Water Absorption Properties of Heat-Treated Bamboo Fiber and High Density Polyethylene Composites

Lanxing Du,[a,b] Yanjun Li,[a,]* Sunyoung Lee [c], and Qinglin Wu [d,]*

To modify water absorption properties of bamboo fiber (BF) and high density polyethylene (HDPE) composites, heat treatment of BFs was performed prior to compounding them with HDPE to form the composites. The moisture sorption property of the composites was measured and their diffusion coefficients (D_m) were evaluated using a one-dimensional diffusion model. Moisture diffusion coefficient values of all composites were in the range of 0.115×10^{-8} to 1.267×10^{-8} cm^2/s. The values of D_m decreased with increasing BF heat-treatment temperature, and increased with increasing BF loading level. The D_m value of 40 wt% bamboo fiber/HDPE composites with BFs treated with 100 ^oC was the greatest (*i.e.,* $1.267 \times 10^{-8} cm^2/s$). Morphology analysis showed increased fiber-matrix interfacial bonding damage due to fiber swelling and shrinking from water uptaking and drying. The mechanism of water absorption of the composite, indicated a general Fickian diffusion process.

Keywords: Heat-treatment; Bamboo fiber; HDPE; Moisture sorption; Diffusion coefficient

*Contact information: a: School of Engineering, Zhejiang Agriculture and Forestry University, Lin An 311300, China; b: College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China; c: Korea Forest Research Institute, Seoul, Korea; d: School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA; *Corresponding authors: wuqing@lsu.edu; lalyj@126.com*

INTRODUCTION

Natural fiber-reinforced plastic composites gain extended development primarily due to their strength property and sustainability. Among these natural materials, bamboo possesses high strength-to-weight ratio because of its longitudinally aligned fiber (Abdul *et al.* 2012). Currently, bamboo-based materials have been used in windows, outdoor flooring, kitchen and bath components, pavilions, and parts in automobiles, ships and other transportation equipment (Kushwaha and Kumar). The materials in all these applications inevitably absorb moisture, which has profound effects on their mechanical properties, dimensional stability, and decay resistance (Tsenoglou *et al.* 2006). For example, it has been shown that the flexural modulus and strength of wood-polymer composites after extended moisture immersion were remarkably decreased, while the freeze-thaw cycling did not significantly affect their mechanical properties (Stark and Gardner 2008; Tamrakar and Lopez-Anido 2011).

Many modification methods have been used to alter the water absorption process of the composites. For example, clay as a nanofiller has been used in wood flour and polypropylene (PP) composites, and the water absorption of the composites was shown to decrease with increasing clay loading (Ghasemi *et al.* 2009). Pressurized and regular hot water extraction of hemicelluloses from wood/natural fibers and addition of coupling agents to the composites have been shown to help enhance composite water resistance as these processes reduce the hydrophilic properties of the fiber and improve bonding between the matrix and fibers (Hosseinaei *et al.* 2012; Karmaker 1997). In addition, reducing fiber size has also been seen as an effective way to reduce the water uptake of the composites (Bouafif *et al.* 2009) as smaller fiber particulates can be encapsulated better by the plastic compared with larger ones.

Previous research indicated that heat treatment improves the water absorption resistance and dimensional stability of various wood samples. For instance, one study showed that the ability to absorb water decreased after 140, 160, 180, and 200 ^{o}C heat treatment of cypress wood (Obataya *et al.* 2000). Beech wood under inert gas also presented a low water absorption rate and reduced the swelling rate, possibly because of the enhanced plasticity (Hakkou *et al.* 2005). After steam treatment and heat treatment, bamboo material showed a similar reduced hygroscopicity (Jiang *et al.* 2008; Qin 2010). Thus, introducing heat treatment to the fibers to help reduce the water absorption of natural fiber-reinforced plastic composites may be an effective physical modification technology for natural fibers used in these composites. In an earlier study, thermal decomposition, crystallization, and mechanical properties of heat-treated bamboo fiber (BF)-reinforced high density polyethylene (HDPE) composites were investigated to identify the specific variation by the heat treatment on thermal degradation process of the composites (Li *et al.* 2013; Du 2013). It was shown that the activation energy (E_a) values of composites from thermal degradation were between 225 and 236 kJ/mol and decreased with increasing fiber heat-treatment temperature (Li *et al.* 2013). Crystallization of the HDPE in the composites under the influence of heat-treated BFs occurred within a temperature range between 106 and 126 ^{o}C. The values of the Avrami exponent of the crystallization model slightly increased with increasing heat-treatment temperature (Du 2013).

