Chelating efficiency and thermal, mechanical and decay resistance performances of chitosan copper complex in wood–polymer composites

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Abstract

Wood–polymer composites (WPC) have been extensively used for building products, outdoor decking, automotive, packaging materials, and other applications. WPC is subject to fungal and termite attacks due to wood components enveloped in the thermoplastic matrix. Much effort has been made to improve decay resistance of WPC using zinc borate and other chemicals. In this study, chitosan copper complex (CCC) compounds were used as a potential preservative for wood–HDPE composites. CCC was formulated by reacting chitosan with copper salts under controlled conditions. Inductively coupled plasma (ICP) analytical results indicated that chitosan had high chelating efficiency with copper cations. CCC-treated wood–HDPE composites had a thermal behavior similar to untreated and zinc borate-treated wood–HDPE composites. Incorporation of CCC in wood–HDPE composites did not significantly influence board density of the resultant composites, but had a negative effect on tensile strength at high CCC concentration. In comparison with solid wood and the untreated wood–HDPE composites, 3% CCC-treated wood–HDPE composites significantly improved the decay resistance against white rot fungus Trametes versicolor and brown rot fungus Gloeophyllum trabeum. Especially, CCC-treated wood–HDPE composites were more effectively against the brown rot than the untreated and chitosan-treated wood–HDPE composites. Moreover, CCC-treated wood–HDPE composites performed well as zinc borate-treated wood–HDPE composites on fungal decay resistance. Accordingly, CCC can be effectively used as a preservative for WPC.

Keywords: Chelating; Chemical modification; Fungal decay resistance; Mechanical and thermal properties; Wood–polymer composites

1. Introduction

WPC is one of the most dynamic growing materials in wood and plastic industry. It has been extensively used for automotive, building products, packaging materials, and other applications (Youngquist, 1995). It is estimated that the demand for WPC will be over 1.4 billion dollars worldwide by 2007 (Lee and McDonald, 2000). Like wood and wood-based composites, WPC is subject to fungal and termite attacks due to the wood components enveloped in the thermoplastic matrix (Laks and Verhey, 2000; Mankowski and Morrell, 2000). A number of researches have shown that more wood content in WPC is accessible to the fungi on the surfaces and along the composite produced with the large particle. Moreover, the decay susceptibility increased with the wood content and particle size (Mankowski and Morrell, 2000; Khavkine et al., 2000; Verhey and Laks, 2002; Simonsen et al., 2004). Recently, more effort has been made to improve fungal decay resistance of WPC with zinc borate (ZB) and other chemicals (Verhey et al., 2001; Verhey and Laks, 2002; Simonsen et al., 2004).
Chitin and chitosan are commonly known as natural biopolymers. Chitin is the second most abundant natural polymer in the world and mainly exists in crustacean shells (Sanford, 1989; Todd et al., 1997; Duan, 1998). Chitosan, poly-[β(1→4)-2-amino-2-deoxy-D-glucopyranose, is a nontoxic natural product. It is derived from chitin and has a polyamino-carbohydrate structure (Fig. 1). Chitosan is insoluble in water, alkali, and organic solvents, but soluble in some diluted organic and inorganic solutions (Brine, 1984; Sanford, 1989). Chitosan normally decomposes at around 310 °C (Kittur et al., 2002). It also has high reactive adsorptive ability, antimicrobial capability, radiation stability, biocompatibility, and bioinertness (Brine, 1984; Sanford, 1989; Muzzarelli et al., 1995).

Since there are a number of amino groups (–NH2) in its macromolecular structure, chitosan easily chelates with metal salts (such as copper chloride or zinc chloride) to form a polymer metal complex, i.e., chitosan metal complex compounds (CMC) (Muzzarelli et al., 1995). Recently, CMC [e.g., chitosan copper complex (CCC) and chitosan zinc complex (CZC)] have been used as a catalyst for organic synthesis, medicine, antimicrobial fiber and hydro-metallurgy (Hu et al., 2000; Jiang, 2001). CMC also stimulates the enzyme function to accelerate the reaction (Jiang, 2001; Schmuhl et al., 2001).

