

The Effect of Bamboo Charcoal on Water Absorption, Contact Angle, and the Physical-Mechanical Properties of Bamboo/Low-Density Polyethylene Composites

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The use of bamboo charcoal (BC) was investigated as a filler in bamboo-plastic composites (BPCs) to achieve improved water resistance, physical-mechanical properties, and reduced hydrophilicity. The influence of the BC content and size on the water absorption, contact angle, density, and mechanical properties of bamboo flour/low-density polyethylene (LDPE) composites was tested. Scanning electron microscopy was used to analyse fractured and flat composite surfaces. The results indicated that the BC increased water resistance, achieving optimal results at 8% content. The BC particles that ranged in size from 60 to 100 mesh were more water-resistant than other sized BC. The water contact angle increased with an increase in the BC content or a decrease in the particle size. These results indicated that BC reduced the composite hydrophilicity and that the smaller BC particles improved this effect. The BC strongly connected with the LDPE composites, and the BC contents below 12% improved the flexural properties and increased the density of the BPCs. Also, the impact strength of the BPCs decreased dramatically with a decrease in the BC particle size. These results demonstrated that the integration of BC with BPCs resulted in strengthened water resistance and physical-mechanical properties and reduced hydrophilicity.

Keywords: Bamboo-plastic composite; Bamboo charcoal; Water absorption; Contact angle; Physical-mechanical properties

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INTRODUCTION

Bamboo is an important natural resource that grows faster than trees and is stronger than wood (Jiang 2007). Bamboo-plastic composites (BPCs) are manufactured *via* hot pressing and extrusion or injection moulding using thermoplastics and bamboo instead of wood (Yeh *et al.* 2009; Wu *et al.* 2013). BPCs are widely used in decorations, outdoors, and as non-structural components of buildings (Xian *et al.* 2015) because they are biodegradable, renewable, and environmentally friendly materials (Zhou *et al.* 2015a). However, the interface between the polar, hydrophilic bamboo fibres and the non-polar, hydrophobic low-density polyethylene (LDPE) is weak, which leads to the formation of many gaps and pores between the two materials. This incompatibility results in poor mechanical properties and renders the composites vulnerable to water penetration and fungal attack (Hosseinihashemi *et al.* 2011; Mbarek *et al.* 2013). Bamboo fibre processing (Li *et al.* 2013) and coupling agent addition (Tran *et al.* 2013) are widely used

techniques for improving the compatibility of plant fibres and polymers. Another method of eliminating gaps is filler addition, which is a simple and low-cost way to effectively improve the composite morphology and mechanical properties. Nanofillers (Deka and Maji 2012), glass fibres (Zolfaghari *et al.* 2013), and carbon (Li *et al.* 2014) are among the most widely used reinforcement fillers.

Bamboo and the remainders of processed bamboo can be used to prepare bamboo charcoal (BC) at high temperatures under a nitrogen atmosphere. Bamboo carbonization could alleviate the high demand for wood charcoal and increase the utilization of bamboo resources. Furthermore, BC is a good reinforcement material for all types of polymers (Lou *et al.* 2007; Kittinaovarat and Suthamnoi 2009; Ho and Lau 2014; You and Li 2014; Ho *et al.* 2015), wood-plastic composites (WPCs) (Li *et al.* 2014), and BPC (Zhu *et al.* 2016). In addition to being a stiff material, BC also exhibits unique properties, including high porosity, high moisture resistance, odour control, bacterial and fungal growth inhibition, and heavy metal absorption (Kittinaovarat and Suthamnoi 2009; Ho and Lau 2014). Because BC is very porous, polymers can permeate these pores, strengthening the BC-polymer interface and thus enhancing the mechanical properties of the composites. Li *et al.* (2014) reported that the mechanical properties, water resistance, and thermal properties of WPC with BC were higher than WPCs, and Zhu *et al.* (2016) also found the same results while the BC nanoparticles enhance BPCs. You *et al.* (2014) reported a strong interfacial interaction between BC and polymers because the $\tan\delta$ decreased with an increase in the BC content. Thus, Tang *et al.* (2015) thought that the OH groups of the BC nanoparticles may strongly interact with the polymer. Furthermore, hydrophilic groups are reduced during the process of bamboo carbonization (Jianbin 2005), which improves the water resistance of composites containing the BC. Zhang *et al.* (2016) reported that carbon nanotubes could increase the water resistance due to the hydrophobicity. Overall, BC is an excellent filler for enhancing the mechanical properties as well as water resistance of composite materials.

While fibre size is known to affect composite properties (Migneault *et al.* 2009; Tisserat *et al.* 2014), this study confirmed that the BC particle size also affects composite strength. Larger BC particles are high-aspect-ratio strips that enhance composite strength, while smaller BC particles have a larger specific surface area and absorption capacity (Sun *et al.* 2010). To date, few studies have investigated the influence of BC size on BPC properties or examined how different BC filler contents and sizes impact the strength of BPCs. Therefore, the objectives of this research were to explore the influence of BC content and size on the water absorption, contact angle, density, mechanical properties, and morphology of BPCs.

EXPERIMENTAL

Materials

Bamboo flour (BF) was purchased from the Wood River Weihua Spices Factory (Jiangmen City, Xinhui District, Shuangshui Town, Guangdong Province, China). LDPE was purchased from SuZhou Joe Shun Plastic Co., Ltd. (Suzhou, China). The bamboo charcoal (BC) was purchased from QuZhou Nine Wave E-commerce Co., Ltd. (Zhejiang, China). A coupling agent was purchased from NanJing YouPu Chemical. Co., Ltd. (Nanjing, Jiangsu, China). Ethanol and acetic acid was purchased from Beijing Chemical Co., Ltd. (Beijing, China).

Specimen Preparation

The tested formulations of the BPCs with BC are shown in Table 1. The BF was treated with silane coupling agent (vinyltrimethoxysilane). The coupling agent was dissolved in ethanol with the concentration of 4 wt.%, and the pH of the solution was adjusted to the range 4.5 to 5.5 by adding acetic acid. The coupling agent solution was heated to 60 °C for 10 min, then the solution was sprayed onto the BF uniformly at room temperature with the mass ratio of coupling agent to BF 1:1. The treated BF was placed under ventilation to allow the alcohol to evaporate and was subsequently oven-dried for 24 h at 100 °C ± 1 °C. The BF, LDPE, and BC were then premixed for 30 min in a malaxator (NH-1, Guancheng Machine Co., Ltd., JiangSu, China) at 50 °C (i.e., the temperature of the materials). The mixtures were placed in a mould and hot-pressed at 150 °C for 30 min. Finally, the composites were removed while the temperature was reduced to 35 °C.