The objective of this study was to study the effects of heat treatment of BFs on the water absorption properties of the BF/HDPE composites. A one-dimensional diffusion model was used to fit the experimental weight gain and time data, and the water diffusion mechanism in the composite was analyzed. The obtained data can help better understand the moisture sorption process in the BF-polymer composites to aid the development of the durability improvement strategies for the composite system.

EXPERIMENTAL

Raw Material and Preparation

Moso bamboo (*Phyllostachys edulis*) was used for the study. Green bamboo sections with diameters varying from 70 to 100 mm were collected, cross-cut, and sawed into strips. All strips were dried at 100±2 ^{o}C for 48 h to reduce the moisture content to about 6%. The strips were then randomly divided into three equal groups. One group was used as a control, and two other groups were subjected to heat treatment at 150 and

180 ^{o}C for 2 h. All three groups were them hammermilled, and the crushed material was screened to pass a 40-mesh screen.

High density polyethylene (HDPE AD60-007 with MFR=0.7 g/10 min at 190 ^{o}C/2.16 kg, density=0.96 g/cm^3) was provided by Exxon Mobile Chemical Co. (Houston, TX, USA). Maleic anhydride grafted polyethylene (MAPE - Epolene^{TM} G2608 with MFR = 6~10 g/10 min at 190 °C/2.16 kg, M_F = 65,000 g/mol, and acid number = 8 mg KOH/g) from Eastman Chemical Co. (Madison, TN, USA) was utilized to increase the compatibility between the fillers and plastic matrix.

Composite Sample Preparation

Melt compounds with different heat-treated bamboo fiber loading levels (10, 20, 30, and 40 wt%) were formed using an intermesh, counter-rotating Brabender twin-screw extruder (Brabender Instruments Inc., Hackensack, NJ) with a screw speed of 40 rpm. The temperature profile of barrels was 150-175-175-175-175 °C. The extrudates were quenched in a cold water bath and then pelletized into granules, which were oven-dried at 100 °C for 12 h and bagged for further testing.

Water Absorption Test and Data Analysis

The samples were stored for a month in ambient conditions prior to testing (temperature = 20 to 23 ^{o}C, relative humidity = 30 to 35%). The measurement of water absorption in distilled water was prepared with rectangular samples of 160 x 15 x 3 mm^3 (length x width x thickness). All samples were submerged in the distilled water surface at least 5 cm below the water surface in a temperature range of 20 to 22 ^{o}C. At each target sampling time, the samples were removed from the water soaking tank. The surfaces of the samples were lightly wiped using a clean towel to remove the surface water, and the samples were kept at room conditions for one minute to allow the surface water to dry. The sample weight was then recorded, and all samples were placed back in the distilled water after completing all measurements. The process was repeated until the sample weight reached a constant value. The final equilibrium moisture content was then determined by the oven-drying method. The moisture diffusion characteristic parameters were calculated using a specially designed program in Origin 7.5 with a one-dimensional diffusion model as described below.

Moisture diffusion coefficient (D_m) is defined as the total mass of water crossing the diffusion direction of the test material in a unit area during a unit time. A higher value of D_m reflects a stronger ability of the material to absorb water. In this work, a one-dimensional moisture diffusion process was used to determine the coefficient of diffusion. Fick's second law can depict the water diffusion from outside to the inside of the materials as:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \tag{1}$$

with boundary conditions:

$$c = c_i \qquad 0 < x < h \qquad t < 0 \tag{2a}$$

$$c = c_0 \qquad x = 0; x = h \qquad t > 0 \tag{2b}$$

where t is time (h), x is the spatial coordinate in the sample thickness direction (m), c is the moisture concentration (kg/m^3), and D_x is the diffusion coefficient along the sample thickness direction (m^2/s).

