

Article

Castor oil-based Polyurethane Resin for Low-density Composites with Bamboo Charcoal

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Abstract: Polyurethane (PU) foam adhesives were prepared from castor oil as a polyol with isocyanate poly (4,4'-methylene diphenyl isocyanate) (PMDI) using a solvent-free process. The NCO/OH molar ratio used for the preparation of PU foams was 1.5. Water, organosiloxane and dibutyltin dilaurate were blowing agent, surfactant and catalyst, respectively. Effects of the ratio of blowing agent and catalyst were adjusted to optimize the properties. The results show that 4 wt% of castor oil of catalyst and blowing agent minimizes water absorption and maximizes volume expansion in the PU foams. FT-IR analysis shows that urethane bond was formed by hydroxyl group of castor oil and –NCO group of isocyanate PMDI. More blowing agent and catalyst could improve the volume expansion ratio and reduce water retention of PU foams. It was found that Moso bamboo charcoal (*Phyllostachys pubescens*) or/and China fir wood particle (*Cunninghamia lanceolata*) composites with setting densities of 500 and 600 kg/m³ can be prepared from optimized castor oil-based PU foam adhesive at 100 °C for 5 min under a pressure of 1.5 MPa. Increasing the amount of bamboo charcoal decreases the equilibrium moisture content, water absorption and internal bonding strength of the composite. Notably, bamboo charcoal composite exhibits excellent dimensional stability. The optimized density and bamboo charcoal percentages of the composite were 500 kg/m³ and 50 to 100%. The castor oil-based PU composites containing bamboo charcoal fulfilled the CNS 2215 standards for particleboard. This dimensionally stable, low-density bamboo charcoal composite has high potential to replace current indoor building materials.

Keywords: Adhesive; bamboo charcoal; castor oil; composites; polyurethane

1. Introduction

Biomass is an abundant renewable resource that differs from dwindling petroleum-based materials since the main component of biomass is hydrocarbons, which can be converted to industrial raw materials. Thus a primary goal for biologically-based chemicals is to produce them directly from biomass, and the bio-refinery is a facility that uses biomass raw materials for bio-based products [1]. Biomass has great potential to help shift consumption towards sustainability in chemicals [2], fuels [3] and other materials [4]. Liquid biomass, such as plant oil, is an excellent candidate to efficiently produce bio-based chemicals, and plant oils have been used as a commercial source of biomass-derived polyols for polyurethane (PU) [5]. Currently, PU resin with a urethane linkage molecular structure is one of the most important polymers for industrial products.

Castor oil, a non-food plant oil, intrinsically contains hydroxyl groups and thus can be used directly as a polyol in chemical industries. Hence, castor oil-based PU resins are an active area of research because of their universal availability, potential biodegradability and low price [6]. PU resin has been used as adhesive, especially as a woodworking, and recent studies have focused on castor oil-based PU adhesives. Somani (2003) indicated castor oil based PU adhesives prepared from aromatic isocyanate show good adhesion strength and chemical resistance [7]. Fiorelli (2012) used castor oil based PU adhesive to prepare coconut fiber-based particulate composite [8]. Cravo et al.

(2015) used cement packaging residues to manufacture particleboards with castor-based PU resin [9]. Tenorio-Alfonso et al. (2017) prepared castor oil-based PU adhesives with cellulose acetate for bonding wood [10]. These results show castor oil can be used for PU adhesive studies. On the other hand, solvents and formaldehyde already are used in a variety of adhesives. But these low-molecular-weight organic compounds are volatile organic compounds (VOCs), which are major air pollutants, especially for indoor environments [11]. Moreover, a previous study indicated solventless castor oil-based PU adhesive joints showed peeling strength values 75% higher than a solvent-based commercial adhesive [12]. Thus castor oil-based PU resin can be an eco-friendly, bio-based adhesive.

Composites combine a fiber and a resin to prepare a matrix with significantly different physical or chemical properties, and PU resin has been used to manufacture lignocellulosic composites. Most previous studies have focused on woody composites, finding that PU and lignocellulosic fibers develop an interfacial interaction for a successful reinforced matrix [8,13,14]. Bamboo charcoal is produced from bamboo, which is a fast-growing speed plant. Bamboo charcoal has many attractive properties, such as high absorption for harmful gases, humidity regulation, emission of far infrared rays, and high thermal stability, making it an excellent candidate for an indoor building material [15-17]. However, there are only very limited studies on bio-based PU resin for bamboo charcoal composite made with a solvent-free process.

