Effect of Durability Treatment on Moisture Sorption Properties of Wood-Plastic Composites

Huiyuan Li, a Kunlin Song, b Dingguo Zhou, a, * and Qinglin Wu b, *

In this study, water absorption and desorption behaviors of wood-plastic composites (WPCs) treated with ultraviolet agents and zinc borate were investigated. Water diffusion characteristics in the composites were analyzed using a one-dimensional diffusion model. The mechanism of water sorption for all composites deviated from Fick’s law of diffusion. Much larger diffusion coefficient values are observed from the desorption process when compared to the absorption process. Measured final equilibrium moisture content and calculated diffusion coefficients varied with sample formulation in a non-consistent manner; this indicated that the durability treatment used in the current study did not negatively affect the water sorption behavior of WPCs. The results of this study help to clarify the effect of durability treatment on the dynamic moisture sorption process of WPCs.

Keywords: Wood-plastic composites; UV-stabilizer; Zinc borate; Water sorption; Diffusion coefficient

INTRODUCTION

The use of wood-plastic composites (WPCs) has increased considerably in recent years. The composites are currently utilized as decking, siding, roof tiles, and window frames. These applications help promote WPCs as low-maintenance and high-durability products when compared to traditional lumber products (Klyosov 2007). However, increased use of WPCs in the construction field has resulted in concerns about its exterior durability (Stark and Matuana 2006; Tascioglu et al. 2013).

WPCs typically consist of thermoplastics, wood fibers (WFs), and processing additives. Both plastics and wood are susceptible to ultraviolet (UV) irradiation. The UV-degradation of thermoplastic, such as polyethylene, results in polymer chain scission that causes surface cracking and strength loss. Wood also undergoes photo-degradation after being exposed to UV light. The exposed surfaces become cellulose-rich and more wettable (Stark and Matuana 2006). To protect WPCs from UV degradation, UV stabilizing agents, including hindered amine light stabilizer (HALS) and ultraviolet absorber (UVA), have been used to minimize the adverse effects of UV radiation (Stark and Matuana 2004). Other additives, such as lubricants and coupling agents, have also been used to improve interfacial bonding and fiber dispersion in WPCs. Previous studies show that wood particles in these materials remain susceptible to moisture and fungal attack under certain conditions (Rangaraj and Smith 2000) because not all the fibers are fully encapsulated by the thermoplastic matrix. Uncoated wood particles and extensive voids in the material provide a continuous pathway for moisture and oxygen to diffuse (Mankowski and Morrell 2000). Biological agents such as decay fungi attack the wetted WPCs, leading to reduced...
mechanical properties. It was concluded that higher wood flour content resulted in greater decay susceptibility and mass losses because the major part of water absorption happened in wood (Pendelton et al. 2002; Kiani et al. 2011). Several borate-based biocides, such as zinc borate (ZnB) and calcium/sodium borate, have been added to WPCs to provide decay (and termite) resistance (Tascioglu et al. 2013). Compared with other compounds, ZnB has the characteristics of low water solubility, high processing temperature, and low environmental toxicity and cost. These advantages make ZnB a common biocide used for WPC products (Tascioglu et al. 2013).

Water in composite facilitates deeper light penetration and provides sites for fungal degradation. WPCs can be detrimentally affected by the presence of excess water. Dynamic water absorption within the composites is intrinsically related to the degradation process (Tsenoglou et al. 2006; Steckle et al. 2007). Thus, understanding the water absorption process in WPCs is very important for the prediction of their application behaviors in highly humid environments (Chen and Shaler 2010). Stark and Matuana (2006) reported the influence of water on the properties of artificially aged WPCs. The authors pointed out that the addition of a UV absorber reduced the loss of strength. Taib et al. (2010) compared the effect of HALS and UVA on the properties of WPCs exposed to natural weathering with high humidity. The results indicated that UVA showed the best results with respect to preventing the loss of flexural modulus. However, none of these studies dealt with the effect of UVA on dynamic water sorption. The effect of ZnB on water absorption of WPCs was studied by Gnatowski (2009). The results showed that two commercial WPC boards containing ZnB absorbed less moisture during exterior exposure. Although the study showed that the use of ZnB decreased water absorption in the test formulations, the dynamic water sorption processes were not determined. Jahadi et al. (2010) investigated the moisture diffusion coefficient of WPCs containing high-density polyethylene (HDPE) and ZnB. The results showed that the addition of ZnB (1%) to the composites decreased the diffusion constant. However, the effects of ZnB concentration were not reported.

