

## Effect of Low-Concentration Alkali Solution Pretreatment on the Properties of Bamboo Particles Reinforced Poly(lactic acid) Composites

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**ABSTRACT:** Bamboo particles (BP) were treated with 0.3N (1.20 wt %) low-concentration alkali solution for different times (0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 24 h) as reinforcements in poly(lactic acid) (PLA) biodegradable composites. Characteristics of BP by composition analysis, scanning electron microscopy, Brunauer-Emmett Teller test, and Fourier transform infrared spectroscopy, showed that low-concentration alkali treatment had a significant influence on the microstructure, specific surface area, and chemical groups of BP. PLA/treated-BP and PLA/untreated-BP composites were both produced with 30 wt % BP contents. Mechanical measurements showed that tensile strength, tensile modulus, and elongation at break of PLA/BP composites increased when the alkali treatment time reached 3.0 h with maximal values of 44.21, 406.41 MPa, and 6.22%, respectively. Maximal flexural strength and flexural modulus of 83.85 MPa and 4.50 GPa were also found after 3.0-h alkali treatment. Differential scanning calorimetric analysis illustrated that PLA/BP composites had a better compatibility and larger PLA crystallinity after 3.0-h treatment. Overall, low concentration alkali treatment was a feasible technology in creating BP reinforced PLA composites. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1667–1674, 2013

**KEYWORDS:** cellulose and other wood products; thermal properties; biodegradable; compatibilization; mechanical properties

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### INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable and environment-friendly polymer material with excellent processing properties including compressing and heating, extrusion, blow molding or injection modeling, relatively high strength and modulus of elasticity, complete biodegradation, and favorable chemical inertness.<sup>1–4</sup> Therefore, it is considered as a new ecological and green material with the most development potential in the 21st century.<sup>5–7</sup> However, PLA has high cost (approximately 2.2 \$kg<sup>-1</sup>)<sup>5</sup> and defects like relatively low heat resistance, which limit its broader applications.<sup>4,5</sup>

As a kind of cheap fiber reinforcement and ease of access,<sup>8,9</sup> bamboo particle (BP) can be combined with various resin matrices to create composites.<sup>10–13</sup> However, BP is a kind of uneven anisotropic material,<sup>8</sup> which is composed of cellulose, lignin, hemicellulose, and various extractives.<sup>14–16</sup> As abundant functional groups like polar hydroxyl and phenolic hydroxyl group contained in cellulose, lignin, and hemicelluloses, the surface of BP presents relatively strong chemical polarity and hydrophilicity.<sup>17</sup> Therefore, during the preparation of composites, the interfacial interaction between BP reinforcement and PLA matrix is relatively poor, leading to the failure of effective delivery of stress in the interface and decline of mechanical strength.<sup>18,19</sup> Furthermore, a clear interface separation might even exist

between BP reinforcement and PLA matrix because of the low compatibility.<sup>20,21</sup>

The alkali pretreatment of plant fiber surface is an effective approach to improve interfacial compatibility between plant fiber and polymer matrix.<sup>22–25</sup> Several studies have been reported on the effect of alkali treatment on the fine structure and mechanical properties of bamboo fibers. Kang and Kim observed enhancement in the mechanical properties of BF/PLA composite treated by sodium chlorite and/or a silane coupling agent. Similar enhancement was also obtained by treating with silane coupling after plasma treatment and silane coupling during UV irradiation.<sup>26</sup> Das and Chakraborty compared the fine structure and morphology of bamboo fibers in the form of strips and dust treated with NaOH solution of varying concentrations (10%, 15%, and 20%).<sup>27</sup> Although, there are many views on the effects of alkali treatment on bamboo fibers with various methods, information and its explanation for low concentration of NaOH solution treating BP is scanty.

In this article, an attempt was made to prepare BPs reinforced PLA composites using 0.30N (1.20 wt %) low-concentration NaOH solution with different treatment times as the particles surface modifier. The purpose of using low-concentration alkali was to improve the compatibility between BP and PLA without significantly destroying BP structure. The particles were

**Table I.** Cellulose, Hemicellulose and Lignin Content of the Untreated and Alkali Treated BPs

Treated time (h)	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)
0	36.18 ± 0.30	23.11 ± 0.21	39.24 ± 0.24
3.0	39.89 ± 0.19	19.73 ± 0.30	41.46 ± 0.28
8.0	41.02 ± 0.17	19.84 ± 0.21	40.60 ± 0.18
24.0	41.36 ± 0.22	19.47 ± 0.33	40.49 ± 0.23

mercerized by alkali treatment and the fibers maintained original form with its relative high mechanical property. The effect of alkalization with NaOH on BPs was explored by analyzing its morphology, surface charge, available functional groups, mechanical and thermal properties, and the optimal treatment time therefore was found.