Table 1. The Formulations of BPCs with BC

	BF (wt.%)	LDPE (wt.%)	BC (wt.%)	BC (mesh)
BPC	60	40	0	/
BPC-BC _{4%}	56	40	4	>40
BPC-BC _{8%}	52	40	8	>40
BPC-BC _{12%}	48	40	12	>40
BPC-BC _{16%}	44	40	16	>40
BPC-BC _{40 to 60}	50	40	10	40 to 60
BPC-BC _{60 to 80}	50	40	10	60 to 80
BPC-BC _{80 to 100}	50	40	10	80 to 100
BPC-BC _{>100}	50	40	10	>100

Specimen testing

Water absorption

The water absorption test was carried out according to ASTM D 570 (2005). The dimensions of samples were 45 × 45 × 4.5 mm (length × width × thickness). Five samples of one set were tested using deionized water. Before starting the test, all specimens were placed in an oven at 50 ± 1 °C for 24 h, followed by immersion in the deionized water at 21 °C. Readings were after 1h, 4h, 9h, 16h, 25h *et al.* until the test end since the initial part of water absorption versus \sqrt{t} plot is fairly linear (Tamrakar *et al.* 2011). The specimens were periodically removed from the water and wiped off with blotting paper to measure the weight, and then replaced in the water.

The percentage of water absorbed ($M\%$) was calculated using Eq. 1,

$$M\% = (m_t - m_0) / m_0 \quad (1)$$

where m_0 and m_t are the mass of the composite before and after immersion in water, respectively, for the indicated periods.

Contact angle

Three different types of liquids were used to test the contact angle: distilled water, a strongly polar liquid ($r_p = 51$ mN/m, $r_d = 21.8$ mN/m), formamide, a weakly polar liquid ($r_p = 19$ mN/m, $r_d = 39$ mN/m), and diiodomethane, a non-polar liquid ($r_p = 0$ mN/m, $r_d = 50.8$ mN/m).

An OCA20 video-based instrument from Dataphysics (DSA100, Hamburg, Germany) was used to measure the contact angle optically. The volumes of water, formamide, and diiodomethane used for each test were 3 μL , 3 μL , and 0.8 μL , respectively. Three samples from each group were tested, and three points were included from each specimen. During the tests, the temperature was 26 $^{\circ}\text{C}$, and the humidity was 15%.

Density

The density of the materials was assessed using a Solid Densimeter (GH-120E, Taiwan Matsu Haku Scientific Instrument Co., Ltd., Xiamen, China). Prior to this test, all specimens were oven-dried to a constant weight at 100 ± 1 $^{\circ}\text{C}$. The results represent the average of at least five samples.

Mechanical properties

Flexural testing was performed in accordance with the ASTM D 790 (2010) using a universal testing machine (Instron 5582, Norwood, MA, USA). The length \times width \times thickness of samples were $90 \times 15 \times 4.5$ mm, and the test speed was 10 mm/min. Notched impact tests were conducted in accordance with the ASTM D 6110 (2010) standard using an impact-type testing machine (XJJ-5, Kecheng Testing Machine Co., Ltd., Chengdu, China). The dimensions of impact test samples were same as flexural test samples. At least five samples were used for each test type.

Characterization

The surfaces of the samples subjected to impact testing were first sputtered with a layer of golden and then analysed using a scanning electron microscope (JSM-6310F, JEOL, Tokyo, Japan) at an accelerating voltage of 10.0 kV.

Statistical analysis

Statistical differences among the variables were analysed using analysis of variance (ANOVA) and SPSS software (SPSS Inc., Chicago, USA). The statistical significance was determined using a 95% confidence interval.

RESULTS AND DISCUSSION

The ANOVA results are shown in Table 2.

Table 2. ANOVA Results Describing the Effects of BC Content and Size on the Properties of BPCs

Properties	BC Content		BC Size	
	F-value	P-value	F-value	P-value
Water absorption	140.854	0.000**	19.756	0.000**
Contact angle (water)	32.245	0.000**	7.398	0.001*
Density	19.579	0.000**	6.432	0.05*
MOR	21.720	0.000**	9.140	0.001*
MOE	39.602	0.000**	3.192	0.52 ^{ns}
Impact strength	2.669	0.062 ^{ns}	48.798	0.000**

*Significant difference at the 95% level; **significant difference at the 99% level; ns= not significant

The water absorption, contact angle, density, and flexural properties all varied greatly with the changes in the BC content. However, the effect of the BC content on the impact strength was not significant. In contrast, the effect of the BC particle size on the impact strength was significant, while the BC particle size had influenced the water absorption, contact angle, density and modulus of rupture (MOR) to a lesser extent. The effect of the BC particle size on the modulus of elasticity (MOE) was not significant.

Water absorption

Water absorption was tested in deionized water for 779 h at 21 °C, and the water absorption percentages are shown in Fig. 1. Almost all of the specimens absorbed the water rapidly in the early stages of immersion, and then the absorption slowed until equilibrium conditions were reached.

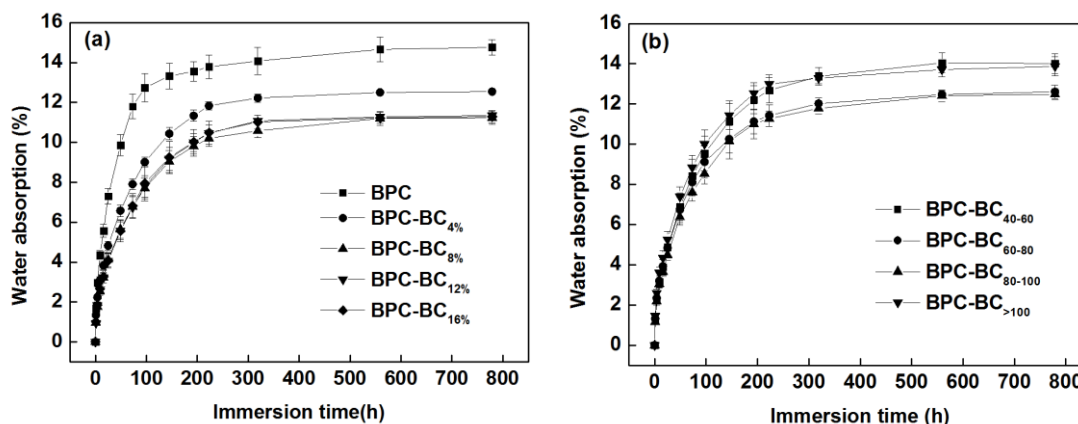


Fig. 1. Water absorption curves of BPC with different BC contents (a), and sizes (b)