In our previous research, a full-factorial experimental design was used to examine the effects of HALS, UVA, and ZnB on the anti-aging properties of WPCs (Li et al. 2014). However, the influence of these additives on water sorption has not been studied. The objective of this work was to provide a comparative analysis of the water sorption behaviors and to determine the moisture diffusion coefficient of WPCs treated with these durability additives.

**EXPERIMENTAL**

**Materials**

High-density polyethylene (AD60 and HD0760, with MFR = 0.7 g/10 min at 190 °C/2.16 kg, density = 0.96 g/cm³) was provided by Exxon Mobile Chemical Co. (Houston, TX, USA). Pine wood flour (WF; 20-mesh particle size) was supplied by American Wood Fiber Inc. (Schofield, WI, USA). Maleic anhydride polyethylene (MAPE; Epolene™ G2608 with melt flow rate of 6 to 10 g/10 min at 190 °C/2.16 kg, Mw = 65,000 g/mol) was utilized to increase the compatibility between fillers and plastic matrix. Lubricant (TPW 306 from Struktol Co., Stow, OH, USA) was used to improve the processing ability of WPC profile. Colorant was added to improve the aesthetics of the WPCs. One UVA (Tinuvin 326 (AT)) and two HALS (Tinuvin 783 (HT), Chimassorb 944 (HC)) were chosen for this study based on differences in molecular structure. All of the HALS and UVA additives were supplied by Ciba Specialty Chemicals, Inc. (Mississauga, Ontario, Canada).
Zinc borate (Borogard-2ZnO·3B₂O₃·3.5H₂O) was obtained from US Borax Inc. (Valencia, CA, USA).

**Table 1. Formulations of Wood-Plastic Composites Used in This Study**

<table>
<thead>
<tr>
<th>Sample</th>
<th>WF &amp; Addictive (wt %)*</th>
<th>HDPE (wt %)</th>
<th>HALS (wt %)</th>
<th>UVA (wt %)</th>
<th>ZnB (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tin783</td>
<td>Chi944</td>
<td>Tin326</td>
</tr>
<tr>
<td>Control</td>
<td>1</td>
<td>31</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>31</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>30</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>29</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>29</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>30</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>29</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>30</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>29</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: *The content was based on the total composite weight

HT = Tinuvin 783; HC = Chimassorb 944; AT = Tinuvin 326; ZnB = zinc borate

**Methods**

*Composite manufacturing*

The WF/HDPE/additive pellets were prepared using a Leistritz Micro-27 co-rotating parallel twin-screw extruder (Leistritz Corporation, Allendale, NJ, USA) according to the formulations shown in Table 1. The extrusion temperatures were controlled at 155 °C (feeder) and 160, 165, 170, 170, 170, 150, 140, 130, and 155 °C (die); the extruder rotation speed was 60 rpm. Profile extrusion was done using an Intelli-Torque Twin-Screw Extruder (CW Brabender Instruments, South Hackensack, NJ, USA) and a 5 × 50 mm die. Manufacturing temperatures for the profile extrusion were varied from 150 °C (feeder) to 165, 160, and 155 °C (die). The profile was air cooled and cut into various lengths for further testing.

*Water absorption and desorption test*

WPC samples of 152 mm × 50 mm × 5 mm were conditioned in an oven at 80 ± 2 °C until constant weights were obtained. Water absorption tests were conducted according to ASTM D 570-98 (2010). All the specimens were placed horizontally on metal test frames in two temperature-controlled (24 ± 0.5 °C) water baths. Both baths were filled with water to a depth of 25 cm. At the end of each target immersion period, the specimens were removed from the containers and surface water was wiped off with paper tissues. The sample weights were measured using a Sartorius-BP analytical balance with an accuracy of 0.001 g. After completing the water soaking tests, water was removed from the test containers. The samples were placed back on the test frame and allowed to dry at the same temperature as that used for water absorption. The samples were periodically weighed during drying until their final equilibrium weight was reached.

The cumulative percentage moisture gain or loss at any time $t$ as a result of moisture absorption or desorption was calculated using the following formula:

$$M_t(\%) = \left(\frac{W_t - W_i}{W_i}\right) \times 100$$

(1)
where $M_t$ is sample moisture content (MC) at time $t$ (%), and $W_i$ and $W_f$ are the initial weight of test samples (initial oven-dry sample weight for absorption or soaked weight for desorption) and weight of test samples at a given time $t$, respectively. For each experimental condition, the average of three samples was used to determine the weight change.

**Composite morphology analysis**

The morphologies of unsoaked control and soaked/re-dried composite samples were observed using a model XL30 environmental scanning electron microscope (SEM) (FEI, Hillsboro, OR, USA) operating at an accelerating voltage of 7 kV.