Introducing the initial and boundary conditions into Eq. (1), Eq. (1) is solved as:

$$\frac{C_0 - C_i}{C_m - C_i} = 1 - \frac{4}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)}\frac{(2j+1)n\pi X}{h}\exp\left[-(2j+1)^2 n^2 \frac{D_x t}{h^2}\right] \tag{3}$$

where the parameter C_o is the initial moisture concentration in the material (kg/m^3), C_m is the equilibrium moisture concentration (kg/m^3), C_i is the moisture concentration at a given time t (kg/m^3), t is the diffusion time (s), X is the thickness of moisture diffusion path (m), D_x is the diffusion coefficient along the x direction (m^2/s), and h is the thickness of the material (m).

The total weight of moisture absorbed is obtained by integrating Eq. (3) over the sample thickness h.

$$M = A\int_0^h c\,dx \tag{4}$$

where A is the exposed surface area. Eq. (3) can then be written as:

$$G = \frac{M_i - M_0}{M_m - M_0} = 1 - \frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{\left[-(2j+1)^2\left(\frac{D_x t}{h^2}\right)^2\right]}{(2j+1)} \tag{5}$$

where M_o, M_m, and M_i in percent are the moisture contents (MCs) corresponding to t=0, t= +∞, and t=t, respectively. The final equation of the diffusion coefficient along the x direction (sample thickness) is expressed as:

$$D_x = \pi\left(\frac{h}{4M_m}\right)^2\left[\left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2\right] \tag{6}$$

where D_x is determined from the slope of the linear region in the testing data (*i.e.*, fractional moisture content vs square root of time). The obtained moisture diffusion coefficient through the material can be adjusted using a geometric edge correction factor (ECF) given by:

$$\mathrm{ECF} = (1 + \frac{h}{L} + \frac{h}{W})^2 \tag{7}$$

where L and W are the length and width of the samples, respectively. The final material diffusion coefficient can be written as:

$$D_m = D_x / \mathrm{ECF} \tag{8}$$

It is well known that possible mechanisms for water absorption in composites include Fickian diffusion, relaxation-controlled, and non-Fickian or anomalous diffusion process. The actual mechanism can be distinguished theoretically by the shape of the sorption curve represented by the following equation:

$$\log(\frac{M_t}{M_m}) = \log(k) + n\log(t) \tag{9}$$

The values of n reflect different sorption mechanisms. n=0.5 represents a Fickian diffusion process, $n > 0.5$ is relaxation process, and $0.5 < n < 1$ presents an anomalous transport process. The coefficients were calculated from the slope of $\log(M_t/M_m)$ *versus* $\log(t)$.

Composite Morphology Analysis

The morphology of the composites was measured using a model XL30 environmental scanning electron microscope (SEM) (FEI, Hillsboro, Oregon, USA) with unsoaked and soaked-and-redried composite samples.

RESULTS AND DISCUSSION

Moisture Content-Sorption Time Relationship

Plots of measured MC against $t^{1/2}$ were made to show the relationship between MC change and sorption time. The MCs in the composites linearly increased at the beginning of the soaking process, and the increasing trends gradually slowed down until reaching the final MCs. The MC values at the beginning of the diffusion process were selected to perform a linear fitting of the data. Figure 1(a) shows the initial MC data of the 40 wt% BF/HDPE composites at various BF treatment temperatures. The BF/HDPE composites with BFs treated at higher temperatures experienced a longer sorption time before all the samples reached the same MC level, which suggests that BF heat treatment helped slow down the water uptake of the BF/HDPE composites.

The MC data of the BF/HDPE composites with 100 ^{o}C heat-treated BFs at various BF loading levels is shown in Fig. 1(b). The plots display similar trends of increasing MC with increasing BF loading. The actual MC for the composites with 40 wt% BF was approximately twice as high of that of composites with 30 wt% BF. As expected, the BFs in the composite were the main source for the water absorption.