With a decreasing bamboo fibre content and increasing BC content, the water absorption first decreased and then became nearly invariant (Fig. 1(a)). The lowest water absorption was 11.23%, which occurred with a BC content of 8%, and the highest water absorption was 14.77%, which was observed in the BPC samples without BC. These results indicated that the addition of BC increased the composite water resistance, as it could fill the gaps within the BPC (Zhou *et al.* 2015b). The results showed that the water absorption remained steady, even with a BC content of 8%. This effect occurred because when the BC content in the composite was high, it could aggregate (Zhou *et al.* 2015b) and generate many channels and gaps. Water could be absorbed through these channels and fill the gaps (Bouafif *et al.* 2009), so water absorption increased. But the decreasing of bamboo fibre could lead to the decreasing of water absorption. It could be speculated that these two factors function together so that the equilibrium water absorption appeared to be the same when the BC content increased from 8% to 16%.

Figure 1(b) shows the effect of BC particle size on water absorption when the content was maintained at 10%. With a decreasing BC particle size, the water absorption first decreased and then increased. While the content of the BC was invariant, the changes in the water absorption were caused by the presence of the channels and gaps in the composites (Bouafif *et al.* 2009). Neither the larger nor the smaller BC particles could fill the gaps between the LDPE and bamboo fibres. Thus, the water absorption also decreased with decreased BC particle size. However, the smaller BC particles have a larger specific surface area and absorption capacity (Sun *et al.* 2010). Furthermore, the

water resistance decreased when the BC particles that were larger than 100-mesh were present in the composites.

Fickian diffusion is suitable for describing water absorption behavior (Espert *et al.* 2004; Adhikary *et al.* 2008; Zabihzadeh *et al.* 2010; Tamrakar *et al.* 2011). As such, the diffusion coefficient (D_x) was calculated using the following equation,

$$D_x = \frac{\pi}{16M_\infty^2} \left[\frac{M_t}{\sqrt{t}/h} \right] \quad (2)$$

where M_t is the water content at a specific time, t ; M_∞ is the maximum water content, and h is the thickness of the specimens, in mm. The value of $M_t / (\sqrt{t}/h)$ can be determined from the slope of M_t vs. \sqrt{t}/h .

The resulting diffusion coefficients are shown in Table 3. The highest value of D_x was observed for the BPCs not containing BC. With the temperature and medium remaining constant, the lower D_x values represent denser composites, indicating that the BC filled gaps within the BPC. The variation of D_x with an increasing BC content was almost the same as that of the water absorption. When the BC content was greater than 8%, the exposed bamboo fibres and newly formed gaps had an increased D_x .

Table 3. Diffusion Coefficients for BPCs with Different BC Contents and Mesh Sizes

Composite	h (mm)	M_∞ (%)	D_x (10^{-12} m ² /s)
BPC	4.5	14.77	1.63
BPC-BC _{4%}		12.58	1.61
BPC-BC _{8%}		11.23	1.54
BPC-BC _{12%}		11.35	1.58
BPC-BC _{16%}		11.29	1.61
WPC-BC ₄₀₋₆₀		14.01	1.25
WPC-BC ₆₀₋₈₀		12.61	1.56
WPC-BC ₈₀₋₁₀₀		12.48	1.48
WPC-BC _{>100}		13.87	1.42

The D_x values of the BPCs containing the BC of different particle sizes are also shown in Table 3. Interestingly, the effect of the BC particle size on the D_x was the opposite of its effect on the water absorption. This difference may be the result of several factors related to the BC particle size, including the specific surface area and particle distribution within the composites; however, further investigations are needed to identify the exact cause.

Contact angle

The water contact angle of these composites essentially reflects the hydrophilicity of the surface. Water droplets have difficulty spreading on hydrophobic surfaces, and the more rounded water that droplets remain, the larger the contact angle becomes. Because LDPE is a non-polar and hydrophobic material, the water contact angles of the tested BPCs (Table 4) were higher than that of bamboo, which ranges from 50° to 70° (Ahmad and Kamke 2003; Fuentes *et al.* 2011). The water contact angle increased with the

increasing BC content. However, the increase was found to be slower with a BC content below 8%, and above 8% the growth began to accelerate. This trend could have been caused by the reduction in hydrophilic groups during carbonization, leading to reduced BPC hydrophilicity with an increasing BC content and decreasing BF content. The plant fibre content is important for improving the hydrophilicity and reducing the contact angle of composites (Ayrilmis 2011).

The BC particle size also had little influence on the water contact angle, while the BC content in the BPCs was maintained at 10%. Table 4 shows that the water contact angle increased slowly with decreasing BC particle size. While the hydrophilicity of the composite surface was invariant, the surface roughness was another factor that influenced the water contact angle (Ayrilmis 2011). The composite surface roughness increases with an increasing particle size, indicating that the surface roughness of the BPCs increased with an increasing BC particle size (Ayrilmis 2011; Ayrilmis *et al.* 2012). A greater surface roughness leads to smaller contact angles; thus, while the BC particle size increased, the contact angle decreased. However, in general, the hydrophilicity of the materials exerted the greatest influence on the contact angle.

Table 4. Contact Angles of Three Test Liquids on the BPC Surfaces (°)

Composite	Water	Formamide	Diiodomethane
BPC	85.3	53.8	76.3
BPC-BC _{4%}	86.8	54.4	77.0
BPC-BC _{8%}	88.0	55.0	75.4
BPC-BC _{12%}	96.2	56.6	79.8
BPC-BC _{16%}	101.5	55.5	72.8
BPC-BC ₄₀₋₆₀	97.6	56.3	81.8
BPC-BC ₆₀₋₈₀	98.2	50.3	76.0
BPC-BC ₈₀₋₁₀₀	98.0	47.4	75.0
BPC-BC _{>100}	99.4	45.0	77.5

The surface tension can be calculated using the contact angle and can be divided into dispersion (non-polar) and polar components according to Eqs. 3 and 4 (Young 1805; Fowkes 1963; Wu 1971):

$$\gamma = \gamma^d + \gamma^p \quad (3)$$

$$(1 + \cos\theta)\gamma_L = 2\sqrt{\gamma_S^d \cdot \gamma_L^d} + 2\sqrt{\gamma_S^p \cdot \gamma_L^p} \quad (4)$$

where γ is the surface tension, and γ^d and γ^p represent the dispersion and polar components, respectively. The γ_S and γ_L are the surface tension of the solid and liquid, respectively, and θ is the contact angle.

