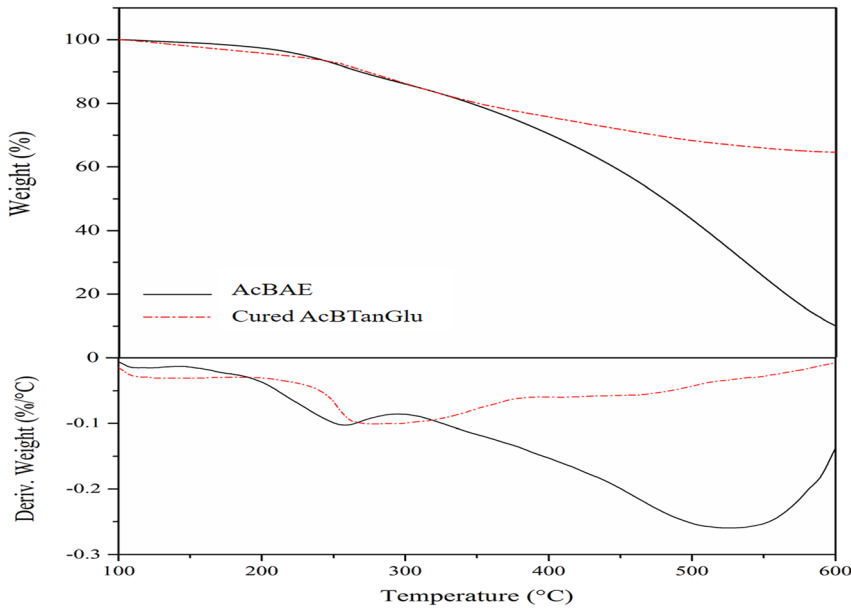


Figure 8: Thermal stability of AcBAE and cured AcBTanGlu.

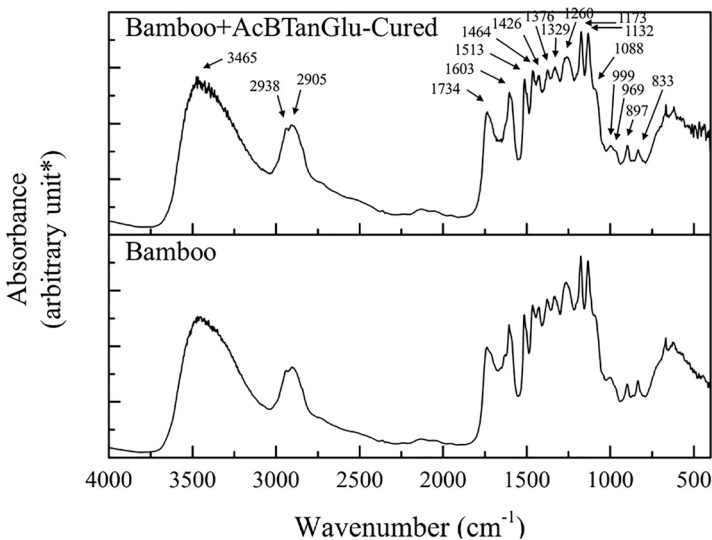


Figure 9: DRIFT spectra of AcBTanGlu-glued OBSB and untreated bamboo samples.

Table 2: MOE, MOR and nail withdrawal resistance of OBSBs glued with three types of adhesives.

Adhesive	Density (g/cm ³)	MOE (GPa)	MOR (MPa)	Nail withdrawal resistance (kgf)
AcBTanGlu	1.02 (0.01) ^a	17.2 (1.3) ^b	172.5 (5.7) ^c	160.0 (4.3) ^a
UF	1.03 (0.02) ^a	19.6 (1.2) ^{ab}	196.5 (6.4) ^b	152.4 (6.5) ^b
PF	1.03 (0.04) ^a	20.7 (2.0) ^a	210.5 (6.3) ^a	158.6 (4.9) ^a

Numbers followed by the letter “a, b, and c” are statistically different at the probability level of $P < 0.05$ according to Tukey’s test and ANOVA.

strength in nail withdrawal resistance. They all exceeded 51 kgf/cm², the CNS 2215 standard on the particle boards of type 35–15.

4 Conclusions

The bark of *A. confusa* was rich in phenolics and condensed tannins comprising mainly B-type flavonoid bonds as measured by analysis using ¹³C NMR and DRIFT-IR. According to CP/MAS ¹³C-NMR analysis, the condensed tannin of AcBAE could react well with hexamethylenetetramine to form a cross-link structure through the polymerization reaction. GC-MS analysis of AcBTanGlu-glued OBSB showed

no formaldehyde emitted in VOCs. The thermal stability was significantly improved in cured AcBTanGlu of high residual weight (65 wt%) maintained at 600 °C. A comparison of the difference in DRIFT-IR spectra between AcBTanGlu-glued OBSB and untreated bamboo indicated that bonding with Acacia tannin glue had no significant influence on the chemical functional properties of bamboo. After statistical analysis of variability, AcBTanGlu-glued OBSBs had lower MOE and modulus of rupture ($P < 0.05$), but same higher nail withdraw resistance with PF-glued OBSBs.

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