Effects of Preservative Pretreatments on Moisture Adsorption and Desorption Properties of Corn Stalk Fiber/High-density Polyethylene Composites

Lihui Xuan, Dongxue Hui, Dong Wang, Wanli Cheng, and Guangping Han*

The impact of alkaline copper quat (ACQ) and zinc borate (ZB) on the moisture adsorption and desorption properties and leaching resistance of corn stalk fiber (CSF) reinforced high-density polyethylene (HDPE) composites was investigated. The equilibrium moisture content (EMC) was fitted by the Nelson model, and the interaction between the CSF component and the preservatives was characterized by Fourier transform infrared spectroscopy (FTIR). The effective components of the preservative were successfully immobilized on the CSF, which was observed by FTIR analysis. The leaching resistant analysis showed that the leaching amount of copper and boron elements reached a plateau, and that the leaching resistant performance in the ACQ treatment was better than in ZB. The moisture adsorption of CSF/HDPE composites was significantly reduced with ACQ treatment at low CSF content, but clearly increased in ZB treatment at high CSF content. The moisture adsorption and desorption EMC increased with the increased preservative (ACQ or ZB) embedding at a given CSF/HDPE component ratio. The experimental values were fitted well with the Nelson model; thereby this model could be used to predict the moisture adsorption and desorption EMC of CSF/HDPE composites at various relative humidity.

Contact information: Key Laboratory of Bio-based Material Science and Technology (Ministry of Education), Northeast Forestry University, Harbin 150040 China;
* Corresponding author: guangping.han@nefu.edu.cn

INTRODUCTION

Corn straw is one of the main components of agricultural residues in China. It is very important and necessary to utilize corn stalk in a scientific and efficient way. With the development of wood-plastic composites' (WPCs) technology and environmental protection requirements, the emerging study of agricultural fiber reinforced plastic composites has developed rapidly in recent years (El-Saied *et al*. 2012; El-Shekeil *et al*. 2012; Liu *et al*. 2012).

Agricultural fiber reinforced plastic composites have been widely used in garden architectures and fencings, but they are adversely affected by seasonal variations, ultraviolet radiation, and fungal deterioration (Verhey *et al*. 2001). As reported, the water adsorption rate of natural fiber for 24 h is 7% to 20% (Väisänen *et al*. 2016). The water adsorption for natural fiber/polymer composites varied considerably depending on the fiber species and preconditioning process. The maximum moisture adsorption for the natural fiber/polypropylene composites with several types of fiber reinforcements (wood fiber, rice husks, newsprint fibers, and kenaf fibers) is approximately 1.1% to 13.2%.

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Moreover, there is almost a linear relationship between fiber loading and the moisture adsorption of natural fiber/polypropylene composites (George *et al.* 1998). Wang and Morrell (2004) reported that the wood plastic composites exposed in a higher relative humidity environment tended to have a higher surface moisture content, and the water was distributed equally through the cross-section of the composites. Significant weight losses were found once the moisture content of composites reached approximately 12% to 15%, as revealed by the study of laboratory fungal resistance (Clemons and Ibach 2004). Chen *et al.* (2009) evaluated the influence of moisture sorption on the interfacial shear strength of bamboo/vinyl ester composites. They noted that the moisture adsorption decreased the interfacial bonding strength between bamboo and vinyl ester and caused warping, expansion, and a reduction in the mechanical properties. Pendleton *et al.* (2002) concluded that higher moisture uptake resulted in greater decay of WPCs. Furthermore, Defoirdt *et al.* (2010) also described the moisture content as an important factor in the microbial growth and suggested it could be a critical factor in the service life of WPCs. In a parallel study, it was observed that the WPCs were susceptible to fungal attack with the moisture of the wood component near the fiber saturation point (Clemson and Ibach 2004). Therefore, the moisture adsorption is one of the main influencing factors for the properties of composites, especially for the resistance to deterioration.

A preservative treatment could endow wood materials with a resistance to biodegradation and an extension of service life. The primary preservative for wood is chromated copper arsenate, and other preservatives, such as alkaline copper quat (ACQ), ammoniacal copper zinc, copper boron azole, and zinc borate (ZB), were also used (Martin *et al.* 2005). Wood preservative is widely used in wood industry production because of the low costs, high safety, low corrosiveness, strong preservative retention, and environmentally-friendly performance. The WPCs impregnated with a water-solution preservative will achieve better durability than the untreated WPCs. Loading the preservative is a traditional way to improve anti-degradation and anti-decay performance. Kamdem *et al.* (2004) reported that the mechanical properties, deterioration resistance, and photodegradation of WPCs were enhanced after they were treated by the chromated copper arsenate. Pendleton *et al.* (2002) found that biological resistance was exhibited in the wood/high-density polyethylene (HDPE) composites containing ZB. Stable mechanical properties, similar moisture sorption behaviors, and improved biological performances were shown in the HDPE-based composites treated with ACQ and micronized copper quaternary, as reported by Shang *et al.* (2012). Similarly, Tascioglu *et al.* (2013) reported that addition of ZB at a 1% retention level decreased the mass loss of WPCs when exposed to laboratory decay and termite tests. Now that the moisture is one of the main affecting factors for resistance to deterioration, what is the effect of preservative pretreatment on the moisture adsorption properties of the agriculture fiber/plastic composites? This will aid in the research on the applicable conditions of preservative composites.

Thus, the objective of this study was to investigate the effect of preservatives and corn stalk fiber (CSF) loading levels on the moisture adsorption and desorption of the CSF/HDPE composites. The feasibility of Nelson's model in predicting the equilibrium moisture content (EMC) of the CSF/HDPE composites was also evaluated. Basic research on the application of preservatives incorporated into CSF/HDPE composites was conducted and represents a potentially viable way to convert an agricultural waste product into value-added composites.