## EXPERIMENTAL

### Materials

PLA pellets (ES701) obtained from Tongjieliang Biomaterials, Shanghai, were used as matrix material. PLA had a number average molecular weight of 52,000 g mol<sup>-1</sup>, *T<sub>g</sub>* of 57.5°C and melting point (*T<sub>m</sub>*) of 153.9°C. BP was obtained from Bamboo Processing Factory, Zhejiang Province.

### Alkali Treatment of BP

BP was ground to 250–425 μm with a hammer mill, then immersed in NaOH solution with the concentration of 0.30N in a 40.0°C water batch with a solid-to-liquid ratio of 1:15 for different times (0.25, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 24 h). After that, BP was rinsed with distilled water and then washed with acetic acid solution for neutralization. Then they were further rinsed with distilled water and filtered under vacuum for 5 min and finally dried at 105°C for 24 h.

### Composition Analysis of the BP

Lignin and cellulose content analysis of the fibers was carried out at Biomaterial and Bioenergy Laboratory at Zhejiang University with Raw Fiber test machine (FIWE-6, VELP), in accordance with the method of Van Soest.<sup>28,29</sup> About 1.00 g of sample was ground into fine powder, and the content of neutral detergent fiber, acid detergent fiber, acid detergent lignin, and acid-insoluble ash, respectively, was extracted by a series of solutions and solvents. Through conversion, the content of cellulose, hemi-cellulose, and lignin was obtained.

### Surface Morphology Observation

Surface morphology of BP was observed by using launch scanning electron microscope (S-4800, Hitachi, Japan). The samples were coated with gold before observing. The launching voltage of electron microscope was 10.0 kV. The fractured surface of BP/PLA composite was observed by a super resolution digital microscope (VHX-1000, Keyence, Japan).

### Specific Surface Area of BP

Static nitrogen absorption instrument (JW-BK, Beijing) was used to measure the specific surface area of BP. Brunauer-Emmett Teller method was used to calculate the specific surface area.

### Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) (Nicolet-380, Thermofisher Scientific) was adopted for infrared representation with the scanning range of 4000–400 cm<sup>-1</sup>. The spectra were obtained with the KBr pellet technique. Untreated and alkali-treated particles were ground into powder, then mixed and compressed with KBr powder into thin discs. A total of 16 scans were co-added.

### Preparation of PLA/BP Composites

BP to PLA ratio was kept constant at 30% BP (by weight) in all composites. The blends were prepared in a double roll lab-scale compounder under the conditions of 180°C and 50 rpm. The samples after compounding were placed in the desiccator for 24 h and then paved to the mold. The mold was exactly the size of specimens. Vulcanization molding machine (GT-7014-A50C, GTM) was adopted to preheat the samples for 10 min at a temperature of 180°C first and then conducted hot pressing on the samples under the conditions of 180°C and 2.0 MPa. The pressure was maintained for 5 min and then the sample was cooled with water circulation in the press platen. The sizes of samples for tensile and bending tests were 165 × 13 × 4 mm<sup>3</sup> and 127 × 10 × 4 mm<sup>3</sup>, respectively, on the basis of ASTM D638 and ASTM D790. All samples were kept in desiccator for further characterization.

### Composite Mechanical Testing

Tensile and bending tests of PLA/BP composite were carried out by using universal testing machine (CMT4503, MTS) according to ASTM D638 and ASTM D790, the gauge length and the crosshead speed for tensile test were set to 50 mm and 5 mm min<sup>-1</sup>, the support span and the crosshead speed for bending test were set to 64 mm and 5 mm min<sup>-1</sup>, respectively. Five specimens were used for each test.