Dimensionally stable and low-density ($400\text{--}600\text{ kg/m}^3$) composites are desired to replace conventional plywood panels [18], and bio-based PU foam adhesives from castor oil and PMDI were used to reduce the density. The properties of bio-based PU foams prepared with various dosages of blowing agent and catalyst were measured to determine the optimal conditions for their preparation.

This study develops a solvent-free method and hot-pressing process to prepare low-density bamboo charcoal-PU resin composites that also increases forestry resource utilization. Bamboo charcoal, small-diameter timbers and castor-oil based polyurethane resins were applied for the composite. Castor oil is renewable resource and can be used as a polyol in industry. The water absorption, hygroscopicity, dimensional stability and internal bond strength of the composites were investigated.

2. Materials and Methods

2.1 Materials

China fir (*Cunninghamia lanceolata*) was obtained from the Hui-Sun Experimental Forest Station, and wood particles were ground to pass through a 2.4-mm screen. Bamboo charcoal was prepared from Moso Bamboo (*Phyllostachys pubesens*) in an earth oven between $650\text{--}800\text{ }^{\circ}\text{C}$. The bamboo charcoal was ground to pass between 2.4- to 3.4-mm diameter screens. The wood and bamboo charcoal were dehydrated in an oven at 105°C for 12 h. Castor oil was purchased from First Chemical. Potassium hydroxide (KOH) and pyridine and acetic anhydride were reagent-grade chemicals used without pretreatment. PMDI with the NCO content was used as an isocyanate compound. Organosiloxane and dibutyltin dilaurate were used as surfactant and catalyst, respectively.

2.2 Properties of castor oil and PMDI

Castor oil and PMDI were used directly in the experiments. The acid and hydroxyl value of castor oil and PMDI of NCO% were measured by standard methods [19]. Moisture content of castor oil was measured by Metrohm 703 Ti Stand. Castor oil and PMDI were diluted with THF and deposited on KBr tablets for FTIR analysis. The FT-IR spectra were measured using a Fourier transform infrared spectrometer (Mattson Genesis II) with a diffuse reflectance accessory, and a deuterated triglycine sulfate detector. The spectra were measured within the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} .

2.3 Preparation of PU resins

To prepare the PU resins, molar ratios of the functional group of NCO for isocyanate to OH for castor oil were set as 1.5. Organosiloxane, dibutyltin dilaurate and water were added as the surfactant, the catalyst, and bubble agent, with the formulation shown in Table 1. Castor oil with the bubble agent, surfactant and catalyst were mixed thoroughly first, and then the isocyanate was added and stirring continued. Following previous studies [20,21], the cream time, end of rise time, tack-free time of mixtures and volume expansion were recorded during the foaming process.

Table 1. PU resins formulation.

Code ¹	PMDI (%)	Castor oil (%)	Surfactant (%)	Bubble agent (%)	Catalyst (%)
P-2-2	43.2	64.4	2.58	1.29	1.29
P-2-3	43.2	64.4	2.58	1.29	1.93
P-2-4	43.2	64.4	2.58	1.29	2.58
P-3-2	43.2	64.4	2.58	1.93	1.29
P-3-3	43.2	64.4	2.58	1.93	1.93
P-3-4	43.2	64.4	2.58	1.93	2.58
P-4-2	43.2	64.4	2.58	2.58	1.29
P-4-3	43.2	64.4	2.58	2.58	1.93
P-4-4	43.2	64.4	2.58	2.58	2.58

¹P-x-y: Amounts of bubble agent and catalyst are x and y wt% of castor oil.

2.2 Characterization of PU resins.

2.2.1. FT-IR analysis

PU resins were ground to pass through a 150-μm screen and remove water by vacuum drying oven at 40 °C overnight. The samples were mixed with KBr powder at a weight ratio of 1:100. The subsequent method was the same as that previously mentioned in properties of castor oil and PMDI.