EXPERIMENTAL

Materials

Raw materials and preparation

Corn stalks were collected from a farmland in Harbin, China. After removing the inner pith, the corn stalks were granulated to the size required, approximately 1 mm in length and 0.1 mm in diameter, and the ground materials were dried to a moisture content of approximately 3% prior to use. The ACQ and ZB as preservatives were purchased from Star Wyatt Wood Preserving Co., Ltd. (Guangzhou, China). Preservative-treated CSF used for the study was vacuum impregnated by ACQ or ZB. The CSF in the beaker was exposed to an initial vacuum at 0.01 MPa for 30 min. Then, preservative at three loading values (1 phm, 2 phm, 3 phm) were, respectively, added to completely immerse the CSF, and then the pressure was treated at 0.6 MPa for 1 h. After impregnation, the CSF was taken out using a sieve and was oven dried at 103 ± 2 °C to a moisture content of 3% prior to use. High-density polyethylene (density = 954 kg/m³, melt flow index (MFI) = 0.7 g/10 min at 190 °C/2.16 kg) was used as the matrix. Maleated polyethylene (MAPE) (Harbin Institute of Chemical Industry, Harbin, China) (Epolene® CMG9804 with a grafting degree of 0.9%) was applied to increase the compatibility between the corn stalk fibers and the plastic matrix. Paraffin was used as lubricant. The magnesium chloride ($MgCl_2$), sodium nitrite ($NaNO_2$), sodium chloride (NaCl), potassium chloride (KCl), and sodium sulfate (Na_2SO_4) were purchased from Aladdin Reagent (Shanghai, China).

Blend design and sample fabrication

The composite blends were prepared in the Engineering Composite Laboratory of Northeast Forestry University using an SJSH30/SJ45 twin-screw extruder (Nanjing Rubber Machinery Plant, Nanjing, China). The eight blending temperature zones were controlled at 145 °C, 155 °C, 160 °C, 165 °C, 165 °C, 155 °C, 150 °C, and 145 °C from the feeding zone to the die.

Table 1. Formulations of Various Samples for the Preparation of the CSF/HDPE Composites

Code	CSF (wt.%)	HDPE (wt.%)	ACQ (phm*)	ZB (phm*)	MAPE (wt.%)	Paraffin (wt.%)
A	50	47	1	-	2	1
B	50	47	2	-	2	1
C	50	47	3	-	2	1
D	60	37	1	-	2	1
E	60	37	2	-	2	1
F	60	37	3	-	2	1
G	50	47	-	1	2	1
H	50	47	-	2	2	1
I	50	47	-	3	2	1
J	60	37	-	1	2	1
K	60	37	-	2	2	1
L	60	37	-	3	2	1
M	50	47	-	-	2	1
N	60	37	-	-	2	1
*phm: parts per hundreds of mixture (CSF, HDPE, MAPE, and Paraffin)						

Preservative-treated CSF, HDPE, and other processing agents (MAPE 2%, Paraffin 1%), were mixed thoroughly in a high-speed mixer and added to the extruder. The CSF/HPDE profile, with approximately 4-mm thickness, was cut into various lengths for further testing following air cooling. Control boards were manufactured with no AQC or ZB addition. Table 1 shows the design for various blends of all formulations.

Methods

FTIR study

The treated and untreated CSF/HDPE composites were ground and Fourier transform infrared spectroscopy (FTIR) absorbance data were obtained using a Nicolet 6700 FTIR spectrometer (Thermo Fisher Science, Agawam, MA, USA) with an ATR unit (Universal ATR Diamond Zn/Se, Thermo Fisher Science, Agawam, MA, USA) at a resolution of 4 cm^{-1} for 32 scans in the spectral range of 600 cm^{-1} to 4000 cm^{-1}.

Leaching resistance test

The leaching resistance test for CSF/HPDE composites was similar to AWPA E11-97 (American Wood-Preserver's Association, E11-1997, Granbury, TX, USA) to determine the levels of preservative retention for the different composites. Replicated (n = 5) test blocks of each type of ACQ-treated CSF/HDPE, ZB-treated CSF/HDPE, and untreated CSF/HDPE with different formulations were placed in beakers. Then, 350 mL of distilled water was poured into the beakers to ensure the specimens were submerged below the liquid surface, and every beaker bottle was finally sealed with a waterproof paper to prevent the evaporation of water. This test was conducted for 1200 h under the constant temperature of 20 °C ± 2 °C, and the water was changed in intervals of 6 h, 24 h, and 48 h for the leaching solution. The percentages of copper and boron were determined by the atomic absorption spectrometer (PerkinElmer, Waltham, MA, USA).

Moisture adsorption test- EMC measurement

The moisture adsorption test was carried out according to Liu *et al.* (2015). The saturated aqueous solutions of different chemicals formed different levels of relative humidity (RH) in closed containers. The moisture adsorption test consisted of an adsorption process and a desorption process. Thus, 10 dryers were prepared for the saturated saline solution of $MgCl_2$, $NaNO_2$, $NaCl$, KCl, and Na_2SO_4 with the RH of 33%, 66%, 75%, 85%, and 93%, respectively. The specimens (10 mm × 10 mm × 4 mm) were separated into two groups, and eight replicates were run for each formulation. The details were as follows: (1) At RH = 0%, the samples were oven-dried at 103 °C ± 2 °C for 48 h to reach the moisture content of 0%; and (2) At RH = 100%, the samples were immersed in distilled water to reach the equilibrium state; the change in the quality of each specimen was less than 0.002 g.

The treated specimens were placed in the corresponding dryer sealed with Vaseline. Each specimen was weighted once a week until reaching the equilibrium state at the ambient temperature of 20 °C. After conditioning, the specimens were oven-dried at 103 °C ± 2 °C for 24 h. The EMC of each specimen was calculated as follows,

$$EMC\ (\%) = \frac{W_t - W_0}{W_0} \times 100\% \tag{1}$$

where W_t is the equilibrium weight (g) and W_o is the oven dry weight (g).