### Thermal Analysis

Differential scanning calorimeter (200F3, Netzsch) was adopted to study the thermal properties of pure PLA, untreated BP/PLA composite and treated 3 h BP/PLA composite. About 10.0 mg sample was weighed and sealed. The sample was kept at a constant temperature of 0°C for 5 min and then increased at a rate of 10°C min<sup>-1</sup> to 200°C. Nitrogen was used as purging gas at a rate of 50 mL min<sup>-1</sup>. Crystallinity (*X<sub>c</sub>*) was estimated according to the following equation:

$$X_c(\%) = \frac{\Delta H_c}{\Delta H_0 \times X_{PLA}} \times 100\% \quad (1)$$

where  $\Delta H_c$  refers to the crystallization enthalpy of PLA/BP composite;  $\Delta H_0$  refers to the enthalpy value during 100% crystallization of PLA, which is 93.6 J/g<sup>30</sup>;  $X_{PLA}$  refers to the weight ratio of PLA in PLA/BP composite.

## RESULTS AND DISCUSSION

### Composition Analysis

The cellulose, hemicelluloses, and lignin content of untreated and treated BP are summarized in Table I. It was observed that cellulose, hemicellulose, lignin content of untreated BP was

36.18%, 23.11%, 39.24%, respectively. Alkali treatment removed about 3% of hemicelluloses from BP within the first 3-h treatment. Cellulose and lignin content increased because of the mass loss of BP, indicating that the hemicelluloses were decomposed on the surface of BP and impurities, such as wax from surface of lignocellulosic materials were wiped off, but later the lignin content decreased because of its own decomposition. It can be verified by the following micromorphology analysis that the structure of fiber was not destroyed, indicating that mercerization treatment increased the amount of cellulose exposed on the fibrous surface, thus increasing the number of possible reaction sites.