2.2.2. Density, Water absorption and water retention

The methods of water absorption and water retention of PU foams followed a previous study [19]. PU foam specimens with of 2 × 2 × 2 cm³ were used for density and water immersion testing. The density was calculated by the weight and the volume of the foams, with average values are reported. The water immersion testing was carried out by dipping the specimens into de-ionized water and measuring the degree of water absorption and water retention after 7 days at room temperature. Water absorption (%) and water retention (g/cm³) were calculated as follows: Water absorption (%) = (W₁–W₀)/W₀×100 and Water retention (g/cm³) = W₁/V₀; where W₀, W₁ and V₀ denote initial weights, wet weights and volumes of PU foams, respectively.

2.2.3. Weight retention

The measurement of weight follows a previous investigation [22]. PU foam specimens with dimensions of 1 × 1 × 1 cm³ were used to measure weight retention after water immersion. The specimens were immersed into 600 mL of water at 50 °C for 1 h followed by vacuum oven drying at 60°C and calculating weight retention. Weight retention (%) = (W₃–W₂)/W₂×100; where W₂ and W₃ denote initial and oven-dried weights of PU foams.

Five specimens were tested for each experiment.

2.3. Preparation of bamboo charcoal/wood composites

PU resins were prepared by castor oil with PMDI with R of 1.5. Amounts of the organosiloxane, dibutyltin dilaurate and water were 4 wt % of castor oil. The PU resin was mixed with bamboo charcoal or/and wood particle a 15:10 weight ratio. Percentages of bamboo charcoal particles were set to 100, 75, 50 and 0 %. Densities of composites were set to 0.5 and 0.6 g/cm³. To manufacture the

composites, castor oil, surfactant, and catalyst were mixed and stirred, and then the isocyanate and bamboo charcoal/wood particles were added and stirred thoroughly again. The reactive mixture was put into a metal mold $15 \times 15 \times 1.2 \text{ cm}^3$, and the samples were cured at 100°C for 5 min under a pressure of 1.5 MPa.

2.4. Characterizations of bamboo charcoal/wood composites.

Bamboo charcoal/wood composites of $5 \times 5 \times 1.2 \text{ cm}^3$ were used for all testing. Composites were held at 70% relative humidity (RH) and 27°C until weight stability. Then equilibrium moisture content was determined using an oven drying method at 103°C until an approximately constant weight was measured. Density and water immersion testing used the same methods as PU foams. Thickness swelling and internal bond strength were measured following the CNS2215:2017 standard [39].

2.5. Statistical analyses

Results for PU resin and composites are shown as mean and standard deviation. Statistical analysis was performed using SPSS software version 20 (SPSS Inc., Chicago, IL, USA). Tukey's multiple range test was used to find the statistical significance ($P = 0.05$) between pairs.

3. Results and Discussion

3.1. Basic Properties and Reactivity of Castor oils and PMDI

Acid value and hydroxyl value are related to the degradation degree of the $-\text{COOH}$ and $-\text{OH}$ groups from castor oil. To prepare PU resins, castor oil is an excellent candidate because it is rich in OH groups. The acid value and hydroxyl value of castor oil were 1.8 and 193.8 $-\text{KOH/g}$, similar to a previous study [23]. The moisture content of castor oil was 0.12%. In addition, isocyanate contains $-\text{NCO}$ groups that could react with $-\text{COOH}$ and $-\text{OH}$ groups to yield a urethane linkage, and the $-\text{NCO}$ of PMDI is 28.9%. Results for the raw materials indicated the functional groups of raw materials agreed with the prepared PU resins.

Table 2 shows the foaming behavior of PU resin with respect to the reactivity of castor oils and PMDI by an exothermic process. Cream time, end of rise time and tack-free time can be shortened with increased bubble agent, and the results indicated increasing bubble agent can help the rate of expansion and gelation rate. [24] On other hand, catalyst concentration did not yield a significant foaming behavior. The volume expansion of PU resins is greater than 250%. These phenomena may be due to $-\text{OH}$ groups of castor oils reacting with $-\text{NCO}$ groups of PMDI.

Table 2. Foaming behavior of the PU resins.