The surface tension values calculated using the contact angles and following Eq. 4 are shown in Table 5. The surface tension of the BPCs containing different amounts and sizes of the BC ranged from 30 mJ/m² to 40 mJ/m², which were similar to the results reported by Wolkenhauer *et al.* (2008). The surface tension decreased slightly when the BC content increased from 0% to 16%; the neat BPCs exhibited the highest surface tension. In addition, the γ^d did not vary much with the BC content, mainly because the γ^p had decreased. The surface of the BC has fewer polar groups than that of the bamboo fibre. By increasing the amount of BC and reducing the amount of bamboo fibre, the number of polar groups becomes lower, therefore decreasing the γ^p .

Table 5. Surface Tension of BPCs (mJ/m²)

Composite	γ^d	γ^p	γ
BPC	32.13	3.27	35.40
BPC-BC _{4%}	31.79	2.87	34.66
BPC-BC _{8%}	31.45	2.59	34.03
BPC-BC _{12%}	30.53	0.87	31.40
BPC-BC _{16%}	31.16	0.19	31.35
BPC-BC ₄₀₋₆₀	30.70	0.64	31.34
BPC-BC ₆₀₋₈₀	34.11	0.30	34.41
BPC-BC ₈₀₋₁₀₀	35.71	0.23	35.94
BPC-BC _{>100}	37.01	0.08	37.09

Note: Surface tension was calculated using the average contact angle values (distilled water and diiodomethane)

The surface tension values of the composites containing BC particles of different sizes are shown in Table 5. The results suggested that the BC particle size influenced the surface tension more than the BC content, and that the main factor was the γ^d . As the content of the BC was invariant, the γ^p of the surface did not greatly vary; however, the value of γ^d increased gradually with a decreasing BC particle size.

Physical-mechanical properties

The densities of the BPCs with different BC contents are shown in Fig. 2(a). The trend observed for density was similar to that observed for the modulus of elasticity (MOE) and modulus of rupture (MOR). A maximum density of 1.09 g/cm³ was achieved with a BC content of 12%. These results demonstrated that with BC contents below 12%, the BC could fill the gaps within the BPC, and in turn the density increased.

The effects of the BC particle size on the composite density are shown in Fig. 2(b). The results demonstrated that BC particles larger than 100-mesh did not significantly affect density, as all of the values were approximately 1.05 g/cm³. However, the density abruptly increased to 1.08 g/cm³ with the BC particles that were smaller than 100-mesh. The larger BC particles are not able to fill the gaps between LDPE and bamboo fibre as well as the smaller BC particles.

The effects of the BC content on the composite flexural properties are illustrated in Fig. 2. The MOR of the BPCs first increased and then decreased with an increasing BC content. The MOR increased by 29.2% from 13.60 MPa for neat BPCs to 17.57 MPa for BPCs with 12% BC.

The BC was able to reinforce the BPC because the BC filled the gaps within the BPC and because the polymer permeated the BC through the pores (Li *et al.* 2014), which strengthened the BC. Thus, the stress transferred to the stiffer BC, and the MOR improved. However, the MOR decreased when the BC content was greater than 12% because of the weaker interfaces that were formed (Ho and Lau 2014). Chen *et al.* (2015) studied the reinforcement of WPCs with waste fibre and found that excessive amounts of waste fibre were difficult to disperse. When the external stress was transferred to those weak interfaces, the BC would detach and be pulled out from the matrix, thus impairing the stress transfer and decreasing the MOR.