Nelson's Model

The Nelson model is an adsorption isotherm model. It was fitted at different values of RH according to the EMC Eq. 2, which is suitable for isotherms for Type Ⅱ sorption,

$$\frac{RH}{100} = exp\left\{\left(-\frac{W_w}{RT}\right)exp\left[A\left(1.0 - \frac{EMC}{M_v}\right)\right]\right\} \tag{2}$$

where *RH* is the relative humidity (%), *exp* is the exponential function, M_v is the material constant, which is similar to the fiber saturation point for desorption, *A* is the natural logarithm of the Gibbs free energy per gram of sorbed water as *RH* approaches zero ($\triangle G_0$, cal/g, $A = \ln(\triangle G_0)$), *R* is the universal gas constant, 1.9858 cal/mol/°K, *T* is the absolute temperature (°K), and W_w is the molecular weight of water, 18.1 g/mol.

A linear regression analysis was performed with the measured EMC as the dependent variable and RH as the independent variable, according to Eq. 3,

$$EMC = M_v\left\{1.0 - \frac{1}{A}\ln\left[\left(-\frac{RT}{W_w}\right)\ln\frac{RH}{100}\right]\right\} \tag{3}$$

where M_v is the material constant (%), and the same for all remaining variables.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra for the control and treated groups are presented in Fig. 1. In the control group (curve 1a), the stretching vibration of C=C presented in the HDPE is confirmed by the peaks at 2915.36 cm⁻¹, 2847.38 cm⁻¹, 1471.90 cm⁻¹, and 1462.26 cm⁻¹ (Pagès *et al.* 1996).

The CSF component is characterized by the absorbance bands that appeared at 3484.257 cm⁻¹ to 3159.793 cm⁻¹, which is associated with the stretching vibration band of intramolecular -OH of cellulose. The -COOH stretching vibration presented in hemicellulose is confirmed by the peak at 1742.37 cm⁻¹. The bands observed at 1593.88 cm⁻¹ correspond to the C=O stretch from the CSF components (Xiao *et al.* 2012). For ACQ-treated CSF/HDPE composites (curve 1b), the absorbance peak at 1742.37 cm⁻¹ was clearly weakened, which indicates the interaction of Cu^{2+} with a carboxyl group. The intensity of the 1593.88 cm⁻¹ band was diminished. Ung and Cooper (2005) showed that both -COOH groups and -OH groups could have been responsible for the Cu-monoethanolamine fixation, and the ACQ is immobilized on the CSF by ion exchange. Lee (2011) also reported that the cation sorption sites in wood were saturated with copper even at low concentrations. In addition, Zhang and Kamdem (2007) concluded that copper ethanolamine interacted with carboxylic groups, phenolic hydroxyl groups, and ester groups from lignin to form copper carboxylate and phenolate complexes.

After treatment by ZB, as presented in spectral curve 1c, the intensity of the peak at 1742.37 cm⁻¹ is slightly increased. This is explained by the fact that there are active sites in the carboxyl groups for the interactions with borate. The carboxyl absorbance peaks for ZB-treated composites are more intense than those for ACQ-treated composites, because the borate as an anion cannot be attached to the carboxyl group directly (Cui and Kamdem 1999). The intensity of the band at 1593.88 cm⁻¹ was slightly shifted towards lower wavenumbers, which shows that the interaction between the CSF component and ZB occurred.

The characteristic bands of 872.63 cm^{-1} are attributed to the stretching vibration absorbance peak of $[BO_3]^{3-}$, which demonstrates that the functional groups in ZB penetrated into the CSF. For ACQ-treated and ZB-treated CSF/HDPE composites, the -OH absorbance bands are weakened, which indicates that the quantity of -OH presented in CSF was changed by the ACQ and ZB agent.
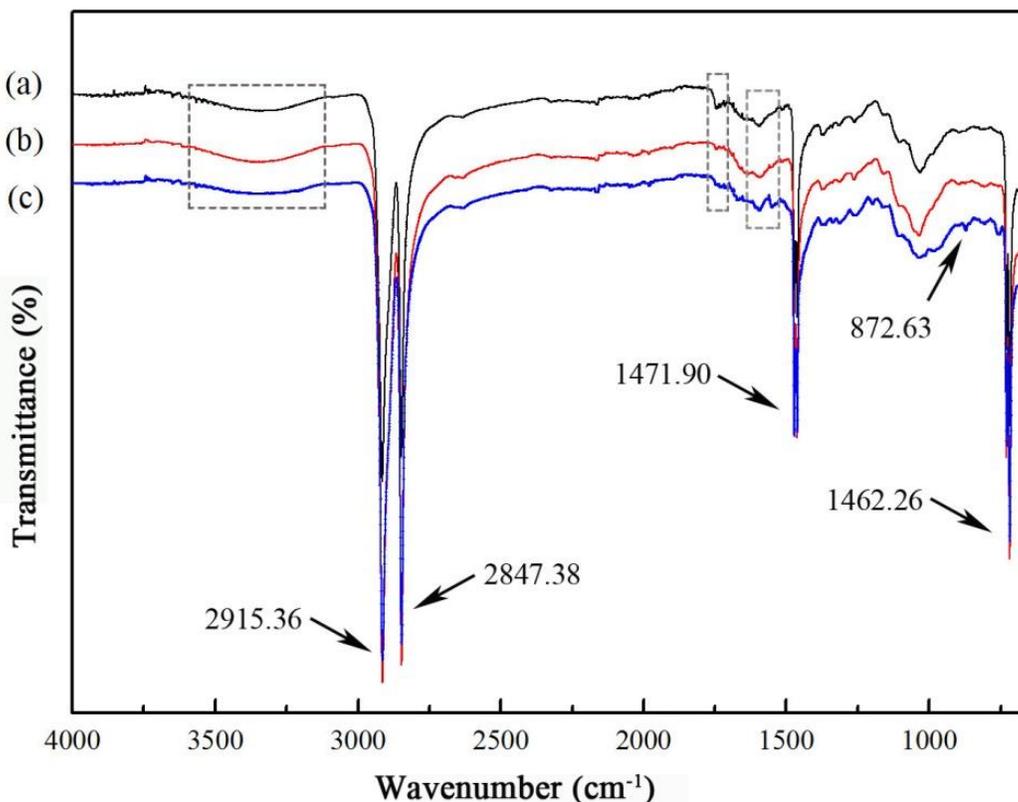

Fig. 1. FTIR spectra of (a) untreated CSF/HDPE composites, (b) ACQ-treated CSF/HDPE composites, and (c) ZB-treated CSF/HDPE composites

A schematic diagram of the interaction mechanism between CSF and ACQ is shown in Fig. 2a. In a complexation reaction mechanism, the substance of ACQ is transformed into charged copper-amine complexes [(1) and (2)] during the treatment with CSF.