As an excellent chelator to copper, zinc, and other metal cations, CMC has a potential and important use in wood preservation. Lee et al. (1992, 1993) determined the preservative effectiveness against Tyromyces palustris and microdistribution of elements in wood after the wood specimens were pretreated with chitosan and impregnated with chromated copper arsenate (CCA). They found that the wood preserving effectiveness by the treatment with chitosan and CCA was better than that by the treatment with chitosan alone with the improved leaching resistance of CCA. Kobayashi et al. (1995) reported the termiticidal and decay-resistant effectiveness of CMC. Their results showed that the effectiveness against Formosan subterranean termites (Coptotermes formosanus Shirak) on Pinus densiflora wood treated with CMC in both laboratory and field was effective. In another study (Kobayashi and Furukawa, 1995), it was found that CMC had a high effectiveness against the wood decay fungi (Coriolus versicolor and Tyromyces palustris) of treated Japanese fir (Cryptomeria japonica). Sun (2000) compared the decay performance of CCC and CZC. The results showed that the decay resistance of the CMC-treated wood was equivalent to that of CCA-treated wood. The effectiveness of CCC and CZC varied with the fungus type. So far, however, there has been no report on preservative performance of CMC-treated WPC products.

The objective of the study was to develop CCC as a potential preservative for WPC. Copper-chelating effectiveness in CCC and its performance on thermal and mechanical properties and fungal decay resistance of the resultant composites were evaluated. CCC was also compared with chitosan- and ZB-treated wood–polymer composites in performance.

2. Experimental

2.1. Materials

Thermomechanical pulp (TMP) fiber of Southern pine was obtained from a local medium density fiberboard factory. The fiber was oven-dried at 100 °C for 24 h prior to use. Its actual moisture content during blending was between 3% and 5%.

High-density polyethylene (HDPE) pellets (PE10462 N, Dow Chemical, Midland, MI) were purchased commercially. The density of HDPE is 962.5 kg/m³. Its melting temperature and melt flow index are 134 °C and 10 g/10 min, respectively. The tensile strength and modulus of PE10462 N are 12 MPa and 0.75 GPa, respectively.

Chitosan was obtained from Vanson HaloSource Company (Seattle, WA). Its deacetylation degree was 90%. Cupric chloride dihydrate (CuCl2·2H2O, analytical reagent) was purchased from Mallinckrodt Baker Inc. (Parism, KY). ZB (Borogard ZB®) was obtained from U.S. Borax Company (Valencia, CA). The specific gravity of ZB was 2790 kg/m³.

Fig. 1. Chemical structure of: (a) chitin and (b) chitosan.
2.2. Preparation of CCC

An amount of 60 g cupric chloride dihydrate (CuCl₂·2H₂O) was placed into a 2,000 ml reaction flask filled with 1200 ml distilled water and continuously stirred with a magnetic stirrer for 5 min until the dihydrate was completely dissolved in water. The same amount of chitosan (60 g) was added into the flask and mixed with the dihydrate. The flask was then placed into a water bath on a hot plate with a magnetic stirrer and heated from room temperature to 50 °C. The reactive solution was continuously stirred at 50 °C for 2 h. During chelation, the pH value of the reactive solution was controlled to be between 5 and 6.

After reaction, the flask was removed from the water bath. The solution was filtrated through a funnel with a filter paper to separate water and sediment under a vacuum condition. The filtrates were rinsed with distilled water to eliminate unreacted chitosan and copper salts. The rinsing procedure was repeated several times until unreacted chitosan was completely removed. After storing for 24 h, the wet CCC powder was oven-dried at 40 °C to reach a constant weight.

The formulated complex compounds were ground with a ball miller and then screened to pass a 40-mesh screen. Finally, the ground powder was oven-dried at 40 °C until it reached a constant weight and sealed into plastic bags prior to use.