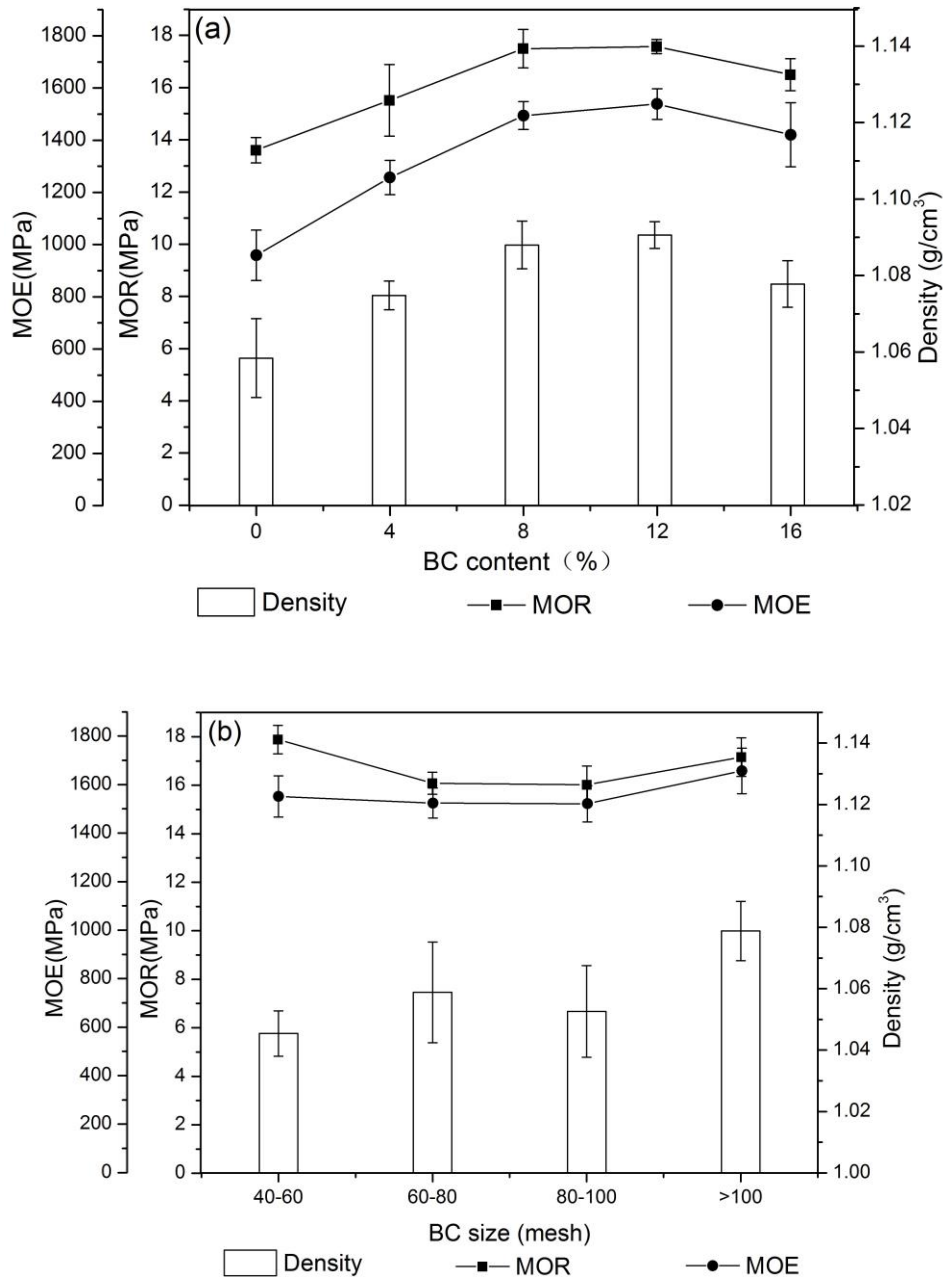


Fig. 2. Comparison of the density and flexural properties of composites with different BC contents (a), and sizes (b)

The MOE represents a material's ability to resist elastic deformation; therefore, larger MOE values indicate better resistance against elastic deformation. In other words, when the load on the materials is kept constant, larger MOE values indicate less elastic deformation. The MOE of the BPCs increased and then decreased with increasing BC content (Fig. 2). At a BC content of 12%, the MOE was 1300 MPa, which was 44.4% greater than the 900 MPa demonstrated by the neat BPCs. The MOE increased not only because the BC was a stiff material, but also because the BC filled the gaps and restricted the motion of polymer chains (Li *et al.* 2014; You and Li 2014), reducing the elastic

deformation of the BPCs. However, the BC became aggregated with an increased BC content, which reduced the restriction of the LDPE chain motion, thus increasing the elastic deformation and decreasing the MOE.

Table 6. BC Enhanced the Flexural Properties of Composites

Composite	BC shape	Molding Method	Flexural strength			Flexural modulus			Ref.
			MOR /MPa	Increase Rate/%	BC content /%	MOE /MPa	Increase Rate/%	BC content/%	
BPC (LDPE)	Fibre	Hot pressing	17.57	29.2	12	1300	44.4	12	-
BPC (HDPE)	Nano-particle	Extrusion	46.01	15.8	7.5	4650	17.5	7.5	Zhu <i>et al.</i> 2016
WPC (LDPE)	Fibre	Injection molding	16.90	19.9	8	1120	10.9	8	Li <i>et al.</i> 2014
PLA	Fibre	Injection molding	38.98	98.9	7.5	789	12.7	10	Ho <i>et al.</i> 2015
UHMWPE	Fibre	Extrusion	91.3	492.9	80	2378	451.7	80	You 2014

The effects of BC as a reinforced material to increase the flexural properties of composites are shown in Table 6. It was shown that adding BC increased flexural properties at differently degree of different composites. The enhancement extent was affected by the factors such as matrix and molding method. And the main factor was the matrix, because while BC enhanced pure UHMWPE, the increase rate could reach 490% (You 2014) and while the matrix was wood/bamboo plastic composites, the highest increase rate was 44%. The increase rate of the flexural properties in this study was higher than other two kinds of wood/bamboo plastic composite (Li *et al.* 2014; Zhu *et al.* 2016). It was probably due to the different molding methods and the different carbonization operating conditions, resulting in BC with different stiffness levels.

The effect of the BC particle size on the composite flexural properties was assessed, keeping the BC content constant at 10%, as shown in Fig. 2. The highest MOR of the BPCs, *i.e.*, 17.88 MPa, was achieved using 40-mesh to 60-mesh BC. This result can be explained by the large, high-aspect-ratio strips of the BC enhancing the composite strength more than the smaller, granular BC particles. The MOR declined with a decrease in the BC particle size, but slightly increased with BC particles smaller than 100-mesh. However, the BC particles smaller than 100-mesh had a larger specific surface area with more channels and gaps (Sun *et al.* 2010). The molten LDPE is able to enter these pores, stiffening the BC (Li *et al.* 2014). As BC particles ranging from 60-mesh to 100-mesh did not have this enhanced lubricity or high porosity, the MOR values of the BPCs containing those BC particles were lower. The effect of the BC particle size on the MOE was not significant (Fig. 2).

The impact strengths of composites with different BC contents are shown in Fig. 3. An irregular trend was observed with an increase in the BC content, indicating that the BC content had no obvious influence on impact strength. It is possible that increasing the BC content simultaneously improved the BPC stiffness and increased the restriction of LDPE motion (You and Li 2014), thereby reducing ductility. The interaction of both factors could have resulted in the irregular impact strength pattern that was observed.

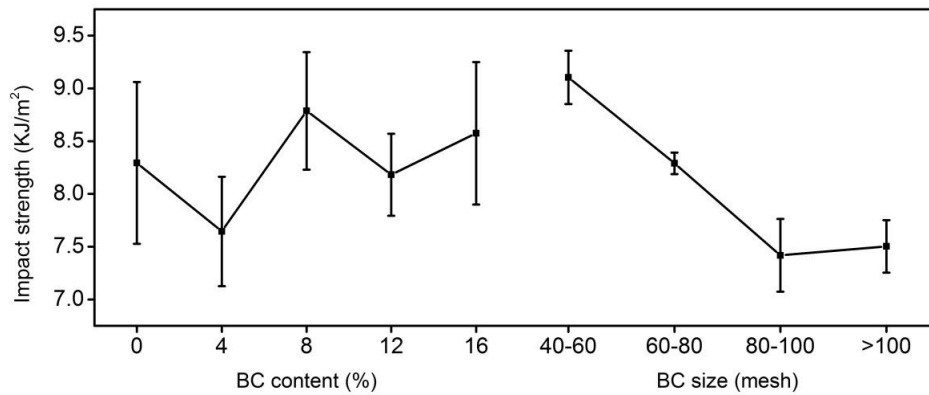


Fig. 3. Comparison of the impact strength of composites with different BC contents and sizes