Then, the two charged copper-amine complexes are reacted with the CSF-carboxylic and CSF-hydroxylic groups to form a stable CSF-copper-amine complex. In a ligand exchange reaction mechanism, the substance of ACQ exchanges ligands with functional groups of CSF and release amine molecules.

The reaction processes of ZB with CSF can be extrapolated, as shown in Fig. 2b. The $B(OH)_3$ is generated by ZB hydrolysis, and a stable complex is formed by $B(OH)_3$, CSF-carboxylic, and CSF-hydroxylic groups.
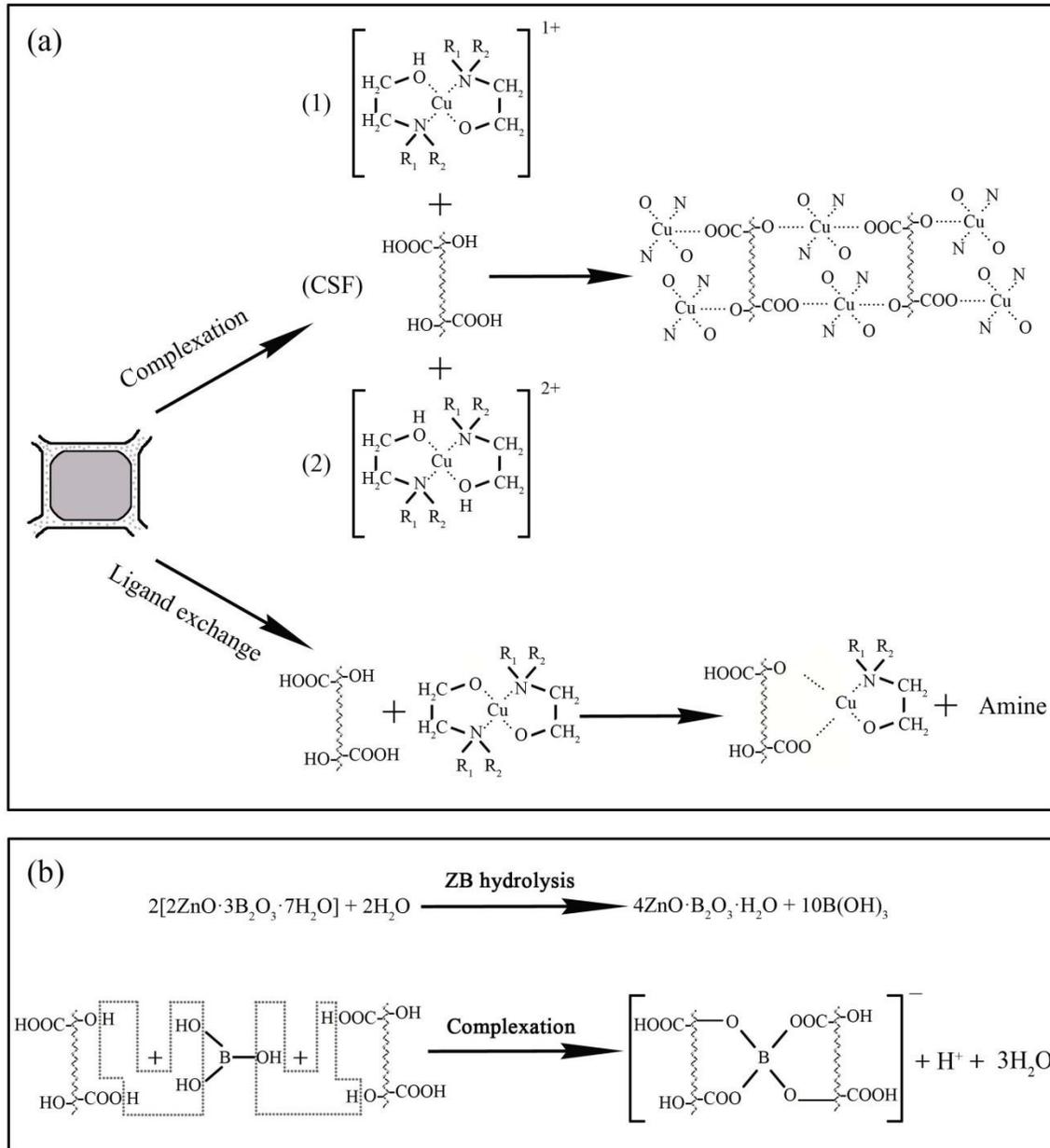
Fig. 2. The schematic diagram of interaction mechanism (a) between CSF and ACQ, (b) between CSF and ZB

Leaching Resistance Analysis

An understanding of the leaching resistance laid the foundation for studying the effect of preservatives on the other properties of composites. The results of the chemical assays about CSF/HDPE with different formulations and control specimens are summarized in Fig. 3. The curvilinear trend of copper leaching was similar to that of boron; the leaching amount of the two chemical elements increased with the increasing test time for all samples. Notably, within the first 400 h, the increment is apparent, and then gradually becomes slower, which was attributed to the chemical reaction of copper and boron in the CSF-HDPE composites. One of the active ingredients, Cu^{2+}, in ACQ is partly deposited in the wood cell wall, and the others form stable hydrogen bonding with