Code	Cream time (s)	End of rise time (s)	Tack free time (s)	Volume expansion (%)
P-2-2	32	62	90	250
P-2-3	33	62	81	360
P-2-4	31	62	83	500
P-3-2	26	46	58	300
P-3-3	26	48	60	340
P-3-4	29	56	80	380
P-4-2	22	47	54	300
P-4-3	28	47	60	330
P-4-4	23	41	59	350

3.2. Properties of PU resins

This investigation used castor oil as a raw material for polyol, PMDI as isocyanate, water as a blowing agent and organosiloxane as a surfactant. In our previous study, the amount of catalyst was optimized and fixed as 4% [25]. Table 3 displays the water absorption and resistance of PU resins prepared with castor oil. The amount of catalyst and bubble agent was adjusted with 2 to 4 wt% of castor oil. With increasing bubble agent, the density of PU resins increased, while their water absorption decreased significantly. On the other hand, water retention of PU resins slightly decreased with increasing surfactant. All weight retentions of PU resins are similar and higher than 98.5 %. Therefore, the network structure of PU resins is formed because of a complete crosslink reaction in a well-blended mixture of raw materials. These results demonstrate P-4-4 has low water retention and high volume expansion.

Table 3. Density, water absorption and resistance of PU resins.

Code	Density (kg/m ³)	Water absorption (%)	Water retention (g/cm ³)	Weight retention (%)
P-2-2	25.7±0.6 ^{EF,1}	43.0±4.5 ^{AB}	0.11±0.01 ^B	99.0±0.1 ^A
P-2-3	17.8±0.3 ^B	61.4±4.1 ^{CD}	0.11±0.01 ^B	99.2±0.7 ^A
P-2-4	13.3±0.2 ^A	88.6±3.7 ^E	0.12±0.01 ^B	99.0±0.1 ^A
P-3-2	25.8±0.4 ^F	36.1±2.8 ^A	0.09±0.01 ^{AB}	99.2±0.1 ^A
P-3-3	24.1±0.8 ^E	42.2±3.3 ^{AB}	0.10±0.01 ^{AB}	99.2±0.1 ^A
P-3-4	17.8±0.3 ^B	65.7±5.5 ^D	0.12±0.01 ^B	98.3±1.8 ^A
P-4-2	25.0±1.4 ^{EF}	33.8±3.5 ^A	0.08±0.01 ^A	98.6±0.1 ^A
P-4-3	21.0±0.7 ^C	49.9±6.4 ^{BC}	0.11±0.01 ^B	98.5±0.2 ^A
P-4-4	22.2±0.3 ^D	50.7±6.2 ^{BC}	0.10±0.01 ^{AB}	98.5±0.1 ^A

¹ Means and standard deviation with different capital letters indicate significant differences between PU resins using Tukey's multiple range tests at $p < 0.05$.

3.3. FTIR spectra of PMDI, castor oil and PU resins

The FTIR spectra of castor oil and PMDI are shown in Figure 1a, where 2274 cm⁻¹ is assigned to the -NCO group of isocyanate PMDI. Castor oil shows a broad hydroxyl band between 3640 and 3210 cm⁻¹, and a typical triglyceride ester methyl/methylene and carbonyl at 2927/2274 and 1745 cm⁻¹ [26]. Figure 1b shows the FTIR spectra of PU resins P-4-2, P-4-3 and P-4-4. The spectrum for the PU resins derived from castor oil and PMDI shows a very similar pattern, indicating that the amount of catalyst has no effect on the structure. The broad band around 3344 cm⁻¹ was attributable to the amine group (NH stretch) and existence of the hydroxyl group. Absorption bands were assigned to methyl (2926 cm⁻¹) and methylene (2853 cm⁻¹) groups from castor oil. The very weak absorbance band between 2200–2300 cm⁻¹ was due to the -NCO group. Since PMDI can be a wood adhesive, the -NCO group of PMDI was also demonstrated and its reaction with both the -OH group and water in the PMDI/wood mixtures. Therefore, residual isocyanates were attributed to networks between resin and fillers [27,28]. The absorption band at 1727 cm⁻¹ was due to carbonyl stretching vibration (amide I band) of the urethane linkages [29]. The band at 1524 cm⁻¹ assigned to N-H and C-N bending vibration of urethane linkages [30]. The two bands 1219 and 1047 cm⁻¹ are attributed C-O stretching vibration and C-O-C stretching vibration [31]. The absorption bands at 1727, 1524 and 1219 cm⁻¹ demonstrated urethane linkages that were formed between castor oil and PMDI.