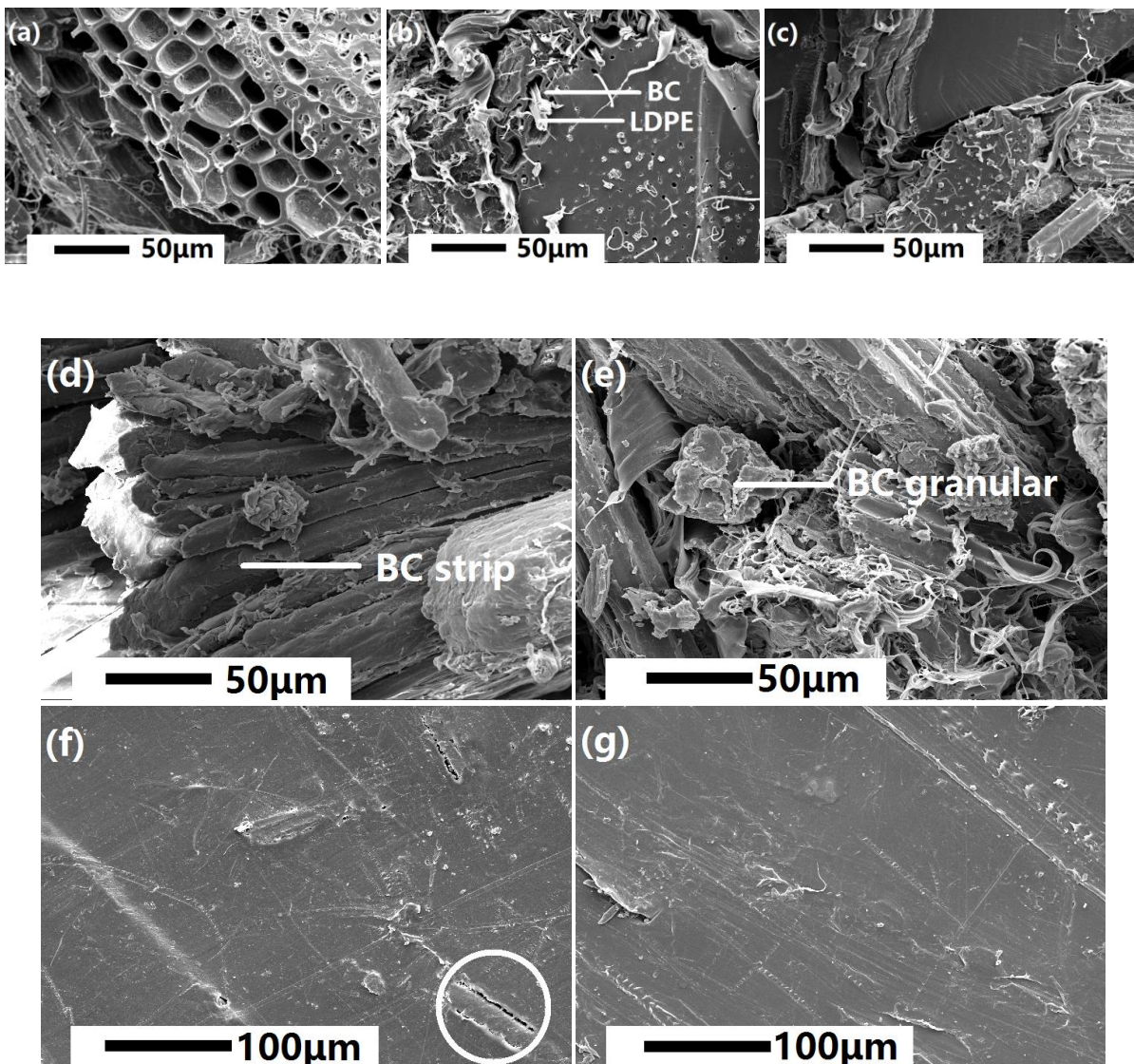


Fig. 4. Scanning electron microscopy (SEM) images of an impact fracture surface of: (a) BPC ($\times 500$), (b) BPC-BC_{8%} ($\times 500$), (c) BPC-BC_{16%} ($\times 500$), (d) BPC-BC₄₀₋₆₀ ($\times 500$), and (e) BPC-BC_{>100} ($\times 500$); a flat surface of (f) BPC-BC₄₀₋₆₀ ($\times 300$), and (g) BPC-BC_{>100} ($\times 300$)

The impact strength of the composites decreased with a decrease in the BC particle size (Fig. 3). The impact strength of the composites with 40-mesh to 60-mesh BC particles was 9.1 kJ/m^2 , which was 21.3% greater than that of composites with particles smaller than 100-mesh. This result was due to the large BC strips being able to absorb more energy than the granular BC particles before the material had fractured. Afrifah (2012) obtained similar results, reporting that for wood flour particles larger than 40-mesh, a decrease in particle size could decrease the impact strength.

Interfacial morphologies

The SEM images of BPCs with different BC contents and sizes are shown in Fig. 4. As shown in Fig. 4(a), 4(b), and 4(c), the content of the BC changed from 0% to 16%. The LDPE and BF had minimal connections because they are two vastly different materials, as shown in Fig. 4(a). In contrast, the LDPE could permeate the pores (Fig. 4(b)) to have a strong connection with the BC and reinforce the materials. This was due to the number of polar groups that become lower after carbonization, which causes the repulsive force to be reduced between the BC and LDPE. Furthermore, the high porosity also resulted in increased interface strength. When the content reached 16%, the BC aggregated (Fig. 4(c)) and weakened the material.

Images of the fractured surfaces of the BPCs containing BC particles of different sizes are shown in Figs. 4(d) and 4(e). The larger BC particles were high-aspect-ratio strips (Fig. 4(d)) that enhanced the material. The smaller BC particles appeared granular (Fig. 4(e)) and could more easily fill the spaces between the LDPE and the BF. The surface of the BPCs (Fig. 4(f)) containing strip-like filler was rougher than that of the BPCs containing grain-like filler (Fig. 4(g)), which could have affected the water contact angle of the materials. The different interfacial morphologies could also explain why the BC content and size could affect the BPC water resistance, contact angle, and physical-mechanical properties.