hydroxyl, as in previous literature (Yu *et al*. 2009). Thus, the leaching for copper and boron took place in the deposition initially during the first 400 h. Afterwards, the leaching rate decreased gradually due to the stable chemical bonds. The leaching amount of the same preservatives was closely related to the CSF content, which demonstrated better encapsulation of CSF by the HDPE matrix. Moreover, the leachability of composites shows a rising tendency along with the increased concentration of preservatives, which is in accordance with previous literature (Ung and Cooper 2004). The samples with ACQ-treated CSF exhibited higher preservative retention than those with ZB-treated CSF, which demonstrates that ACQ exhibited good performance in enhancing preservative retention. One reason for this is the solubility. A lower solubility is accompanied by a better leaching resistance (Furuno *et al*. 2003). Another reason is the different leaching mechanism, for copper leaching there is no adequate sedentary site due to a lack of Cr^{6+} (Li *et al*. 2006). For the leaching of boron, the easily leached species boric acid is generated by ZB hydrolysis (Furuno *et al*. 2003).
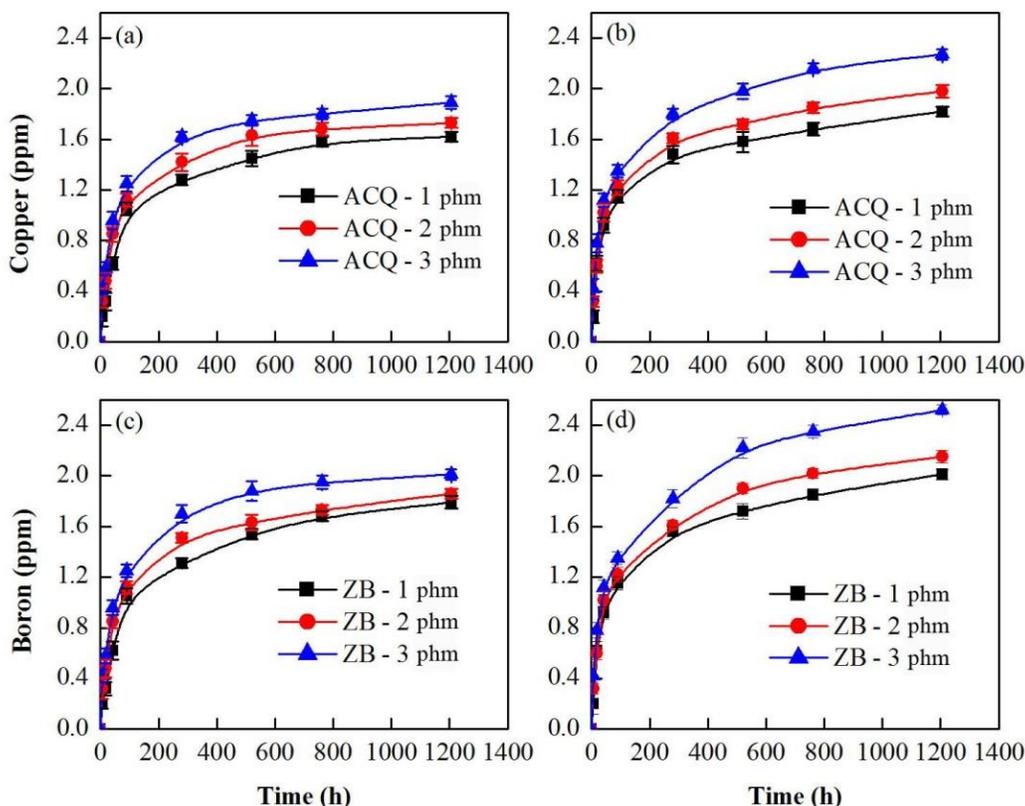

Fig. 3. The leaching resistant property of CSF/HDPE composites for different preservative treated: (a) and (c) CSF/HDPE = 50/50, and (b) and (d) CSF/HDPE = 60/40

Effect of ACQ and CSF Content on the Moisture Adsorption and Desorption Behavior of CSF/HDPE Composites

The moisture adsorption behavior for ACQ-treated CSF-HDPE composites with different formulations is displayed in Fig. 4. No obvious differences were found among the moisture adsorption and desorption properties of CSF/HDPE composites treated with different ACQ concentrations, which indicates that the ACQ concentration had no influence on the mechanism of moisture adsorption. The EMC of the composites varied

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with the CSF/HDPE component ratios and ACQ embedding. At a constant RH, the EMC values increased with increased CSF content for all samples both in the moisture adsorption and desorption process, which is in line with the adsorption phenomenon of the WPCs (Liu *et al*. 2015). The moisture adsorption EMC for the composites treated with ACQ was lower than the untreated composites, which indicates that the moisture resistant abilities of ACQ-treated materials would be enhanced. This could be attributed to the reduction of hydrophilic groups on the CSF surface. Due to the high reactivity of hydroxyl and carboxyl on the CSF surfaces to the Cu^{2+} or quaternary ammonium generated by ACQ hydrolysis, ACQ is immobilized on the CSF surface by chemical bonds. Thus, the moisture adsorption process of ACQ-treated CSF/HDPE composites is inhibited, resulting in the reduction of the EMC.
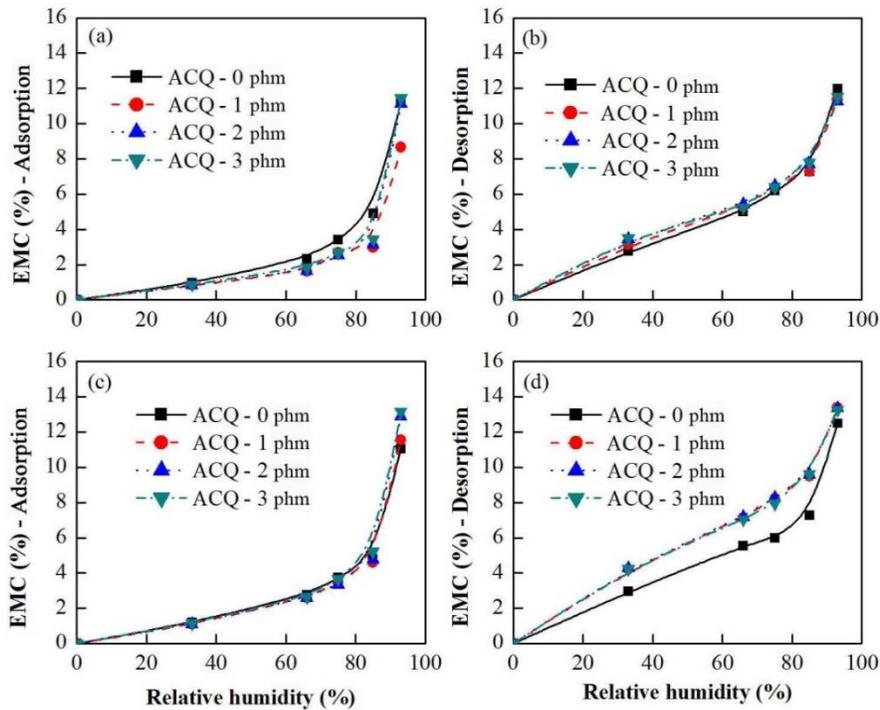