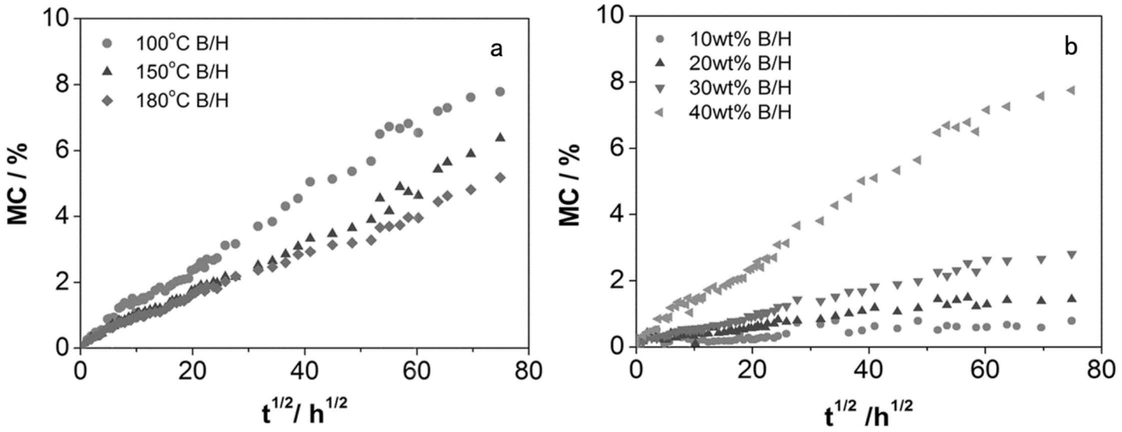

Fig. 1. Comparison of moisture content data for the BF-HDPE composites. (a) MC variations of the 40 wt% BF/HDPE composites with BFs treated at three different temperatures; (b) MC variations of the BF/HDPE composites with 100 °C heat-treated BFs at various BF loadings.

Mechanisms of Moisture Diffusion

Figure 2 shows plots of log(M_t/M_m) against log(t) for composites with various BF loadings and heat treatments. Table 1 shows the n values of various composites. All values are less than n = 0.5; therefore, it can be suggested that the water absorption of the composites primarily followed the Fickian diffusion process. The heat treatment and BF loading did not change the mechanism of water absorption into the composites. Additionally, the n values of the composites treated at 180 °C were lower than those of other composites.

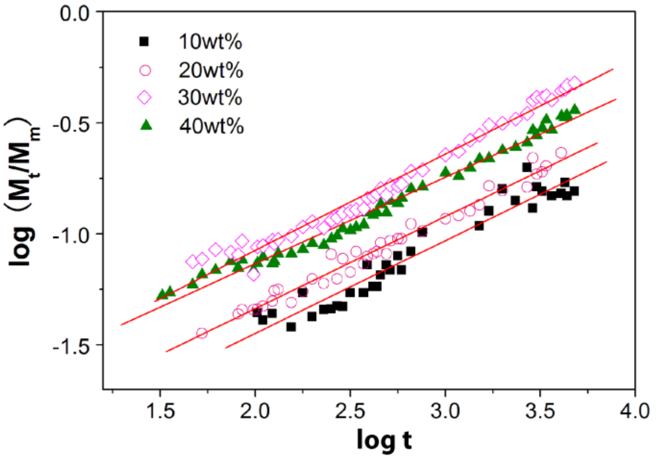

Fig. 2. Plots of log(M_t/M_m) against log(t) for composites with various BF loadings and heat treatments. Lines show the linear fit.

Table 1. Material Constant *n* for Evaluating Diffusion Mechanism of Composites at Various BF Loading and Heat Treatment Temperature Levels.

BF Loading (%)	100 ^{o}C BF/HDPE		150 ^{o}C BF/HDPE		180 ^{o}C BF/HDPE	
	n	R^2	*n*	R^2	*n*	R^2
10%	0.4395	0.9373	0.4191	0.9172	0.3818	0.9489
20%	0.4145	0.9860	0.4894	0.9742	0.3729	0.9538
30%	0.4131	0.9840	0.4031	0.9880	0.3874	0.9898
40%	0.4207	0.9868	0.4229	0.9876	0.4030	0.9938

Moisture Diffusion Parameters

Table 2 shows the diffusion parameters of the heat-treated BF/HDPE composites. The slope of the fractional MC vs square root of time curves (as represented by the α values in Table 2) shows a remarkable decrease with increasing heat-treatment temperature for the BFs, especially that of the heat-treated BF/HDPE composites with 40 wt% BFs. This indicated that the heat-treatment temperature significantly affected the water absorption rate of the BFs and their composites. The final MCs (M_m) of the samples with heat treatment at higher temperatures presented a certain decrease.