CONCLUSIONS

1. Bamboo charcoal (BC) filled the gaps within the bamboo-plastic composites (BPC). While the content below 8%, the water resistance increased. When the BC content was high, it aggregated and formed gaps, so the water resistance decreased. The sizes of the BC affected water resistance by the gaps in the BC and the composites. The larger BC particles could not fill the gaps in the composites. The smaller BC particles had a large absorption capacity, resulting in decreased water resistance of the composites. The BC particles ranged from 40 to 60 mesh and larger than 100-mesh.
2. After the bamboo was carbonized, the hydrophilicity and number of polar groups decreased. The water contact angle increased with increasing BC content. While the content of the BC was invariant, the sizes of the BC affected the contact angle by affecting the surface roughness of the BPCs. The larger sized BC was high-aspect-ratio strips and increased the surface roughness of the BPC, so the contact angle increased.
3. The low-density polyethylene (LDPE) permeated the BC through the pores, enhancing the BC and creating a strong connection with the BC. The BC filled the gaps within the BPC. Thus, the physical-mechanical properties increased. When the

BC content was high, it aggregated and weakened the materials, so the physical-mechanical properties decreased. The size of BC only affected the impact strength of physical-mechanical properties because the larger BC particles could absorb more energy before the BPC fractured.

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REFERENCES CITED

- Adhikary, K., Pang, S., and Staiger, M. (2008). “Long-term moisture absorption and thickness swelling behaviour of recycled thermoplastics reinforced with *Pinus radiata* sawdust,” *Chem. Eng. J.*, 142(2), 190-198. DOI: 10.1016/j.cej.2007.11.024
- Afrifah, K. A. (2012). *Fracture Mechanics and Statistical Modeling of Ternary Blends of Polylactide/Ethylene-acrylate Copolymer /Wood-flour Composites*, Ph.D. Dissertation, Michigan State University, East Lansing, MI, USA.
- Ahmad, M., and Kamke, F. A. (2003). “Analysis of Calcutta bamboo for structural composite materials: Surface characteristics,” *Wood Sci. Technol.* 37(3-4), 233-240. DOI: 10.1007/s00226-003-0172-x
- ASTM D570 (2005). “Standard test method for water absorption of plastic,” ASTM International, West Conshohocken, PA.
- ASTM D6110 (2010). “Standard test method for determining the Charpy impact resistance of notched specimens of plastics,” ASTM International, West Conshohocken, PA.
- ASTM D790 (2010). “Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials,” ASTM International, West Conshohocken, PA.
- Ayrilmis, N. (2011). “Effect of fire retardants on surface roughness and wettability of wood plastic composite panels,” *BioResources* 6(3), 3178-3187. DOI: 10.15376/biores.6.3.3178-3187
- Ayrilmis, N., Benthien, J. T., and Thoemen, H. (2012). “Effects of formulation variables on surface properties of wood plastic composites,” *Compos. Part B- Eng.* 43(2), 325-331. DOI: 10.1016/j.compositesb.2011.07.011
- Bouafif, H., Koubaa, A., Perré, P., and Cloutier, A. (2009). “Effects of fiber characteristics on the physical and mechanical properties of wood plastic composites,” *Compos. Part A-Appl. S.* 40(12), 1975-1981. DOI: 10.1016/j.compositesa.2009.06.003
- Chen, J., Teng, Z., and Wu, J. (2015) “Recycling of waste FRP and corn straw in wood plastic composite,” *Polym. Composite* (Online before print). DOI: 10.1002/pc.23789

- Deka, B. K., and Maji, T. K. (2012). "Effect of silica nanopowder on the properties of wood flour/polymer composite," *Polym. Eng. Sci.* 52(7), 1516-1523. DOI: 10.1002/pen.23097
- Esper, A., Vilaplana, F., and Karlsson, S. (2004) "Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties," *Compos. Part A-Appl. Sci.* 35(11), 1267-1276. DOI: 10.1016/j.compositesa.2004.04.004
- Fowkes, F. M. (1963). "Additivity of intermolecular forces at interfaces. I. Determination of the contribution to surface and interfacial tensions of dispersion forces in various liquids," *J. Phys. Chem.* 67(12), 2538-2541. DOI: 10.1021/j100806a008
- Fuentes, C. A., Tran, L. Q., Dupont-Gillain, C., Vanderlinden, W., De Feyter, S., Van Vuure, A. W., and Verpoest, I. (2011). "Wetting behavior and surface properties of technical bamboo fibers," *Colloid Surface A.* 380(1), 89-99. DOI: 10.1016/j.colsurfa.2011.02.032
- Ho, M. P., Lau, K. T., Wang, H., & Hui, D. (2015). "Improvement on the properties of polylactic acid (pla) using bamboo charcoal particles," *Compos. Part B- Eng.* 81, 14-25. DOI: 10.1016/j.compositesb.2015.05.048
- Ho, M., and Lau, K. (2014). "Enhancement of impact resistance of biodegradable polymer using bamboo charcoal particles," *Mater. Lett.* 136, 122-125. DOI: 10.1016/j.matlet.2014.07.165
- Hosseinihashemi, S. K., Modirzare, M., Safdari, V., and Kord, B. (2011). "Decay resistance, hardness, water absorption, and thickness swelling of a bagasse fiber/plastic composite," *BioResources* 6(3), 3289-3299. DOI: 10.15376/biores.6.3.3289-3299
- Jianbin, Z. (2005). *Study on the Mechanism of Action and Environmental Application of Bamboo Charcoal*, Ph.D. Dissertation, Nanjing Forestry University, Nanjing, China.
- Jiang, Z. (2007). *Bamboo and Rattan in the World*, Forestry Publishing House, Beijing, China, pp. 3-7.
- Kittinaovarat, S., and Suthamnoi, W. (2009). "Physical properties of polyolefin/bamboo charcoal composites," *J. Met. Mater. Miner.* 19, 9-15.
- Li, X., Lei, B., Lin, Z., Huang, L., Tan, S., and Cai, X. (2014). "The utilization of bamboo charcoal enhances wood plastic composites with excellent mechanical and thermal properties," *Mater. Design* 53, 419-424. DOI: 10.1016/j.matdes.2013.07.028
- Li, Y., Du, L., Kai, C., Huang, R., and Wu, Q. (2013). "Bamboo and high-density polyethylene composite with heat-treated bamboo fiber: Thermal decomposition properties," *BioResources* 8(1), 900-912. DOI: 10.15376/biores.8.1.900-912
- Lou, C., Lin, C., Lei, C., Su, K., Hsu, C., Liu, Z., and Lin, J. (2007). "PET/PP blend with bamboo charcoal to produce functional composites," *J. Mater. Process. Tech.* 192-193, 428-433. DOI: 10.1016/j.jmatprotec.2007.04.018
- Mbarek, T. B., Robert, L., Sammouda, H., Charrier, B., Orteu, J.-J., and Hugot, F. (2013). "Effect of acetylation and additive on the tensile properties of wood fiber-high-density polyethylene composite," *J. Reinf. Plast. Compos.* 32(21), 1646-1655. DOI: 10.1177/0731684413505256
- Migneault, S., Koubaa, A., Erchiqui, F., Chaala, A., Englund, K., and Wolcott, M. P. (2009). "Effects of processing method and fiber size on the structure and properties of wood-plastic composites," *Compos. Part-A. Appl. Sci.* 40(1), 80-85. DOI: 10.1016/j.compositesa.2008.10.004