Fig. 4. Adsorption and desorption properties of CSF/HDPE composites treated with different ACQ concentrations: (a) and (b) CSF/HDPE = 50/50, and (c) and (d) CSF/HDPE = 60/40

However, with the increase of ACQ embedding, the moisture resistant abilities decreased in the same formulation. From the above analysis, the hydrophilicity of the chemical groups in ACQ played a role in the moisture adsorption behavior of the composites. Although the hydrophilic groups on the CSF surface were reduced, there are more active hydrophilic substances in the water-soluble ACQ embedded in the compound system, which could be wetted by water molecules. In addition, the composites had two main constituents, the HDPE matrix and the reinforcement CSF. The hygroscopicity is not only related to the various components, but also has a close relationship with the interfacial strength between the HDPE matrix and the CSF (Espert *et al*. 2004). Embedding ACQ increases the interfacial energy at the CSF/HDPE interface, but it weakens the interfacial incorporation and adhesion between CSF and HDPE (Baysal *et al*. 2007), which results in an increase in the water uptake capacity. Therefore, the EMC rose with the increased ACQ. In high CSF content samples, a slight reduction in EMC was

observed for the ACQ-treated CSF/HDPE composites, and no significant differences were found among the ACQ-treated and untreated samples. While a distinctly higher desorption EMC was observed for the composites with the ACQ-treated CSF component, the desorption isotherms were gradually separated from the untreated composites. Therefore, the CSF content also had an obvious influence on the moisture adsorption behavior of composites.

The sorption (adsorption and desorption) isotherms of 1 phm ACQ-treated and untreated composites with different CSF content are summarized in Fig. 5. Similar to the untreated composites, the moisture adsorption (and desorption) isotherms of ACQ-treated CSF/HDPE composites were characterized by sigmoid curves. The EMC values obtained through the moisture adsorption process were lower than those achieved from desorption at the same RH, which indicates the sorption hysteresis still was evident in the ACQ-treated composites. In comparison with the untreated composites, 1 phm ACQ-treated CSF/HDPE composites had a higher hysteresis ratio. The probable reason for this is that the internal water access channel of fiber was occupied by the ACQ, which is unfavorable for the adsorption of water molecules by the composites.
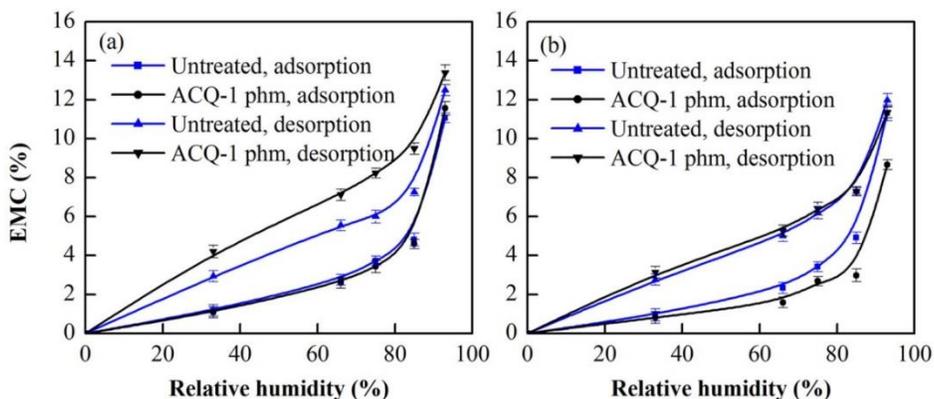

Fig. 5. Comparison of moisture adsorption and desorption of CSF/HDPE composites with 1phm ACQ treatment and without preservative treatment: (a) CSF/HDPE = 50/50 and (b) CSF/HDPE = 60/40

Effect of ZB and CSF Content on the Moisture Adsorption Behavior of CSF/HDPE Composites