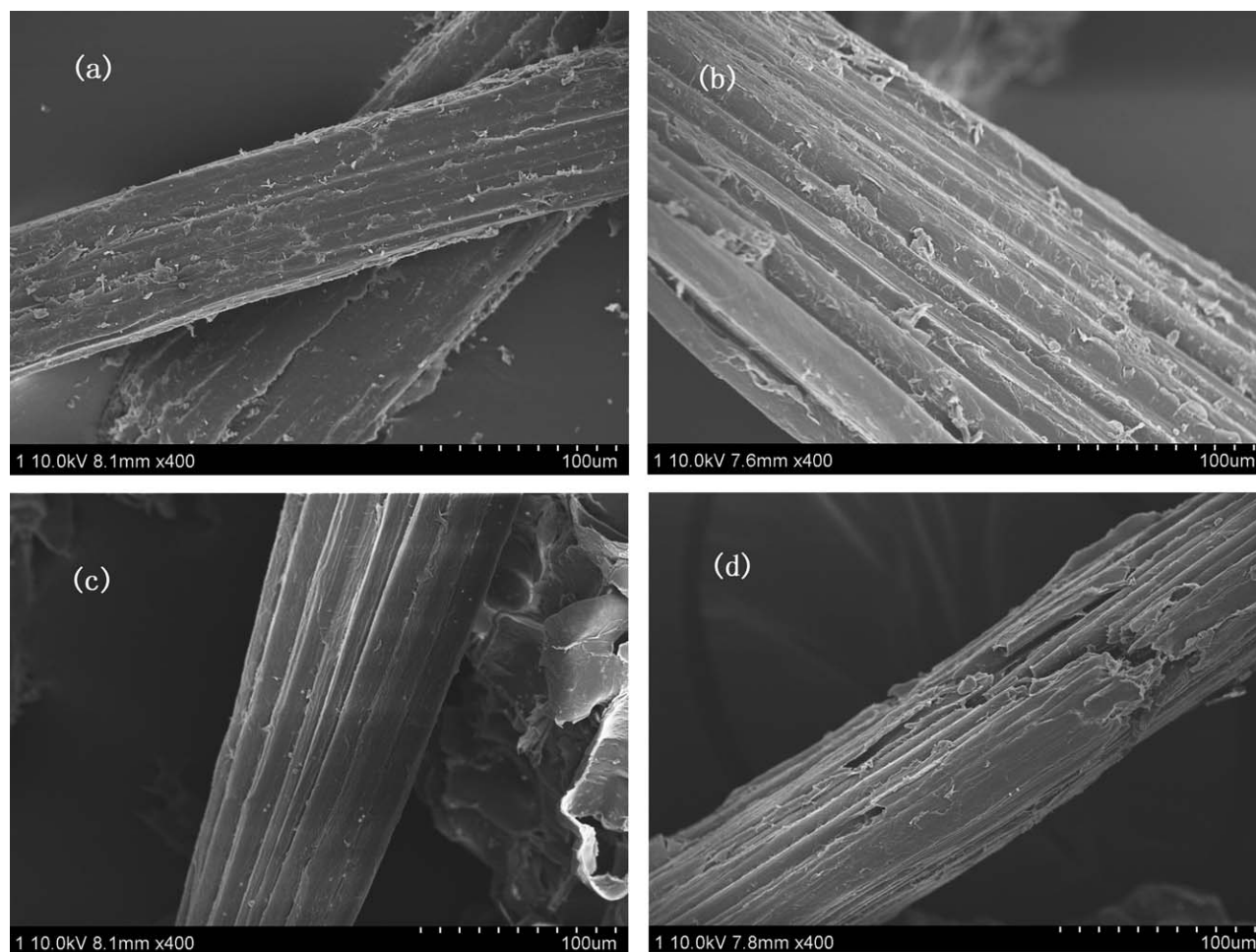
#### Micromorphology Analysis on BP

The scanning electron microscopy results of untreated BP and BP after different times of alkali treatment are shown in Figure 1. The surface of untreated BP was relatively rough with some fine disorderly microfibril. With the increase of alkali treatment time (1.0, 3.0, and 8.0 h), the inorganic impurities on the fiber surface were eliminated and gradually mercerized. Obvious grooves were also presented, and the overall structure of fiber was partly destroyed after 8-h treatment. A relatively strong

capillary effect, which can improve the invasion effect of PLA matrix, can be generated by the pores formed by these grooves,<sup>24</sup> which will strengthen the interfacial bonding between BP and PLA matrix.

#### Influence of Alkali Treatment on Specific Surface Area of BP

The bigger the specific surface area of reinforcement is, the bigger the probability of matrix infiltration will be well documented.<sup>25,31</sup> The trend of specific surface area of BP after different times of alkali treatment is reflected in Figure 2. The specific surface area of BP without alkali treatment was only  $341.95 \text{ m}^2 \text{ g}^{-1}$ . After alkali treatment, the specific surface area of BP increased gradually and reached the peak value ( $376.92 \text{ m}^2 \text{ g}^{-1}$ ) in 3.0 h. After the peak, the specific surface area of BP presents a stably declining trend. It is mainly because that some hemicelluloses and lignin were decomposed during alkali treatment to generate pores on BP. As the treatment time was too long, the surface fiber structure would be changed, some pores became relative large tear and led to slightly decrease the surface area after 3 h. After alkali treatment, the probability of PLA penetration into the surface of BP during compounding was promoted so as to reinforce the interfacial interaction between BP and PLA.



**Figure 1.** Micro-structure of bamboo fiber: (a) untreated, (b) NaOH solution treated for 1.0 h, (c) NaOH solution treated for 3.0 h, and (d) NaOH solution treated for 8.0 h.

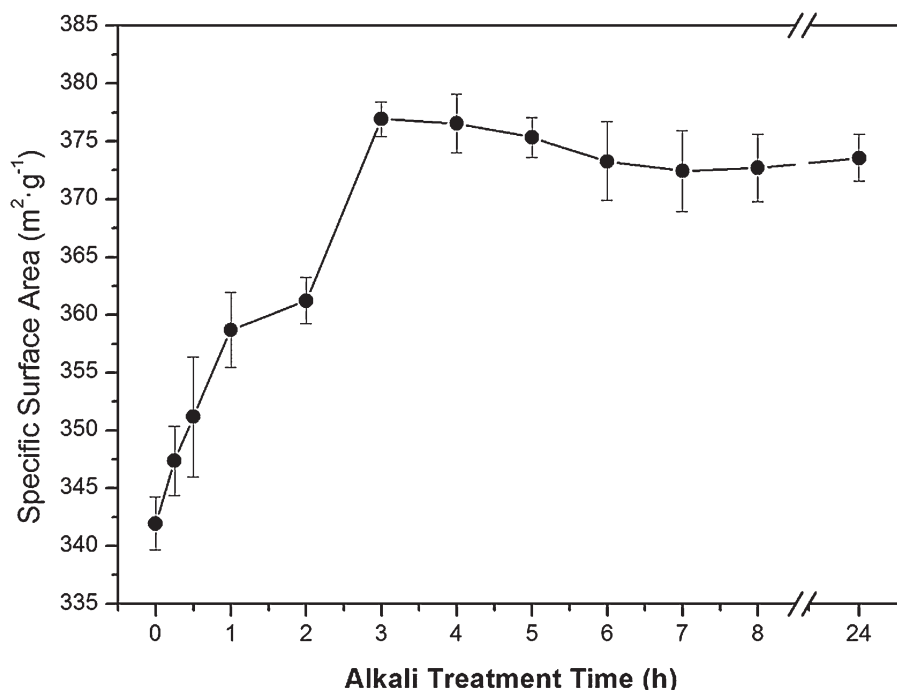


Figure 2. Specific surface area of BP after treatment.