- Sun, S., Wu, G., and Zhang, Q. (2010). "Absorption of organic pollutions in micro-polluted water by bamboo charcoal," *Environ. Sci. Technol. (in Chinese)* 23, 15-18. DOI: 10.3969/j.issn.1674-4829.2010.01.005
- Tamrakar, S., and Lopez-Anido, R. (2011) "Water absorption of wood polypropylene composite sheet piles and its influence on mechanical properties," *Constr. Build. Mater.* 25(10), 3977-3988. DOI: 10.1016/j.conbuildmat.2011.04.031
- Tang, C. M., Tian, Y. H., and Hsu, S. H. (2015). "Poly(vinyl alcohol) nanocomposites reinforced with bamboo charcoal nanoparticles: Mineralization behavior and characterization," *Mater.* 8(8), 4895-4911. DOI: 10.3390/ma8084895
- Tisserat, B., Reifschneider, L., Grewell, D., and Srinivasan, G. (2014). "Effect of particle size, coupling agent, and DDGS additions on Paulownia wood polypropylene composites," *J. Reinf. Plast. Comp.* 33(14), 1279-1293. DOI: 10.1177/0731684414521886
- Tran, D. T., Nguyen, D. M., Ha Thuc, C. N., and Dang, T. T. (2013). "Effect of coupling agents on the properties of bamboo fiber-reinforced unsaturated polyester resin composites," *Compos. Interface.* 20(5), 343-353. DOI: 10.1080/15685543.2013.806100
- Wolkenhauer, A., Avramidis, G., Hauswald, E. Miltz, H., and Viöl, W. (2008) "Plasma treatment of wood-plastic composites to enhance their adhesion properties," *J. Adh. Sci. Technol.* 22(16), 2025-2037. DOI: 10.1163/156856108x332543
- Wu, S. (1971). "Calculation of interfacial tension in polymer systems," *J. Polym. Sci. C Pol. Sym.* 34(1), 19-30. DOI: 10.1002/polc.5070340105
- Wu, T., Chien, Y., Chen, T., and Wu, J. (2013). "The influence of hot-press temperature and cooling rate on thermal and physicomechanical properties of bamboo particle-poly-lactic acid composites," *Holzforschung* 67(3), 325-331. DOI: 10.1515/hf-2012-0087
- Xian, Y., Li, H., Wang, C., Wang, G., Ren, W., and Cheng, H. (2015). "Effect of white mud as a second filler on the mechanical and thermal properties of bamboo residue fiber/polyethylene composites," *BioResources* 10(3), 4263-4276. DOI: 10.15376/biores.10.3.4263-4276
- Yeh, S., Agarwal, S., and Gupta, R. K. (2009). "Wood-plastic composites formulated with virgin and recycled ABS," *Compos. Sci. Technol.* 69(13), 2225-2230. DOI: 10.1016/j.compscitech.2009.06.007
- You, Z. (2014). "The modification study of ultra-high molecular weight polyethylene," Ph.D. Dissertation, Nanjing Forestry University, Nanjing, China.
- You, Z., and Li, D. (2014). "Highly filled bamboo charcoal powder reinforced ultra-high molecular weight polyethylene," *Mater. Lett.* 122, 121-124. DOI: 10.1016/j.matlet.2014.01.010
- Young, T. (1805). "An essay on the cohesion of fluids," *Philos. T. Roy. Soc. A.* 95, 65-87. DOI: 10.1098/rstl.1805.0005
- Zabihzadeh, S., Hosseini, H., Mehregan, N., and Sepidehdam, S. (2010). "Influence of fungal decay on physico-mechanical properties of a commercial extruded bagasse/PP composite," *J. Reinf. Plast. Compos.* 29(29), 1750-1756. DOI: 10.1177/0731684409340596
- Zhang, X., Ya, B., Huang, B., Zhou, B., Pei, L., and Jia, F. (2016). "Study on preparation and properties of carbon nanotubes/hollow glass microspheres/epoxy syntactic foam," *J. Polym. Eng.* 116(3), 1384-1391. DOI: 10.1515/polyeng-2016-0001

- Zhou, Y., Ning, L., Li, X., Zhang, J., Lu, Y., and He, J. (2015a). "Effect of natural flake graphite on triboelectrification electrostatic potential of bamboo flour/high-density polyethylene composites," *Wood Sci. Technol.* 49(6), 1269-1280. DOI: 10.1007/s00226-015-0752-6
- Zhou, Y., Ning, L., Li, X., Zhang, J., Chen, Q., and Yang, X. (2015b). "Bauxite modified bamboo flour/HDPE composites," *Acta. Mater. Compos. Sin. (in Chinese)* 32(4), 977-982. DOI: 10.13801/j.cnki.fhclxb.20141105.005
- Zhu, S., Guo, Y., Chen, Y., Su, N., Zhang, K., & Liu, S. (2016). "Effects of the incorporation of nano-bamboo charcoal on the mechanical properties and thermal behavior of bamboo-plastic composites," *BioResources* 11(1), 2684-2697. DOI: 10.15376/biores.11.1. 2684-2697
- Zolfaghari, A., Behravesh, A. H., Adli, A., and Sarabi, M. T. (2013). "Continuous glass fiber reinforced wood plastic composite in extrusion process: Feasibility and processing," *J. Reinf. Plast. Compos.* 32(1), 52-60. DOI: 10.1177/0731684412461461

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