Table 2. Diffusion Coefficients and Parameters of HDPE and Heat-Treated Bamboo Flour/HDPE Composites in Distilled Water

BF Loading (%)	Moisture Sorption Parameters								
	100 ^{o}C B/H			150 ^{o}C B/H			180 ^{o}C B/H		
	α	M_m (%)	D_m (x10^{-8} cm^2/s)	*α*	M_m (%)	D_m (x10^{-8} cm^2/s)	*α*	M_m (%)	D_m (x10^{-8} cm^2/s)
10	0.012	4.09	0.229	0.010	3.78	0.203	0.009	4.17	0.115
20	0.021	7.16	0.233	0.018	6.45	0.208	0.015	5.62	0.202
30	0.044	8.92	0.673	0.037	8.29	0.548	0.034	11.6	0.230
40	0.114	16.9	1.267	0.081	16.9	0.630	0.064	14.5	0.532

Notes: *α* = the slope of the water absorption curves

The M_m value of 180 ^{o}C treated BF/HDPE composites with 40 wt% BFs was 14.5%, compared with 16.8% for the composites made with 100 ^{o}C treated BFs. The corresponding diffusion coefficient (D_m) values of the composites had similar trends as those of the α values. For composites with 40 wt% BFs, D_m values are, respectively, 53.0, 24.6, and 16.3 x10^{-10} cm^2/s for composite formulations with BFs treated at 100, 150, and 180 ^{o}C.

As shown in Table 2, M_m and D_m values presented a similar trend as affected by BF content, a significant increase with the increasing BF loading level in the composites. All of these illustrated that adding BFs to the composites led to increased diffusion rate of water in the BF/HDPE composites as a result of BFs being a hygroscopic material. The pathway for water into the composites was primarily through spaces between the matrix and the fibers, cell cavities and pits, and primary and secondary sorption sites on the cellulose and hemicellulose of the fibers (Cao and Zhao 2000).

Figure 3 shows the relationship between D_m and BF loading at three different heat treatment temperatures. The exponential function, D_m = A EXP(B*BFContent), fits the D_m - BF loading data well (Table 3). The reason for the observed heat treatment temperature effect on the D_m values might be due to the reduced number of free hydroxyl groups in BFs, resulting in the decrease of the primary sorption sites after the heat treatment of the BFs.

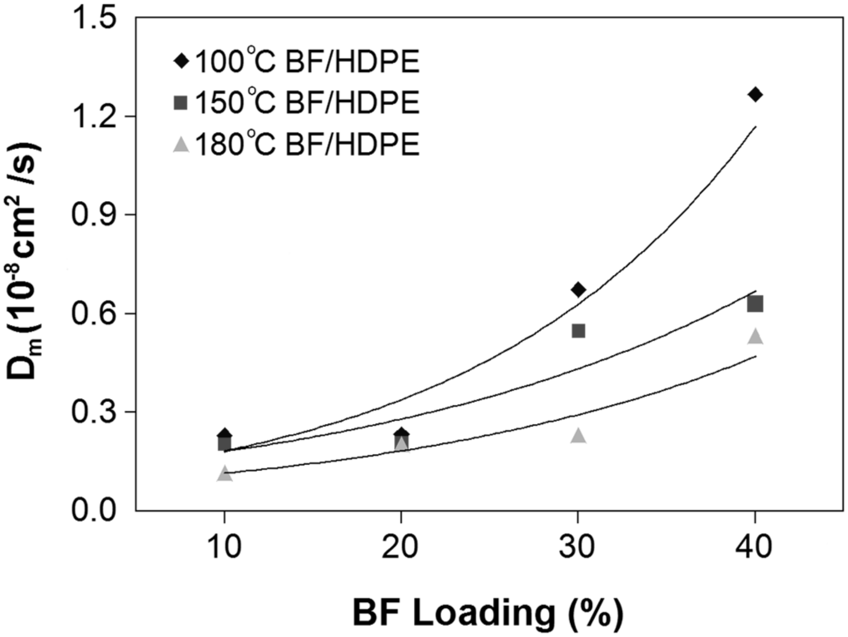

Fig. 3. Plots of D_m versus BF loading for composites made with BFs of different heat treatments; lines show the exponential fit.