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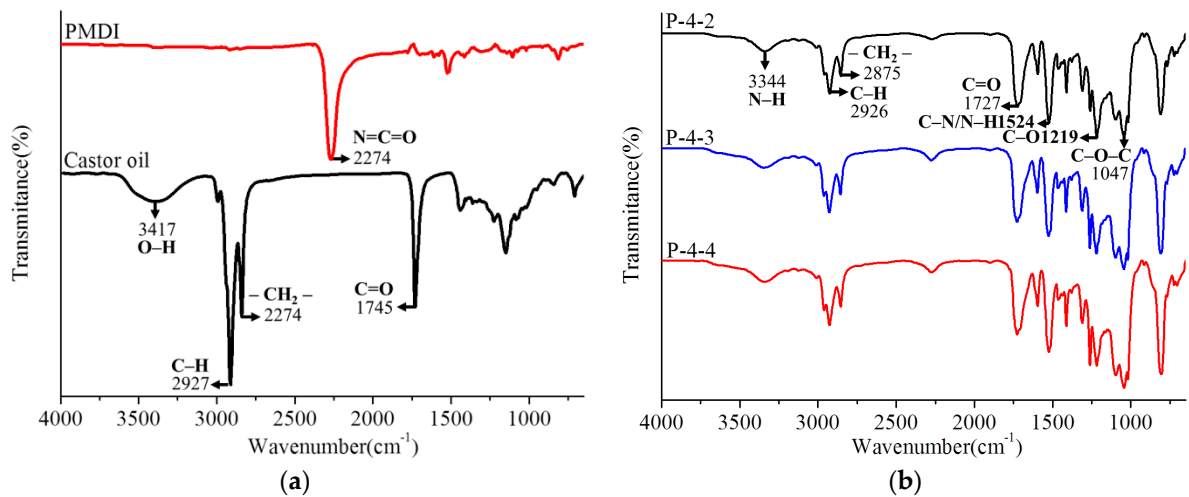


Figure 1. FTIR spectra of PMDI, castor oil (a) and PU resins (b).

3.4. Basic properties of bamboo charcoal/wood composite

The previous results show P-4-4 with high water resistance and low-density is the optimal condition for charcoal/wood composite. Originally, the PU resin was mixed with particles at a 10:10 weight ratio, but the composite collapsed, indicating that PU resin cannot form a stable foam structure with good adhesive property. After modifying the ratio of PU resin and particles to 15:10, bamboo charcoal/wood composites were prepared successfully, as shown in Figure 2. Bamboo charcoal, wood particles and PU resin were homogenously distributed in the low-density composites. Figure 3 shows the densities of bamboo charcoal/wood composite are between 444 and 609 kg/m³. The result shows that densities of wood composites match the setting densities. On the other hand, densities of bamboo charcoal/wood composite decreased significantly when their percentage of charcoal was increased. Densities of P-4-4, bamboo charcoal and wood are 22.2, 690 and 360 kg/m³. Therefore, the bamboo charcoal composite occupies more space than the wood composite and can form PU foam. Wechsler et al. (2013) indicated the density of the castor oil-based macadamia shell and pine wood particleboards were 987 and 691 kg/m³ [32], indicating that castor oil-based PU resin can produce low-density composites in this formulation.