2.3. Copper analysis for CCC

Before ICP analysis, 0.5 g copper complexes were dissolved with a mixing solution of 10% citric acid [HO₂CCH₂C(OH)(CO₂H)CH₂CO₂H, Fisher Chemical, Fairlawn, NJ], 30% hydrogen peroxide (H₂O₂, Fisher Chemical), 2N nitric acid (HNO₃, Fisher Chemical), and distilled water. The sample solution was heated from room temperature and diluted to 0.1% with distilled water. A 7 ml sample solution was transferred with a pipet into a 20 ml test tube. The analyte was analyzed with an inductively coupled plasma-atomic emission spectrometry (ICP-AES) system to determine the actual copper content in CCC. A blank solution only with the mixing solvents was prepared. The copper-chelating efficiency (η) in CCC was calculated using the following equation:

\[ \eta = \frac{C_{AF}}{C_{TF}} \times 100\% \]  

where \( C_{AF} \) is the actually fixed copper ions per chitosan molecule, g, and \( C_{TF} \), the theoretically estimated copper ions per chitosan molecule, g.

2.4. Wood fiber pretreatment

Before the pretreatment, a CCC solution was prepared by the following procedures. A required amount of CCC was placed into a container with 4000 ml tap water and stirred for 5 min with a magnetic stirrer. The concentration levels of CCC were designed to be 6%, 12%, and 18%, based on the weight of oven-dried wood fiber. An amount of 120 g wood fiber was added into the treating solution and continuously stirred for 2 h. The pretreated wood fiber was then filtrated with a screen and stored at room temperature for 24 h, and oven-dried at 70 °C to reach a constant weight. The pretreated wood fiber was ground into powder through a 20-mesh screen with a Thomas Wiley miller (Model 3383L10, Swedesboro, NJ).

2.5. Compounding process

During compounding, wood fiber pretreated with CCC was added into the thermoplastic melts at four concentration levels (0%, 3%, 6%, and 9%). CCC was also directly added into wood and polymer melts at the same concentration levels to compare the influence of wood fiber pretreatment on the performance of CCC in wood–HDPE composites. Zinc borate and chitosan were used as references for CCC. Three concentration levels (0%, 0.75%, 1.5%, 3%, and 6% by weight) were used for zinc borate, but only a 3% concentration level was used for chitosan (Table 1).

The compounding process for wood fiber-HDPE melts followed a one-step process reported by Lu et al. (2004). The HDPE pellets, chemicals, and wood fiber were sequentially fed into a Haake blender (Model Rheomix 600, Dreieich, Germany). The weight ratio of the oven-dried wood fiber and HDPE was 50/50 for all wood–polymer blends. With a rotation speed of 60 rpm, the compounding process was conducted at 165 °C for 10 min. After compounding, the melts were removed from the blender and cooled to room temperature for 2 h. The samples were then placed into a 2,000 ml reaction flask filled with 1200 ml distilled water and continuously stirred for 2 h. The pretreated wood fiber was then filtrated with a screen and stored at room temperature for 24 h, and oven-dried at 70 °C to reach a constant weight. The pretreated wood fiber was ground into powder through a 20-mesh screen with a Thomas Wiley miller (Model 3383L10, Swedesboro, NJ).

Table 1

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Fiber pretreatment</th>
<th>Concentration of chemicals b (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZB</td>
<td>No</td>
<td>0, 0.75, 1.5, and 3</td>
</tr>
<tr>
<td>Chitosan</td>
<td>No</td>
<td>0 and 3</td>
</tr>
<tr>
<td>CCC(Dir)</td>
<td>No</td>
<td>0, 3, 6, and 9</td>
</tr>
<tr>
<td>CCC(Pre)</td>
<td>Yes</td>
<td>0, 3, 6, and 9</td>
</tr>
</tbody>
</table>

The weight ratio of wood fiber and HDPE was 50/50.

* ZB = zinc borate; CCC(Dir) = directly adding CCC during compounding; CCC(Pre) = pretreating wood fiber with CCC before compounding.

b wt% = weight percentage of composites.
room temperature. The melts were then ground into powder (20 meshes in size) with the Thomas–Wiley miller.

2.6. Manufacture of wood–polymer composites

The ground wood–HDPE blends with a required weight were placed into a two-piece aluminum molding set. The mold was pressed with a miniature hot press at 170 °C for 3 min and cooled to room temperature under a pressure for 1 min. The pressure for heating and cooling was controlled to be 0.16 MPa. All specimens were made with the molding set for density measurement and tensile testing. The target density of composite specimens was 1100 kg/m³.