The EMC of CSF/HDPE composites with different formulations is presented in Fig. 6. As shown, the moisture adsorption (and desorption) EMC values of ZB-treated composites showed an increased tendency with the increased RH for all samples. At low CSF content levels, the EMC values were almost the same for the ZB-treated samples and control samples. When the CSF component increased from 50% to 60%, the EMCs caused by moisture adsorption and desorption were uniformly increased for all samples. The larger sorption EMC values are displayed in the ZB-treated samples, but no great differences were recorded among the ZB incorporated formulations. In conclusion, ZB played a key role in the moisture adsorption behavior, and the moisture adsorption of CSF/HDPE composites treated by ZB was remarkably enhanced after increased CSF content. This result was related to the weakened interface caused by the enhanced surface polarity of CSF. Furthermore, natural fiber is the effective water adsorbing component of the composites.
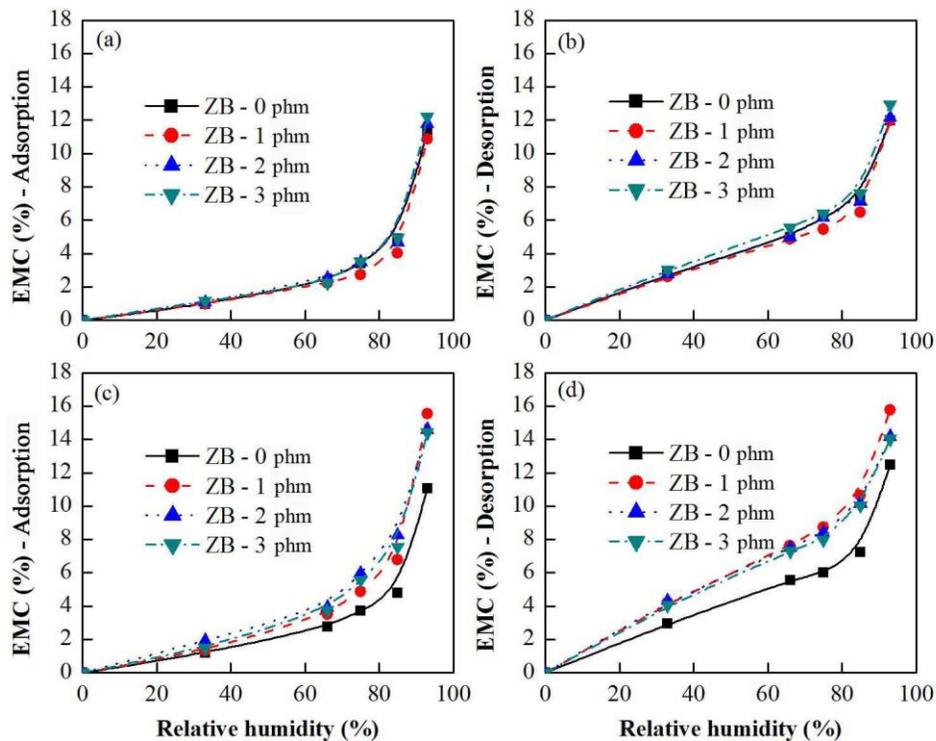
Fig. 6. EMCs of CSF/HDPE composites treated with different ZB concentrations in adsorption and desorption processes: (a) and (b) CSF/HDPE = 50/50 and (c) and (d) CSF/HDPE = 60/40

Fitting of the Nelson Model

As can be seen from the above analysis, the CSF/HDPE composites treated by ACQ exhibited a stronger resistance to moisture adsorption with a low CSF component formulation (50/50). For the 60/40 formulation, the addition of ZB had an obvious effect on the moisture adsorption ability. Therefore, the Nelson model was introduced for the ACQ-treated and ZB-treated CSF/HDPE composites with 50/50 and 60/40 formulations, respectively.

The moisture adsorption isotherm parameters (A and M_v) calculated by the regression analysis and the significant value of fitting effect (F) for different formulations are presented in Table 2. The results show that the values of parameters A and M_v varied with the ACQ embedding and CSF content. The samples with ACQ-treated CSF exhibited lower values of A than those untreated, which indicates the composites treated by ACQ could reach the EMC (for both adsorption and desorption) faster, according to the thermodynamic analysis. Compared with the control samples, the composites treated by ZB had higher values of M_v, which is further demonstrated by how ZB played a role in enhancing the moisture adsorption performance of the composites. For the untreated composites, the value of M_v for desorption process increased with increased CSF loading, which shows that the moisture adsorption of CSF/HDPE composites was highly dependent on the CSF content. Moreover, the value of M_v in the desorption process was higher than in the moisture adsorption process for all of the samples tested at a given RH, which fit the description of sorption hysteresis. From a thermodynamic point of view, if the micro-capillary spaces of the cell wall become smaller as a result of drying, the moisture adsorption process may require a higher energy. The EMC predictive value of

different formulations at a given RH level was calculated by Eq. 3 using the parameters of A and M_v. The linear regression fitting effect of the Nelson model is represented by F. The significance level of this experiment was $a = 0.05$, $F_a(1, n-2) = F_{0.05}(1, 3) = 10.13$. As clearly shown in Table 2, except for the moisture adsorption of CSF/HDPE composites treated by the ACQ level of 2 phm and 3 phm, the value of F was higher than the value of $F_{0.05}(1, 3)$, which indicates the regression equation had a significant effect. The results show that the Nelson model fit well with the experimental data. Therefore, this mathematical model could be used to predict the moisture adsorption and desorption EMCs of CSF/HDPE composites under various RH.

Table 2. Nelson Moisture Isotherms Parameter of CSF/HDPE Composites

Type	Adsorption			Desorption		
	A (cal/g)	M_v (%)	F	A (cal/g)	M_v (%)	F
CSF-50%/ACQ-0phm	3.43	12.53	17.06	4.22	13.73	47.69
CSF-50%/ACQ-1phm	3.42	9.18	10.62	4.48	13.01	56.77
CSF-50%/ACQ-2phm	3.28	11.43	8.05	4.62	12.97	76.18
CSF-50%/ACQ-3phm	3.30	11.88	8.72	4.56	13.19	58.22
CSF-60%/ZB-0phm	3.55	12.19	16.87	4.25	14.05	31.38
CSF-60%/ZB-1phm	3.51	16.4	21.16	4.46	18.38	95.41
CSF-60%/ZB-2phm	3.63	17.82	28.20	4.71	16.59	163.33
CSF-60%/ZB-3phm	3.61	16.39	34.65	4.60	16.51	145.64

CONCLUSIONS

In this study, the effect of various ACQ and ZB loading levels on the moisture adsorption and desorption properties and leaching resistance of the CSF/HDPE composites was investigated. The feasibility of Nelson's model in predicting the EMC of the CSF/HDPE composites was also evaluated. The detailed findings can be drawn as follows:

1. The leaching amount of copper and boron elements reached a plateau, and the preservative retention performance in the ACQ treatment was better than in ZB.

2. At 50% CSF loading levels, the moisture adsorption of the CSF/HDPE composites was greatly reduced with ACQ treatment. The moisture adsorption and desorption EMC was increased with increased ACQ embedding at a given CSF/HDPE component ratio. In conclusion, an ACQ pretreatment effectively reduced the hydrophilic groups and inhibited the moisture adsorption behavior of the composites.

3. At 60% CSF loading levels, the adsorption and desorption EMC of CSF/HDPE composites treated by ZB increased with increased ZB embedding.

4. The adsorption (and desorption) isotherms of CSF/HDPE composites were in line with that of wood, which were characterized by sigmoid curves. The Nelson model could be used to predict the moisture adsorption and desorption EMC of CSF/HDPE composites under various levels of RH.