Table 3. Relationship Between Diffusion Coefficients and BF Content in the Composites for Different Sample Groups.

Sample group	Obtained Exponential Functions	R^2
100 °C B/H	D_m = 0.0977 exp(0.062 BFContent)	0.9612
150 °CB/H	D_m = 0.1167 exp(0.044 BFContent)	0.8600
180 °C B/H	D_m = 0.0709 exp(0.047 BFContent)	0.9101

Table 4 shows a comparison of measured D_m values with published data for wood/natural fiber and HDPE composites in the field. The diffusion coefficient data from this study is within the reported data range, which varied significantly with composite formulations and processing conditions.

Table 4. Comparison of Measured D_m with Values from Previous Studies for Similar Composites.

Source	Ratio Filler/ HDPE	Filler		Polymer	Fabrication Process	D_m $\times 10^{-8} cm^2/s$
		Type	Mesh size			
Current study	40/60	Bamboo (untreated)	40	vHDPE	Extrusion, Injection	1.27
	40/60	Bamboo (treated)	40	vHDPE	Extrusion, Injection	0.53
Wang *et al.* (2006)	40/60	Rice hull	40	vHDPE	Extrusion	0.40
George *et al.* (1998)	30/70	Pineapple-leaf	100-300	vLDPE	Extrusion, Injection	2.13
Najafi and Khademi-Eslam (2011)	60/40	Rice hull	18-100	rHDPE	Dry blends/hot press	5.14
	60/40	Wood sawdust	18-100	rHDPE	Dry blends/hot press	6.97

Notes: v is virgin, and r is recycled.

SEM Micrographs of BFs Reinforced HDPE Composites

Figure 4 shows some typical SEM micrographs of the composites, showing BF distribution in the composites, and its interfacial bonding with HDPE matrix. As expected, an increased number of the fibers were found for composites at the 40 wt% BF loading level. BFs were well dispersed and randomly distributed in the continuous HDPE matrix. The fiber and matrix in the interfacial region was well bonded through the coupling treatment before the water soaking (Fig. 4a, 4c, and 4e). However, the soaked and redried composite samples showed increased separation between the fiber and matrix. This was a result of swelling and shrinking of the BFs from water uptake and redrying (e.g., Fig. 3d and 3f), which damaged the bonding interface. The result indicated that BFs provided a pathway for the water entering and leaving the composite. This is especially true for composites at 40 wt% BF loading level, where the overlapped fibers existed in the composites. The voids between the fiber and matrix also allowed water to pass through the composites.

CONCLUSIONS

1) Bamboo fiber (BF), as a hydrophilic substance, can affect the water absorption behavior of polymer-based composites. Heat treatment as a physical modification technology was used to alter the water absorption properties of bamboo plastic composites.
2) The final equilibrium MC of the composites presented a decreasing trend with increasing fiber heat-treatment temperature, and an increasing trend with increasing BF loading.

3) The moisture diffusion coefficient (D_m) for all the composites was in the range of 0.115×10^{-8} to 1.267×10^{-8} cm^2/s. The D_m values decreased with increasing BF heat-treatment temperature and increased with increasing BF loading level.
4) The mechanism of water absorption represented a general Fickian diffusion process.
5) Morphology analysis showed increased fiber-matrix interfacial bonding damage due to fiber swelling and shrinking from water uptaking and drying.