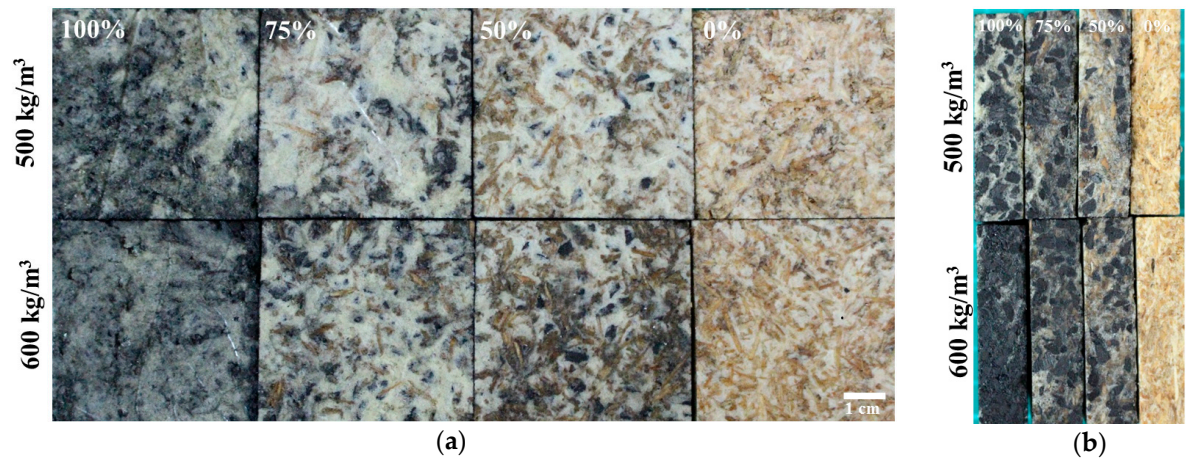


Figure 2. Front view (a) and side view (b) of charcoal/wood composites.

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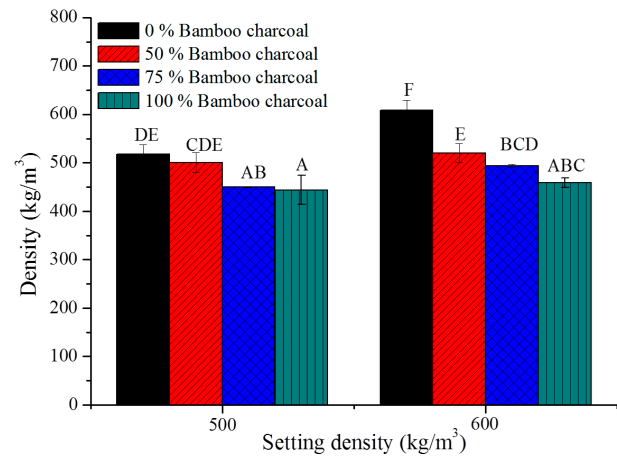


Figure 3. Densities of bamboo charcoal/wood composites. Means with different capital letters indicate significant differences between bamboo charcoal composites using Tukey’s multiple range tests at $p < 0.05$.

221 *3.5. Moisture content and water absorption of bamboo charcoal/wood composites*

222 Lignocellulose materials hold bound water and free water in their cell walls and cavities
223 because of the surface hydroxyl groups. Hygroscopicity influences dimensional stability, mechanical
224 properties, thermal properties and durability [33]. Figure 4(a) shows the equilibrium moisture
225 content of bamboo charcoal/wood composites to be lower than 2.67 %. With the density at 500 kg/m³,
226 the charcoal/wood composite is significantly lower than other specimens. The previous investigation
227 indicated the equilibrium moisture content of raw straw particleboard with methylene diphenyl
228 diisocyanate and urea formaldehyde adhesive to be 7.65 and 7.97% at 65% RH and 23°C. These
229 results are due to low hydroxyl groups binding water on the surface of the composites [34]. Figure
230 4(b) shows the water absorption of bamboo charcoal/wood composites, which are substantially
231 lower than wood composites. The water absorptions of bamboo charcoal composites are 10.8 and
232 8.8% with setting densities of 500 and 600 kg/m³, and the water absorption of PU resins decreased
233 slightly with increased bamboo charcoal content. Cravo et al. (2015) found water absorption of
234 castor-based resin paper residues particleboards to be 70.4 and 56.8% with densities of 500 and 600
235 kg/m³ [9]. Water absorption of conventional particleboard with urea-formaldehyde adhesive is 31.0
236 to 41.0 % with densities of ca. 700 kg/m³ [35]. Bamboo charcoal and castor-oil based PU resin both are
237 highly hydrophobic [5,36]. These results demonstrate that bamboo charcoal-based composites
238 manufactured from castor oil-based PU resin can help reduce water absorption and hygroscopicity
239 of materials.