2.7. Thermal analysis

Thermal analysis was conducted with a TA Instrument TG-DTA coupling system (New castle, DE) to characterize thermal stability of CCC-treated wood–HDPE composites. A small amount of composite sample (ca. 10 mg) was put in a ceramic pan and placed into the testing chamber. A thermogravimetric (TG) analysis was performed by heating a specimen from room temperature to 540 °C at 20 °C/min under a continuous nitrogen stream of 50 ml/min. A differential thermal analysis (DTA) was concurrently conducted under the TG-DTA mode. The temperature difference (ΔT) corresponding to the weight changes (µV/mg) was measured.

2.8. Measurement of mechanical properties

For density measurement, the nominal dimension of each sample was 50 mm × 5.00 mm × 0.7 mm. For tensile testing, dumbbell-shape specimens were made in accordance with the ASTM standard ASTM D638 (ASTM, 1997). For density measurement and tensile testing, four replications were required for each treatment.

The tensile strength of each specimen was tested according to ASTM D638 with an INSTRON (Model 1125) test machine (Canton, MA). The loading speed for each specimen was controlled to be 1 mm/min.

2.9. Decay resistance tests

Soil-block decay tests for wood–HDPE composites samples were conducted in laboratory according to the AWPA standard AWPA E10-01 (AWPA, 2001). Two fungal species were used in this study. One was the white-rot fungus Trametes versicolor (ATCC 42462), while the other was the brown-rot fungus Gloeophyllum trabeum (Madison 617, ATCC 11539). In addition to wood–HDPE composites samples, both yellow poplar and Southern pine blocks were used as a decay reference for wood–HDPE composites. The former were used for the white rot, whereas the latter were used for the brown rot according to AWPA E10-01. For each treatment, three replications were conducted for each fungus species.

Each 250-ml Pyrex® glass jar was filled with 33 g distilled water and 100 g oven-dried fresh forest soil and stored overnight until water was evenly soaked by the soil. A feed strip was then placed on the soil in the jar. The yellow poplar strips were used for the white rot, and the Southern pine strips for the brown rot. All jars closed with plastic caps were steam-sterilized at 122 °C under a steam pressure of 120 kPa for 30 min and gradually cooled to room temperature. The white- and brown-rot fungi were transferred onto a feed strip in each soil-block jar under a sterile hood. The fungi were then incubated at 27 °C and relative humidity 80% for three weeks until each strip was covered with a mycelium mat.

The test samples for the soil-block tests were measured 25 mm long by 16 mm wide by 3 mm thick. Each sample was sanded before exposure to the fungi. Each labeled test specimen was oven-dried at 40 °C to reach a constant weight (W₁), which was the initial weight before the decay test. All test samples were wrapped in groups in aluminum foil and autoclaved at 100 °C for 20 min. After cooling to room temperature, each sample was placed into a soil-block jar under the sterile hood. All test jars were placed in a controlled condition chamber at 27 °C and relative humidity 80% for 12 weeks.

After decay resistance tests, all tested samples were removed from the test jars. Each specimen was carefully cleaned with a piece of soft paper to remove the mycelium from the sample surface. It was then stored at room temperature for 24 h and oven-dried at 40 °C to reach a constant weight (W₂). The weight loss of each tested sample was calculated based on the values of W₁ and W₂.

2.10. Data analysis

Tensile strength and fungal decay resistance were statistically analyzed with Duncan’s grouping tests by means of SAS software (SAS, 2002). The concentration effects of different chemicals on the tensile strength and fungal decay resistance of wood–HDPE composites and the performances on these two properties of different wood–HDPE composites were compared.