#### Influence of Alkali Treatment on Surface Structure of BP

The FT-IR spectra of BP surface are indicated in Figure 3. After 3.0 h of alkali treatment, the peaks in five places, i.e. 3428, 2919, 2854, 1736, and 1049  $\text{cm}^{-1}$  were weakened significantly. The peak located in 3428  $\text{cm}^{-1}$  was a hydroxyl ( $-\text{OH}$ ) stretching vibration peak. Such kind of hydroxyl mainly existed in cellulose, hemicellulose, and lignin, which were removed by sodium hydroxide solution<sup>32,33</sup>; the peak because of the hydrocarbon ( $-\text{CH}$ ) stretching vibration with 2919  $\text{cm}^{-1}$  decreased considerably with the decomposition of hemicellulose and

lignin; a band at 2854  $\text{cm}^{-1}$  in the map attributed to H-bonding present among cellulose, hemicellulose, and lignin molecules of bamboo fiber making the total structure as a network, indicating that the H-bonding were gradually destroyed by alkali treatment.<sup>27</sup> The peak located in 1736  $\text{cm}^{-1}$  was ascribed to carbonyl stretching vibration peak in ester group ( $-\text{CH}_2-\text{COO}-$ ) or carboxyl ( $-\text{COOH}$ ).<sup>17</sup> The peak intensity was gradually reducing as the concentration of the particular group had been reduced because of the removal of hemicelluloses<sup>20</sup>; the peak located in 1049  $\text{cm}^{-1}$  was a stretching vibration peak with a

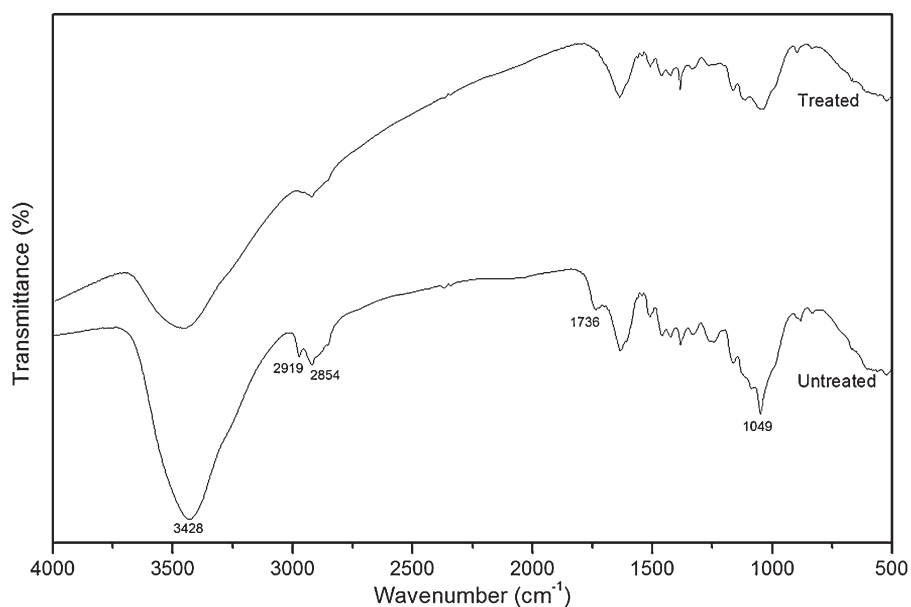
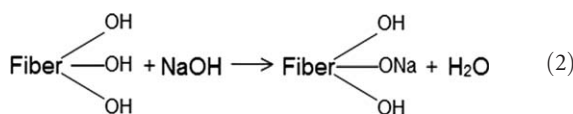


Figure 3. FT-IR spectra of BP.