**Data analysis**

In general, there are three known mechanisms for water transport in polymer composites, including Fick’s diffusion, relaxation-controlled, and non-Fickian or anomalous water transport. These cases can be distinguished theoretically by the shape of the sorption curve represented by the following equation (Adhikary et al. 2008),

$$\log\left(\frac{M_t}{M_\infty}\right) = \log(k) + n \cdot \log(t)$$

where $M_\infty$ (%) is the MC value at the equilibrium condition, and $k$ and $n$ are constants. The value of the constant $n$ is different for the following three cases: in Fickian diffusion, $n = 0.5$; in relaxation, $n \geq 1$; and in the anomalous transport mechanism, $0.5 < n < 1$ (Adhikary et al. 2008).

A Fickian description for water diffusion is given by the following formula (Cheng and Shaler 2010):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\left(-\frac{D (2n+1)^2 t \pi^2}{4 h^2}\right)$$

where $h$ is the original thickness of the sample (mm), $t$ is the time (s), and $D$ is the diffusion coefficient (mm$^2$/s)

To determine Fick’s coefficient of diffusion, the initial stage of moisture sorption is simplified as:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{D t}{\pi h^2}\right)^{1/2}$$

Equation (4) shows that in the initial stage of moisture sorption, the mass uptake has a linear relationship with the square root of the time if moisture diffusion follows Fick’s Law. The diffusion coefficient, $D$, is then calculated using,

$$D = \pi \left(\frac{h \theta}{4 M_\infty}\right)^2$$

where $\theta$ is the slope of the linear portion of the curve. Diffusion through the material can be adjusted using a geometric edge correction factor (ECF), given as,

$$ECF = \left(1 + \frac{h}{L} + \frac{h}{W}\right)$$
where \( L \) and \( W \) are the length and width (mm), respectively, of the samples. Then, the final diffusion coefficient, \( D_m \) in mm\(^2\)/s, can be written as:

\[
D_m = \frac{D}{ECF}
\]  

(7)

RESULTS AND DISCUSSION

Typical Sorption Curves of Treated WPC

Figure 1 shows the mean percentage moisture absorption (Fig. 1a) and desorption (Fig. 1b) versus time for composites with each of the five formulations. Three samples for each formulation were tested, and the mean value for moisture content was determined and reported.

For water absorption, the MC increased as the immersion time was increased. Initial absorption curves for all the samples exhibited a rapid and a linear water uptake during the first 500 h, which was then followed by slower water uptake that approached an asymptotic equilibrium value.

![Typical moisture sorption curves for selected composite formulations. (a) Absorption and (b) desorption](image)

Saturated composites lost their water as they were exposed to a drier environment (desorption). The desorption curves (Fig. 1b) of all the composites had an inverse trend as compared with their corresponding absorption curves (Fig. 1a). The initial desorption curves were approximately linear. As time increased, desorption slowed down until the moisture content reached a final constant value at the equilibrium state.

Interface Evaluation with Scanning Electron Microscope

Figure 2 shows the SEM morphology of unsoaked and soaked/re-dried samples from the untreated control group. As shown in Fig. 2a, the unsoaked control sample had a relatively smooth fiber-plastic interface, where wood components were present on the fracture surface. There were few observed interfacial gaps or separations. In Fig. 2b, it is clear that numerous cracks appeared between the fibers and the matrix after the first cycle.
of absorption and desorption. The result is similar to that observed by Segerholm et al. (2012). At the same time, some wood fibers were pulled out during the fracturing process, leaving holes on the fracture surface (Fig. 2b). Similar behaviors were observed in the corresponding composite samples treated with UV stabilizers and ZnB.

![Fig. 2. Morphology of WPCs from the untreated control group. (a) Unsoaked and (b) soaked and re-dried.](image)

**Mechanisms of Water Sorption**

The fitting of experimental data from the 2% HC-treated WPC is shown in Fig. 3 as an example. General linear lines are observed for the plots of \(\frac{M_t}{M_\infty}\) versus \(\log(t)\). The parameters \(n\) and \(k\) of Eq. 2 were calculated from the slope and the intercept of each curve.

![Fig. 3. Fitting of moisture diffusion data for WPC samples with 2% HC: (A) absorption and (B) desorption.](image)

As shown in Table 2, the \(n\) values of all composites varied from 0.66 to 0.74 for absorption and from 0.33 to 0.46 for desorption. Thus, the observed \(n\) values deviated from the 0.5 value observed for a true Fickian diffusion process. Sample swelling during the absorption and shrinking during desorption probably contributed to the deviation. The data seem to be consistent with previous studies (e.g., Adhikary et al. 2008). Thus, the absorption and desorption processes of WPC samples can only be described by Fick’s law of diffusion as a first approximation; this is especially true for the water absorption during the soaking process. A higher value of \(k\) indicates that the composite requires a shorter time
to reach equilibrium. The \( k \) values are significantly larger from the desorption runs when compared to those from absorption. Thus, water migration from the samples occurred at a much faster rate during desorption under the given exposure conditions.