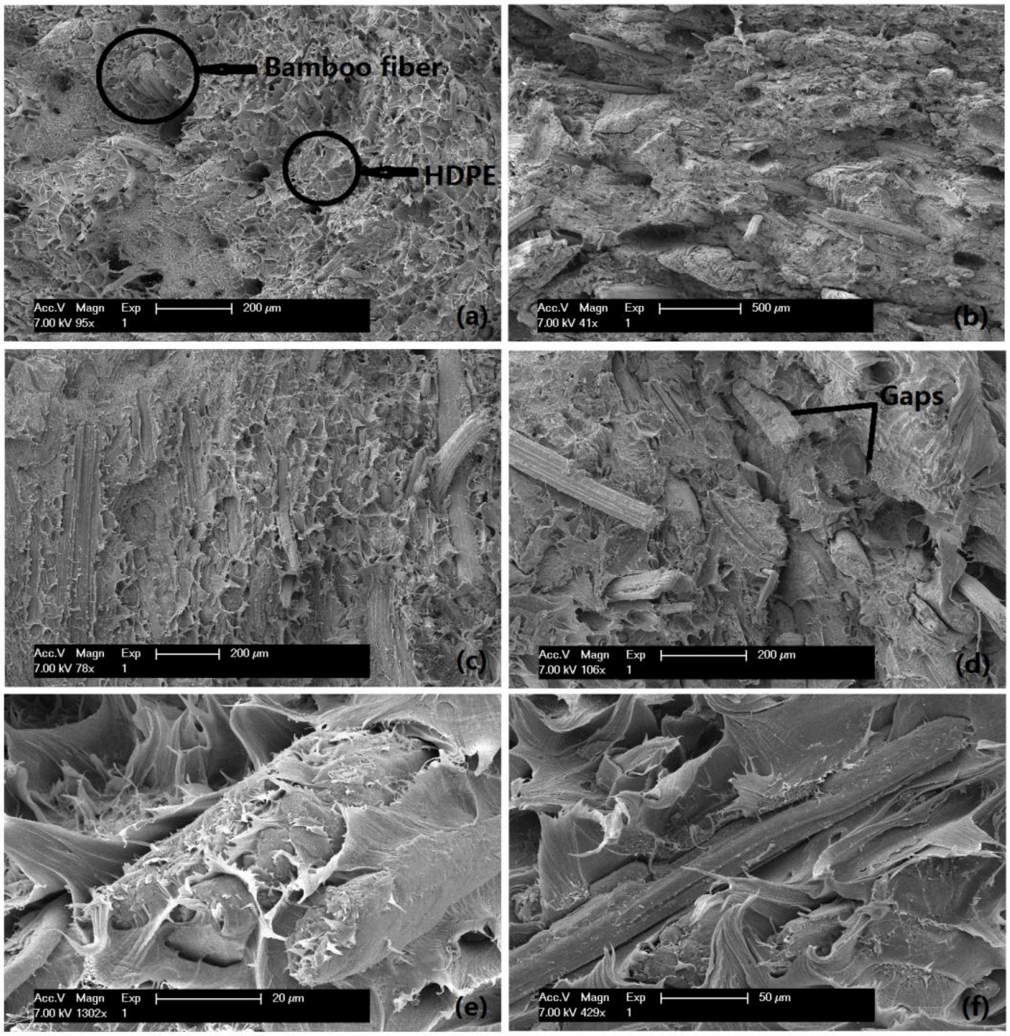

Fig. 4. Typical SEM micrographs of BF reinforced HDPE composites. Unsoaked samples: (a) 180C-40wt% BF, (c) 180C-30wt% BF, and (e)180C-40wt% BF; Soaked-and redried samples: (b) 100C-40wt% BF, d) 150C-40wt% BF, and (f) 180C-20wt% BF.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Project of Science and Technology Department of Zhejiang Province (No. 2012R50023-05), the Project of Undergraduate Science & Technology Creation of Zhejiang Province (No. 2012R412013), the Foundation of Major Discipline of Wood Science & Technology of Zhejiang Province Key Disciplines (No. 201010), and the Foundation of Zhejiang Provincial Natural Science Foundation of China under Grant (No. LZ13C160003).

REFERENCES

Abdul, K. H. P. S, Bhat, I. U. H., Jawaid, M., Zaidonc, A., Hermawand, D., and Hadi Y.S. (2012). "Bamboo fiber reinforced biocomposites: A review," *Materials and Design* 42, 353-368.