3. Results and discussion

3.1. Chelating structure and efficiency of CCC

Copper usually acts as bivalent cations (Cu²⁺) to chelate with electropositive elements (e.g., nitrogen, oxygen, and phosphorus) or other electron pair donors (Solomon, 1981; Bertini et al., 1995). With an electronic configuration of d², Cu²⁺ may form a more stable octahedral structure with six electron pair donors by the d⁵sp³ hybridization under the Jahn-Teller effect (Phipps, 1976). Similar to copper protein and other copper chelating complexes (Pizzi, 1982; Jin and Archer, 1990; Bertini et al., 1995; Lu, 1998), Cu²⁺ can chelate with chitosan to form the coordination compounds. In CCC, Cu²⁺ would primarily chelate with the nitrogen
atoms of amino groups in chitosan. Fig. 2 shows the hypothetical chelating structures of CCC. Generally, a copper cation can chelate with two chitosan molecules and two water molecules to form a stable octahedral structure (Fig. 2a). Two copper cations may link four or more chitosan molecules to form an interlocking structure (Fig. 2b).

According to the aforementioned chelating models for CCC, one copper cation would be fixed by four amino groups. In a 0.5 g CCC sample, the amount of copper cations fixed by chitosan was close to the theoretically estimated value of 0.084 g (Table 2). The copper and nitrogen ratio was 1:4.39 on average and close to 1:4. This result well verified the above proposed chelating models and also implied that there existed some free amino groups in CCC, which did not chelate with any copper cations.

Based on the ICP analysis (Table 2), chitosan had high intimacy with copper. The copper content in copper complexes was 15.3% on average. Chitosan also presented high chelating efficiency with copper. For CCC, the copper-chelating efficiency was as high as 91.3% on average (Table 2).

During wood fiber pretreatment or compounding, CCC was fixed on wood through hydrogen bonding between its amino groups and hydroxyl groups of wood components (e.g., cellulose). It also penetrated into voids and cracks of wood or mechanically deposited in cell lumens. CCC is insoluble in water and has high leaching resistance, thus effectively protecting wood from the fungal attack.

3.2. Thermal performance

According to the DTA spectra, the moisture in the control (i.e., the untreated wood–HDPE composites) started vaporizing at approximately 84 °C (Fig. 3a). The melting peak of HDPE appeared at 141 °C. Lignocellulose started degrading at around 230 °C and the decomposition process of wood was accelerated at 350–400 °C (Shafizadeh, 1984). The peak at 500 °C was mainly due to the decomposition of

![Fig. 2. Hypothetical chelating structures of chitosan copper complexes. The shuttle bars symbolize the parts of chitosan molecule chains.](image)

![Fig. 3. Thermal behavior and stability of different wood–HDPE composites. (a) DTA and TGA spectra of the untreated (control) and treated wood–HDPE composites and (b) DTA spectra of wood–HDPE composites with different CCC concentration levels.](image)

Table 2

<table>
<thead>
<tr>
<th>Order</th>
<th>Sample</th>
<th>Oven-dried sample weight (g)</th>
<th>Solution weight (g)</th>
<th>ICP value (ppm)</th>
<th>( R_v ) (ppm)</th>
<th>Copper concentration (Cu%)</th>
<th>Actually-fixed copper ions in CCC (g)</th>
<th>N:Cu Chelating efficiency, ( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td>–</td>
<td>95.90</td>
<td>0.0027</td>
<td>0</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>CCC</td>
<td>0.503</td>
<td>512.45</td>
<td>143.96</td>
<td>143.96</td>
<td>14.64</td>
<td>0.0736</td>
<td>4.60</td>
</tr>
<tr>
<td>3</td>
<td>CCC</td>
<td>0.504</td>
<td>512.45</td>
<td>152.04</td>
<td>152.04</td>
<td>15.46</td>
<td>0.0779</td>
<td>4.32</td>
</tr>
<tr>
<td>4</td>
<td>CCC</td>
<td>0.504</td>
<td>513.50</td>
<td>153.76</td>
<td>153.76</td>
<td>15.70</td>
<td>0.0791</td>
<td>4.24</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>15.26</td>
<td>0.0769</td>
<td>4.39</td>
</tr>
</tbody>
</table>

Control – the blank solution; CCC – chitosan copper complex.
HDPE (Fig. 3a). For all treated wood–HDPE composites, the above features were not significantly influenced except for the decomposition peak of lignocellulose. ZB- and CCC-treated wood–HDPE composites shifted the decomposition peaks of lignocellulose from 227 °C to 320 °C and 374 °C, respectively (Fig. 3a). The right shift of lignocellulose decomposition peaks in DTA spectra indicates that ZB and CCC may effectively retard the decomposition of wood at high temperatures.