240 *3.6. Dimensional stability of bamboo charcoal/wood composites*

241 For traditional lignocellulose composition, dimensional stability is a basic requirement. Figure
242 4c and d shows the thickness and volume swelling of bamboo charcoal/wood composites after 24 h
243 water soaking. The results indicate thickness and volume swelling decreased significantly with
244 bamboo charcoal added to the composite. Thickness swelling of bamboo charcoal/wood composites
245 is less than 2.41%, and volume swelling of bamboo charcoal/wood composites ranged from 3.83 to
246 -0.14%. Notably, the thickness swelling values of bamboo charcoal composites are -0.27 and -0.02%
247 with densities of 500 and 600 kg/m³. Fabiyi et al. (2011) and Fuentes Talavera et al. (2007) show the
248 thickness swellings of wood and bagasse plastic composite with high-density polyethylene ranged
249 from 1.68 to 5.82% and 6.9 to 15.3% after 1-day water soaking [37,38]. Que et al. (2007) indicated
250 thickness swelling of urea-formaldehyde conventional particleboard is 13.8 and 16.3 % [35]. This
251 result indicates that bamboo charcoal composites are much more dimensionally stable than other
252 wood composites, highlighting the importance of the bamboo charcoal and castor oil-based PU

resin in the formulation. The bamboo charcoal-based composite has high dimensional stability that is attributable to its hydrophobicity.