**Table 2.** Variation of Parameters \( n \) and \( k \) for WPCs with Different Treatments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water absorption ( n )</th>
<th>Water desorption ( n )</th>
<th>Water absorption ( k ) (( h^2 ))</th>
<th>Water desorption ( k ) (( h^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.68 (0.01)</td>
<td>-0.41 (0.03)</td>
<td>0.0090 (0.0001)</td>
<td>17.18 (0.90)</td>
</tr>
<tr>
<td>HT</td>
<td>0.70 (0.03)</td>
<td>-0.44 (0.02)</td>
<td>0.0093 (0.0001)</td>
<td>19.84 (1.68)</td>
</tr>
<tr>
<td>HC</td>
<td>0.69 (0.01)</td>
<td>-0.33 (0.00)</td>
<td>0.0097 (0.0002)</td>
<td>9.89 (0.07)</td>
</tr>
<tr>
<td>AT</td>
<td>0.72 (0.07)</td>
<td>-0.42 (0.01)</td>
<td>0.0091 (0.0002)</td>
<td>18.95 (0.03)</td>
</tr>
<tr>
<td>ZnB</td>
<td>0.67 (0.02)</td>
<td>-0.45 (0.05)</td>
<td>0.0116 (0.0009)</td>
<td>19.76 (4.86)</td>
</tr>
</tbody>
</table>

Mean values of each property; numbers in parentheses are standard deviation based on three specimens.

HT = Tinuvin 783; HC = Chimassorb 944; AT = Tinuvin 326; ZnB = zinc borate

**Final MC and Diffusion Constant**

The final MC values of all composites from both absorption and desorption are given in Table 3.

**Table 3.** Moisture Sorption Parameters of WPCs treated with durability agents

<table>
<thead>
<tr>
<th>Code</th>
<th>Water absorption</th>
<th>Water desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M_w ) (%)</td>
<td>( D_m ) (( \times 10^{-6} ) mm(^2) s(^{-1} ))</td>
</tr>
<tr>
<td>Control</td>
<td>16.3 (0.2)</td>
<td>1.53 (0.10)</td>
</tr>
<tr>
<td>HT</td>
<td>16.5 (0.2)</td>
<td>1.85 (0.18)</td>
</tr>
<tr>
<td>HC</td>
<td>16.0 (0.2)</td>
<td>1.56 (0.18)</td>
</tr>
<tr>
<td>AT</td>
<td>15.6 (0.1)</td>
<td>1.53 (0.1)</td>
</tr>
<tr>
<td>ZnB</td>
<td>15.8 (0.1)</td>
<td>2.09 (0.15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean values of each property; numbers in parenthesis are standard deviation based on three specimens.

HT = Tinuvin 783; HC = Chimassorb 944; AT = Tinuvin 326; ZnB = zinc borate

The mean final MC of the control samples after absorption was 16.3%. The MCs varied from 15.0 to 16.5% for treated composites after absorption. The use of UV agents and ZnB led to a slightly lower MC values in some formulations (e.g., HC1 and HC2 and ZnB1 and ZnB2); however, there was no consistent effect of treatment on the final MC
values after absorption. Composites with 2% AT had the lowest MC of 15.0%. The final MCs after desorption exhibited a similar trend, with values that varied from 1.1 to 2.4% among all the composites. Overall, the effect of durability treatment on the equilibrium MC of WPCs from water-soaked and re-dried samples at the levels used seems to be small when compared to the control samples. Figure 4 shows typical plots of the initial linear portion of MC versus the square root of time curve from absorption (Fig. 4a) and desorption (Fig. 4b), using the composite with 2% HC as an example. Diffusion constants of each composite were calculated, and the mean and standard deviation values are reported.