Bouafif, H., Koubaaa, A., Perré, P., and Cloutier, A. (2009). "Effect of fiber characteristics on the physical and mechanical properties of wood plastic composites," *Composites: Part A*, 40(12), 1975-1981.

Cao, J. Z., and Zhao G. J. (2000). "Dielectric relaxation based on adsorbed water in wood cell wall under non-equilibrium state 1," *Holzforschung*. 54(3), 321-326.

Du, L. X. (2013). "Mechanical and thermal properties of bamboo and high density polyethylene (HDPE) composites with heat-treated bamboo flour," M.S. thesis, Zhejiang A&F University, China.

George, J., Bhagawan, S. S., and Thomas, S. (1998). "Effects of environment on the properties of low-density polyethylene composites reinforced with pineapple-leaf fibre," *Composites Science and Technology* 58(9), 1471-1485.

Ghasemi, I. and Kord, B. Ismaeil, G., and Behzad, K. (2009). "Long-term water absorption behavior of polypropylene/wood four/organoclay hybrid nanocomposites," *Iranian Polymer Journal* 18(9), 683-691.

Hakkou, M., Pe´trissans, M., Zoulalian, A., and Ge´rardin, P. (2005). "Investigation of wood wettability changes during heat treatment on the basis of chemical analysis," *Polymer Degradation and Stability* 89(1), 1-5.

Hosseinaei, O., Wang, S. Q., Taylor, A. M., and Kim, J. (2012). "Effect of hemicellulose extraction on water absorption and mold susceptibility of wood-plastic composites," *International Biodeterioration and Biodegradation* 71, 29-35.

Jiang, S. X., Cheng, D. L., Zhang, X. C., and Cui, H. Y. (2008). "Pilot study on process and properties of high temperature heat-treated reconstituted bamboo lumber," *China Forestry Science and Technology* 6(22), 80-82.

Karmaker, A. C. (1997). "Effect of water absorption on dimensional stability and impact energy of jute fiber reinforced polypropylene," *Journal of Materials Science Letters* 16(6), 462-464.

Kushwaha, P. K. and Kumar, R. (2009). "Enhanced mechanical strength of BFRP composite using modified bamboos," *Journal of Reinforced Plastics and Composites* 28(23), 2851-2859.

Li, Y. J., Du, L. X., Kai, C., Huang, R. Z., and Wu, Q. (2013). "Bamboo and high density polyethylene composites with heat-treated bamboo fiber: thermal decomposition properties," *BioResources* 8(1), 900-912.

Najafi, A. and Khademi-Eslam, H. (2011). "Lignocellulosic filler/recycled HDPE composites: Effect of filler type on physical and flexural properties," *BioResources* 6(3), 2411-2424.

Obataya, E., Fumio, T., and Misato, N. (2000). "Hygroscopicity of heat treated wood I: Effects of after-treatments on the hygroscopicity of heat-treated wood," *Journal of the Japan Wood Research Society* 46(2), 77-87.

Qin, L. (2010). "Effect of thermal-treatment on physical, mechanical properties and durability of reconstituted bamboo lumber," Ph.D. dissertation. Chinese Academy of Forestry, China.

Stark, N. M., and Gardner, D. J. (2008). Outdoor durability of wood-polymer composites. In: Sain, M., Niska, K. O., editors. *Wood-polymer composites,* Cambridge, UK: Wood Head Publishing Limited, 142-165.

Tamrakar, S. and Lopez-Anido, R. A. (2011). "Water absorption of wood polypropylene composites sheet piles and its influence on mechanical properties," *Construction and Building Materials* 25, 3977-3988.

Tsenoglou, C. J., Pavlidou, S., and Papaspyrides, C. D. (2006) "Evaluation of interfacial relaxation due to water absorption on fiber-polymer composites," *Composites Science and Technology* 66, 2855-2864.

Wang, W., Sain, M., and Cooper P.A. (2006). "Study of moisture absorption on natural fiber plastic composites," *Composites Science and Technology* 66(3), 379-386.

Article submitted: October 21, 2013; Peer review completed: December 10, 2013;
Revised version accepted: January 9, 2014; Published: January 14, 2014.