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REFERENCES CITED

Baysal, E., Yalinkilic, M. K., Altinok, M., Sonmez, A., Peker, H., and Colak, M. (2007). "Some physical, biological, mechanical, and fire properties of wood polymer composite (WPC) pretreated with boric acid and borax mixture," *Construction and Building Materials* 21(9), 1879-1885.

Chen, H. Y., Miao, M. H., and Ding, X. (2009). "Influence of moisture absorption on the interfacial strength of bamboo/vinyl ester composites," *Composites Part A: Applied Science and Manufacturing* 40(12), 2013-2019.

Clemons, C. M., and Ibach, R. E. (2004). "Effects of processing method and moisture history on laboratory fungal resistance of wood-HDPE composites," *Forest Products Journal* 54(4), 50-57.

Cui, W., and Kamdem, P. (1999). "Bioefficiency of boric acid grafted onto wood," *International Research Group on Wood Preservation*, Rosenheim, Germany.

Defoirdt, N., Gardin, S., Van den Bulcke, J., and Van Acker, J. (2010). "Moisture dynamics of WPC and the impact on fungal testing," *International Biodeterioration & Biodegradation* 64(1), 65-72.

El-Saied, H., Basta, A. H., Hassanen, M. E., Korte, H., and Helal, A. (2012). "Behaviour of rice-byproducts and optimizing the conditions for production of high performance natural fiber polymer composites," *Journal of Polymers and the Environment* 20(3), 838-847.

El-Shekeil, Y., Sapuan, S. M., Abdan, K., and Zainudin, E. S. (2012). "Influence of fiber content on the mechanical and thermal properties of Kenaf fiber reinforced thermoplastic polyurethane composites," *Materials & Design* 40, 299-303.

Espert, 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," *Composites Part A: Applied Science and Manufacturing* 35, 1267-1276.

Furuno, T., Lin, L., and Katoh, S. (2003). "Leachability, decay, and termite resistance of wood treated with metaborates," *Wood Science and Technology* 49(4), 344-348.

George, J., Bhagawan, 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.

Kamdem, D. P., Jiang, H. H., Cui, W. N., Freed, J., and Matuana, L. M. (2004). "Properties of wood plastic composites made of recycled HDPE and wood flour from CCA-treated wood removed from service," *Composites Part A: Applied Science and Manufacturing* 35(3), 347-355.

Lee, M. J. (2011). *Adsorption of Alkaline Copper Quat Components in Wood– Mechanisms and Influencing Factors*, Ph.D. Dissertation, University of Toronto, Toronto, Canada.

Li, G., Nicholas, D. D., and Schultz, T. P. (2006). "Effect of delayed drying time on copper distribution in the ACQ-treated southern yellow pine research stakes," *Forest Products Journal* 56(3), 29-31.

Liu, D., Song, J., Anderson, D. P., Chang, P. R., and Hua, Y. (2012). "Bamboo fiber and its reinforced composites: Structure and properties," *Cellulose* 19(5), 1449-1480.

Liu, F. H., Han, G. P., Cheng, W. L., and Wu, Q. L. (2015). "Sorption isotherm of southern yellow pine-high density polyethylene composites," *Materials* 8(1), 368-378.

Martin, M. Z., Labbé, N., Rials, T. G., and Wullschleger, S. D. (2005). "Analysis of preservative-treated wood by multivariate analysis of laser-induced breakdown spectroscopy spectra," *Spectrochimica Acta Part B: Atomic Spectroscopy* 60(7), 1179-1185.

Pagès, P., Carrasco, F., Surina, J., and Colom, X. (1996). "FTIR and DSC study of HDPE structural changes and mechanical properties variation when exposed to weathering aging during Canadian winter," *Journal of Applied Polymer Science* 60(2), 153-159.

Pendleton, D. E., Hofford, T. A., Adcock, T., Woodward, B., and Wolcott, M. P. (2002). "Durability of an extruded HDPE/wood composites," *Forest Products Journal* 52(6), 21-27.

Shang, L., Han, G. P., Zhu, F. Z., Ding, J. S., Shupe, T., Wang, Q. W., and Wu, Q. L. (2012). "High-density polyethylene-based composites with pressure-treated wood fibers," *BioResources* 7(4), 5181-5189.

Tascioglu, C., Yoshimuru, T., and Tsunoda, K. (2013). "Biological performance of wood-plastic composites containing zinc borate: Laboratory and 3-year field test results," *Composites Part B: Engineering* 51, 185-190.

Ung, Y. T., and Cooper, P. A. (2004). "Effect of species, retention and conditioning temperature on copper stabilization and leaching for ACQ-D," in: *The 35th Annual Meeting International Research Group on Wood Preservation*, Ljubljana, Slovenia.

Ung, Y. T., and Cooper, P. A. (2005). "Copper stabilization in ACQ-D treated wood: retention, temperature and species effects," *Holz als Roh-und Werkstoff* 63(3), 186-191.

Väisänen, T., Haapala, A., Lappalainen, R., and Tomppo, L. (2016). "Utilization of agricultural and forest industry waste and residues in natural fiber-polymer composites: A review," *Waste Management* 54, 62-73.

Verhey, S., Laks, P., and Richter, D. (2001). "Laboratory decay resistance of woodfiber/thermoplastic composites," *Forest Products Journal* 51(9), 44-49.

Wang, W. H., and Morrell, J. J. (2004). "Water sorption characteristics of two wood-plastic composite," *Forest Products Journal* 54, 209-212.

Xiao, L. G., Li, Y. C., and Li, R. B. (2012). "Influence of corn straw fibers and polymer latexes on vibration damping property of cement-based materials," *Key Engineering Materials* 517, 367-370.

Yu, L. L., Cao, J. Z., Copper, P. A., and Ung, Y. T. (2009). "Effect of hot air post-treatments on copper leaching resistance in ACQ-D treated Chinese fir," *European Journal of Wood Products* 67, 457-463.

Zhang, J., and Kamdem, D. P. (2007). "Interaction of copper-amine with southern pine: Retention and migration," *Wood and Fiber Science* 32(3), 332-339.