**Table II.** Tensile Properties of PLA/BP Composites

Treated time (h)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
0	36.67 ± 1.0	4.51 ± 0.22	406.41 ± 62.0
0.25	40.64 ± 1.3	5.39 ± 0.30	535.04 ± 110
0.5	41.88 ± 1.5	5.59 ± 0.10	587.91 ± 81.0
1	42.01 ± 2.0	5.32 ± 0.15	597.67 ± 110
2	42.21 ± 1.7	5.93 ± 0.20	583.72 ± 98.0
3	44.21 ± 1.0	6.22 ± 0.10	668.30 ± 17.0
4	43.83 ± 2.1	5.84 ± 0.18	624.30 ± 110
5	43.82 ± 1.9	5.59 ± 0.09	610.13 ± 103
6	43.56 ± 1.2	5.41 ± 0.17	553.65 ± 45.0
7	43.31 ± 2.2	5.52 ± 0.12	551.80 ± 121
8	43.35 ± 1.2	5.71 ± 0.21	555.85 ± 122
24	43.25 ± 1.4	5.86 ± 0.10	517.11 ± 50.0

polysaccharide acetal structure (–CO–). It mainly exists in cellulose and hemicellulose.<sup>27</sup> The strength of hydrophilic hydroxyl peak was significantly weakened, which indicated that some hydroxyls in BP were reacted effectively. The followings are possible chemical reactions occurred during alkali treatment of BP<sup>34</sup>:



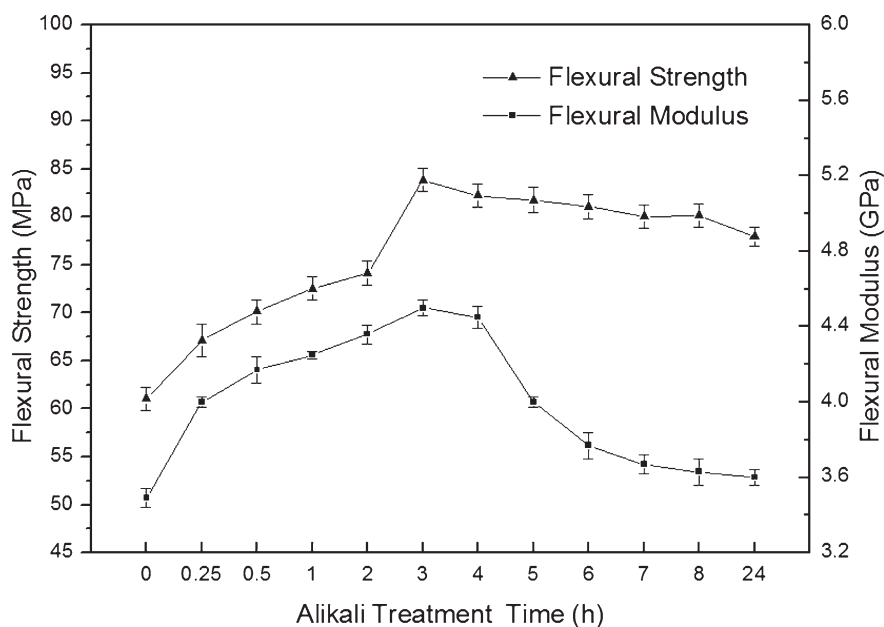
**Mechanical Properties of PLA/BP Composites**

The changes of tensile strength, tensile modulus, and elongation at break of PLA/BP composite with different alkali treatment