Diffusion coefficients, $D_m$, calculated from Eq. 5, are summarized in Table 3. The absorption $D_m$ value of control composites was 1.53×10^{-6} \text{ mm}^2\text{s}^{-1}. The absorption $D_m$ values from treated composites varied from 1.20 to 2.06 mm²s⁻¹, with no particular trend among the various treatments. Among these nine formulations, the composite with 2% AT had the lowest $D_m$ value (1.20×10^{-6} \text{ mm}^2\text{s}^{-1}), while the composites with 2% ZnB had the highest (2.04×10^{-6} \text{ mm}^2\text{s}^{-1}). The desorption process led to much larger diffusion coefficients for the given composite formulations. Microcracks formed in the composites due to fiber swelling and shrinking during absorption and desorption cycle contributed largely to the enlarged diffusion coefficient values in the desorption cycle (Shirangi et al. 2008). Among the treated composites, samples with 2% ZnB had the largest $D_m$ (equal to 9.79×10^{-4} \text{ mm}^2\text{s}^{-1}), while samples with 2% AT had the lowest $D_m$ (1.20×10^{-4} \text{ mm}^2\text{s}^{-1}).

The large variability of $D_m$ values among difference groups could be due to the variation of micro-cracks formed in the sample and/or on the sample surface during the wetting and drying processes as shown by Li et al. (2014). The insoluble ZB particles in the composite could lead to additional micro-gaps between fiber and matrix, which in-turn reduced the bonding strength and helped speed up the water diffusion process.

**Comparison of Water Absorption with Previous Studies**

Comparison of the diffusion coefficients and the saturation water content from previous studies with extruded WPCs materials that contain different fillers and filler loadings are shown in Table 4.
### Table 4. Comparison of Measured $D_m$ and $M_\infty$ Values from This Study and from Previous Studies of WPCs

<table>
<thead>
<tr>
<th>Source</th>
<th>Formulation of WPCs</th>
<th>$D_m$ (mm$^2$·s$^{-1}$)</th>
<th>$M_\infty$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current study</td>
<td>WF/HDPE/MAPP/Additive = 55/31/2/12</td>
<td>1.53×10$^{-6}$</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>WF/HDPE/ZnB/MAPP/Additive = 55/30/1/2/12</td>
<td>2.04×10$^{-6}$</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>WF/HDPE/AT/MAPP/Additive = 55/29/2/2/12</td>
<td>1.20×10$^{-6}$</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>Saw dust/HDPE/Tal/MAPE/Additive = 50/36.5/5/4/5.5</td>
<td>1.37×10$^{-6}$</td>
<td>/</td>
</tr>
<tr>
<td>Jahadi et al.</td>
<td>Saw dust/HDPE/Tal/MAPE/Additive = 50/23.5/15/4/5.5</td>
<td>1.83×10$^{-6}$</td>
<td>/</td>
</tr>
<tr>
<td>2010</td>
<td>Saw dust/HDPE/ZnB/Tal/MAPE = 50/24.5/1/15/4</td>
<td>1.75×10$^{-6}$</td>
<td>/</td>
</tr>
<tr>
<td>Adhikary et al.</td>
<td>WF/HDPE = 40/60</td>
<td>3.95×10$^{-6}$</td>
<td>11.6</td>
</tr>
<tr>
<td>2008</td>
<td>WF/HDPE = 50/50</td>
<td>9.45×10$^{-6}$</td>
<td>23.54</td>
</tr>
</tbody>
</table>

In general, diffusion coefficients and saturated MC levels obtained in the present research had similar values when compared to the results reported by Jahadi et al. (2010). Thus, the results indicated that durability treatment as used in the current study did not negatively affect the water sorption behavior of WPCs. The diffusion coefficient values calculated from this study were somewhat smaller in some formulations when compared to reported values for WPCs with 40% filler loading (without using any coupling treatment) (Adhikary et al. 2008). Thus, the use of a coupling agent in this work to enhance the fiber and matrix bonding can help to reduce the moisture uptake rate of the WPCs.

### CONCLUSIONS

1. The moisture content of WPCs increased as absorption time increased. The absorption curves were linear up to the first 700 h and then asymptotically approached the saturation limit.

2. The moisture content decreased more rapidly as the saturated samples were exposed to a drier environment. The initial desorption curves were also approximately linear; afterwards, the desorption process slowed down until reaching the equilibrium state.

3. The mechanism of water sorption of all the composites deviated from the Fickian diffusion process.

4. Much larger diffusion coefficient values are observed from the desorption process versus the absorption process.

5. The measured final equilibrium moisture contents and calculated diffusion coefficients varied with sample formulation in a non-consistent manner, which indicated that the
durability treatment used in the current study did not negatively affect the water sorption behavior of WPCs.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from “A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD)”, the School of Renewable Natural Resources at Louisiana State University Agricultural Center (Baton Rouge, LA 70803, USA), and the Nanjing Forestry University (Nanjing, China).

REFERENCES CITED


Article submitted: July 10, 2014; Peer review completed: August 9, 2014; Revised version received and accepted: August 28, 2014; Published: September 8, 2014.