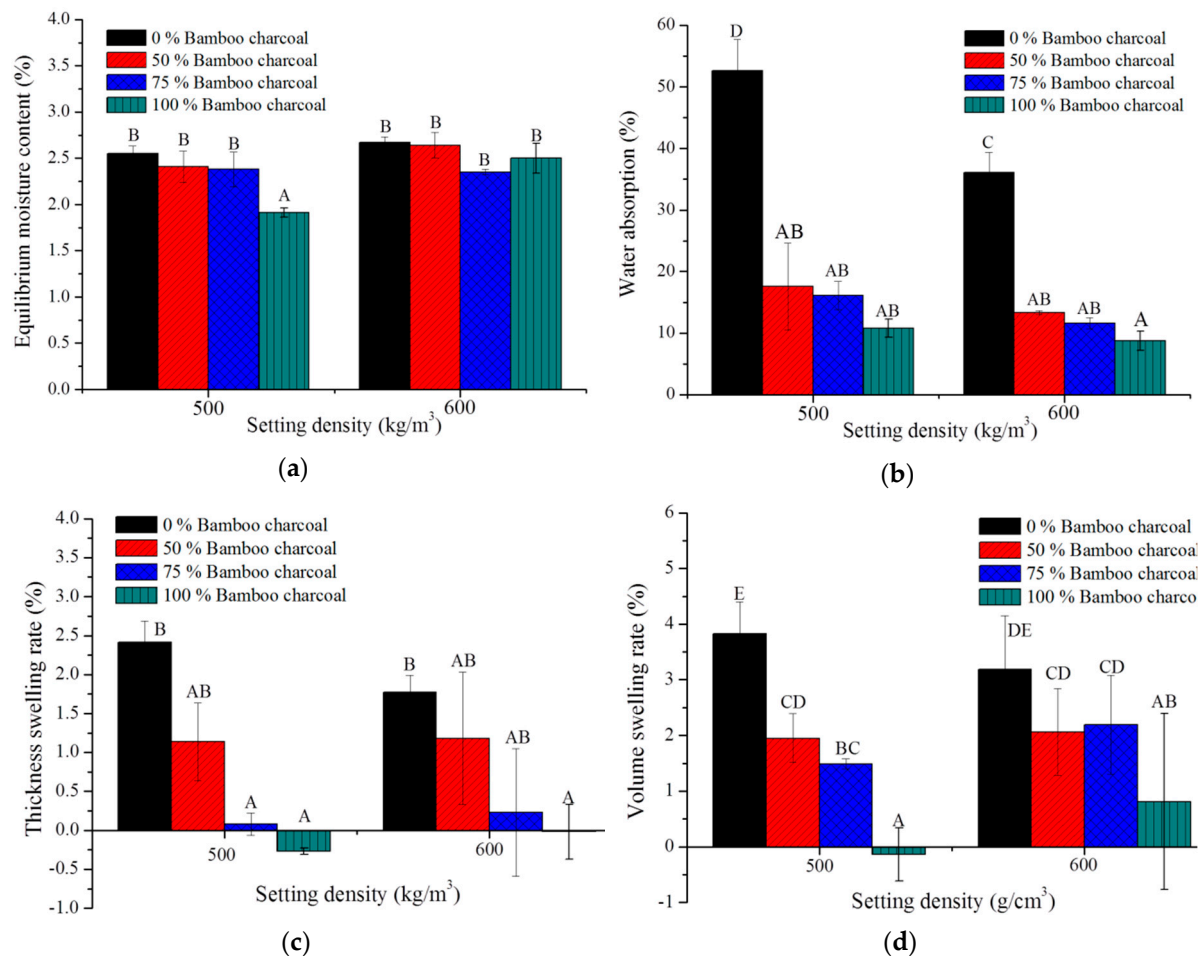


Figure 4 Equilibrium moisture content (a), water absorption (b), Thickness (c) and volume swelling rate (d) of bamboo charcoal/wood composites. Means with different capital letters indicate significant differences between bamboo charcoal composites using Tukey's multiple range tests at $p < 0.05$.

3.7. Internal bond strength of bamboo charcoal/wood composites

The Chinese National Standards, CNS2215:2017 [39], Type 18, 13 and 8 minimum requirements for internal bond strength are 0.3, 0.2 and 0.15 MPa, respectively. Figure 6 shows the internal bond strength of bamboo charcoal/wood composites is from 0.35 to 0.92 MPa. Increased wood content could increase the internal bonding strength. Que et al. (2007) and Wang et al. (2007) show the internal bond strength of conventional particleboard strength with urea-formaldehyde and PMDI to be 0.88 and 0.56 MPa [35,40]. Internal bond strength of all composites can fit the requirements for Type 18 of CNS2215:2017, similar to other composites. For conventional particleboards, internal bonding strength and density are highly correlated in direct proportion [41], and bamboo charcoal composites are similar. The internal bond strength of bamboo charcoal/wood composites with a density of 500 kg/m³ was slightly higher than those with density of 600 kg/m³. The results show the good performance of castor-oil based PU resin for adhering wood and bamboo charcoal.

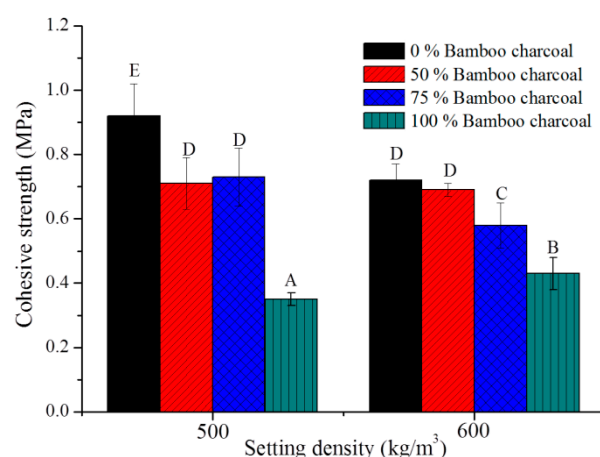


Figure 5. Internal bond strengths of bamboo charcoal/wood composites. Means with different capital letters indicate significant differences between bamboo charcoal composites using Tukey's multiple range tests at $p < 0.05$.

4. Conclusions

PU resins were prepared by blending castor oil with PMDI at a molar ratio of NCO/(COOH+OH) of 1.5. Water, organosiloxane and dibutyltin dilaurate were added as blowing agent, surfactant and catalyst, respectively. Blowing agent and catalyst should be adjusted to optimize the properties as castor oil was used in the manufacturing of PU resins. The results demonstrate that 4% catalyst and blowing agent should be added to minimize water absorption and maximize volume expansion as castor oil was used in the manufacturing of PU foams. The composites had a mixture of PU resin and bamboo charcoal/wood particle of *Cunninghamia lanceolata* with a weight ratio of 1.5/1.0 by hot-pressing. The properties of composites made with different conditions were investigated. Comparing different ratios of wood particle and bamboo charcoal, using completely bamboo charcoal as the raw material had the best dimensional stability. The bamboo charcoal/wood composite with 500 kg/m³ had higher internal bonding strength than particleboards with 600 kg/m³. Internal bonding strength of bamboo charcoal/wood particleboards decreased slightly with higher bamboo charcoal ratio for the particleboards. Internal bonding strength of 50% bamboo charcoal composite was equal to completely wood particleboard. Future functional study of this product can help its applications in the forest product and building material industries.

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