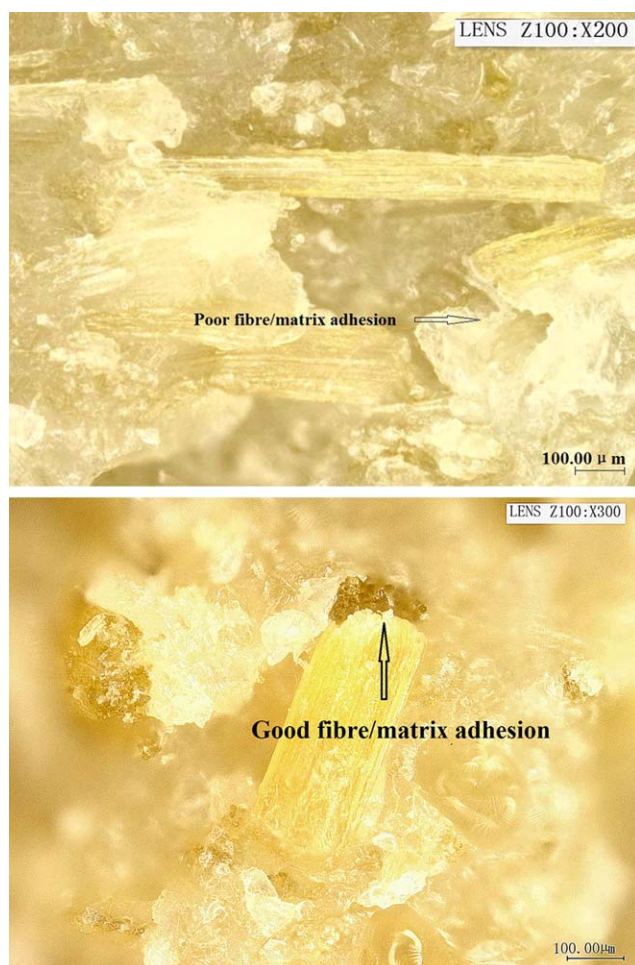
times are shown in Table II. The tensile strength and tensile modulus of untreated PLA/BP composite was only 36.67 and 406.41 MPa, respectively, whereas the elongation at break was 4.51%. The tensile strength, tensile modulus, and elongation at break of composite with alkali-treated BP were improved significantly. Maximal tensile strength of 44.21 MPa, tensile modulus of 668.30 MPa, and elongation at break of 6.22% were obtained with BP with 3.0-h alkali treatment, which were improved by 20.56%, 64.44%, and 37.92%, respectively, compared with the untreated PLA/BP composite. After that, tensile strength, tensile modulus, and elongation at break of PLA/BP composite decreased slightly and began to stabilize. These results suggested that the stress generated by stretch effect had been transferred from matrix PLA to BP through interface, and the complete structure of bamboo fiber strengthened the mechanical properties of composite.

The influence of different alkali treatment times on the flexural strength and flexural modulus of PLA/BP composite are given in Figure 4. The flexural strength and modulus of PLA/untreated-BP composite were 61.07 MPa and 3.49 GPa, respectively, whereas the alkali treatment time increased gradually, the flexural strength of the composite reached the maximum value of 83.85 MPa and the flexural modulus increased to 4.50 GPa. After that, both flexural strength and flexural modulus were gradually decreased.

As the untreated BP surface contained hemicellulose and inorganic impurities and the penetration of PLA matrix was relatively poor, the mechanical properties were not favorable in a macro sense. After alkali treatment for 3.0 h, the surface of BP had a relatively larger specific surface area and relatively abundant pores, thus increasing the infiltration during PLA mixing, generated a relatively strong capillary effect, and reinforced the interface action with PLA matrix. The following were reflected in a macro sense: the tensile strength, tensile modulus,



**Figure 4.** Flexural properties of PLA/BP composites.



**Figure 5.** Micrographs of the freshly fractured surfaces of BP/PLA composites: (I) untreated, and (II) NaOH solution treated for 3.0 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

elongation at break, flexural strength, and flexural modulus of PLA/BP composite had been improved by 20.56%, 64.44%, 37.92%, 37.30%, and 28.94%, respectively. When the treated time went longer, the mechanical properties decreased slightly, because of weakened adhesion between the fibers and the matrix because of the reducing of specific surface area and partly damage of fibrous structure.

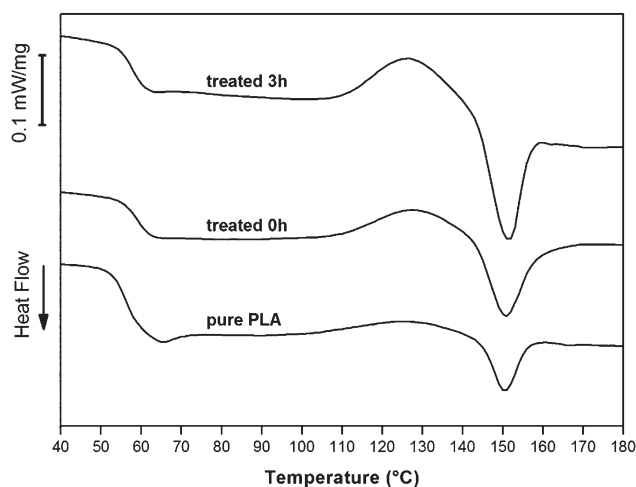
#### Fractured Surfaces Analysis of PLA/BP Composites

Figure 5 shows a comparison of the microscopic photographs of the fracture of the composites with alkali treated and untreated BP/PLA composite. At the interface between PLA and fibers, the cavities, produced by fiber pulling out after fracture, were clearly seen in the untreated fibers reinforced composites, indicating poor interfacial bonding between fibers and PLA. Conversely, almost no cavity was observed in the PLA and fiber interphase structure with 3-h alkali-treated fibers. Moreover, the fibers were snapped when mechanical properties testing and the fiber appeared to densely contact with the PLA matrix, indicating better interfacial adhesion between fibers and PLA.<sup>35</sup>

#### DSC of PLA/BP Composite

PLA is a semicrystalline polymer.<sup>36,37</sup> During heating or cooling, the phenomenon of cold crystallization can be observed in some order areas in the melt.<sup>38–41</sup> The strength and modulus of the material are greatly influenced by the degree of crystallinity ( $X_c$ ).<sup>42,43</sup> DSC thermograms of untreated and 3.0-h-treated BP reinforced PLA composites are given in Figure 6 and the corresponding transition temperatures were summarized in Table III. The neat PLA was characterized by a  $T_g$  at 56.4°C, a cold crystallization peak at 124.8°C, and finally a melting peak at 150.4°C. Thermal behavior of PLA matrix was influenced with the incorporation of untreated BP.  $T_g$  and cold crystallization temperature ( $T_c$ ) of the matrix increased about 2.7°C and 2.5°C because of the restricted chain mobility, because of the physical and/or chemical interactions at the fiber/polymer interphase. The significant change in thermal properties of PLA/BP composite was observed in the case of 3-h alkali-treated BP.  $T_g$  was approximately 3.5°C lower than that of untreated BP/PLA composite. Moreover,  $T_c$  decreased to 120.3°C from 127.3°C. These observations indicate that the presence of byproducts of NaOH treatment can act as plasticizer or impurity for PLA. Therefore, the  $T_g$  lowered because of the enhanced chain mobility and the  $T_c$  lowered because of the nucleating effect of treated BPs and reduced polymer viscosity because of plasticization.<sup>44</sup>

The degree of crystallinity of PLA in composite increased after alkali treatment of BP. The degree of crystalline of PLA in PLA/untreated-BP composite was 6.07%, and that of PLA in composite with 3.0-h alkali-treated BP increased to 14.35%. However, the degree of crystallinity of pure PLA with the same process was only 3.13%. Therefore, BP had a heterogeneous nucleation effect during crystallization of PLA. The crystallization rate of PLA was improved during phase transition. It could attach on BP when the PLA molecular chain segment was relatively short. The fusion enthalpy of PLA/untreated BP composite was 7.28 J g<sup>-1</sup>, whereas that of PLA/BP composite with alkali treatment for 3.0 h was improved to 20.01 J g<sup>-1</sup>, because it was difficult for untreated BP to form crystal nucleus, which influenced the nucleation of crystallization and crystal growth.



**Figure 6.** DSC thermograms of pure PLA and PLA/BP composite.

**Table III.** Thermal Properties of PLA and PLA/BP Composite

Samples	$T_g$ (°C)	$\Delta C_p$ (J (g K) <sup>-1</sup> )	$T_c$ (°C)	$\Delta H_c$ (J g <sup>-1</sup> )	$X_c$ (%)	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )
100% PLA	56.4	0.640	124.8	2.93	3.13	150.4	3.19
PLA/untreated BP	59.1	0.287	127.3	3.98	6.07	150.9	7.28
PLA/alkali treated 3.0 h BP	55.6	0.371	120.3	9.40	14.35	149.5	20.01

## CONCLUSION

After 0.3N alkali solution treatment, the surface of BP was gradually mercerized and obviously vertical grooves were observed. The specific surface area increased significantly and reached the peak value (376.92 m<sup>2</sup> g<sup>-1</sup>) in 3.0 h. Because of the interfacial properties improvement and the original form maintenance of fibers with its relatively high mechanical property, PLA/BP composite exhibited better tensile properties and flexural properties after 3.0 h of alkali treatment. The tensile strength, tensile modulus, elongation at break, flexural strength, and flexural modulus reached maximal values of 44.21 MPa, 668.30 MPa, 6.22%, 83.85 MPa, and 4.50 GPa, respectively. DSC analysis illustrated that PLA/treated-BP composites had a better compatibility and higher degree of crystallinity. Consequently, it is feasible to utilize low-concentration alkali solution to pretreat BPs to reinforce PLA composites.

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