The CCC concentration influenced thermal behavior of the resultant wood–HDPE composites (Fig. 3b). For 3% CCC-treated wood–HDPE composites, the decomposition peak of lignocellulose in the DTA spectra shifted from 227 to 310 °C. At high CCC concentration (>5%), two decomposition peaks of wood converged into a broad peak at ca. 350 °C (Fig. 3b).

All TGA spectra show that there was a 2% weight loss for the treated and untreated wood–HDPE composites at 100 °C due to dehydroxylation of wood (Fig. 3a). The treated and untreated wood–HDPE composites had the first sharp weight loss at around 230 °C due to the decomposition of lignocellulose. The weight loss then slowed down to 30% and 40% at the temperature range between 350 and 450 °C. Another dramatic weight loss occurred at 450–475 °C because of the decomposition and chain scissor of HDPE macromolecules. Wood was finally carbonized over 500 °C and the total weight loss was close to 90% (Fig. 3a).

Consequently, addition of ZB and CCC did not improve thermal stability of the resultant wood–HDPE composites although they retarded the decomposition of wood.

3.3. Mechanical properties

The density of all wood–HDPE composites was 1084 kg/m³ on average with a standard deviation of 70.37. The t-value of t-test for the difference between the density of individual composites and nominal density (i.e., 1100 kg/m³) was equal to −1.0000. The p-value for the one sample t-test was 0.3199, which was larger than z = 0.05. Therefore, the density of most wood–HDPE composite specimens was within the 95% confidence interval of the nominal density.

All ZB-treated wood–HDPE composites had lower means in tensile strength than the control (i.e., the untreated wood–HDPE composites) (Table 3). However, the tensile strengths of all ZB-treated wood–HDPE composites were not significantly different from that of the control in the concentration range between 0% and 9% (Table 4). At 3% CCC(Pre), the tensile strength of CCC-treated wood–HDPE composites was lower than that of the control. The tensile strength of CCC-treated wood–HDPE composites did not significantly change when CCC concentration was between 3% and 6%, but it further significantly decreased at 9% CCC(Pre) (Table 4). The tensile strength of 3% CCC(Pre)-treated wood–HDPE composites was not significantly different from that of the control, but it significantly decreased when CCC(Pre) concentration was increased from 3% to 6%. However, the tensile strength did not significantly change when CCC(Pre) concentration was between 6% and 9%. Hence, CCC had a negative effect on the tensile strength of the resultant wood–HDPE composites at high concentration, regardless of pretreating wood fiber with CCC before compounding or directly adding CCC during compounding.

The negative effect of CCC on the tensile strength of wood–HDPE composites may be due to that unchelated or free copper cations (Cu²⁺) and free chlorine anions (Cl⁻) of copper chloride residuals in CCC impede hydrogen bonding between CCC and cellulose. In addition, these

### Table 3

<table>
<thead>
<tr>
<th>Chemicals¹</th>
<th>Fiber pretreatment</th>
<th>Concentrationb (wt%)</th>
<th>Average board densityc (kg/m³)</th>
<th>Average tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>1107 (35.4)</td>
<td>12.71 (0.93)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>1147 (40.5)</td>
<td>15.54 (1.36)</td>
</tr>
<tr>
<td>ZB</td>
<td>No</td>
<td>0.75</td>
<td>1065 (43.4)</td>
<td>10.66 (0.84)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>1148 (72.8)</td>
<td>12.53 (2.35)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>1158 (55.8)</td>
<td>11.63 (0.64)</td>
</tr>
<tr>
<td>CCC(Dir)</td>
<td>No</td>
<td>3</td>
<td>1003 (52.5)</td>
<td>11.54 (0.11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>1092 (76.8)</td>
<td>11.51 (0.58)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>1044 (62.1)</td>
<td>10.14 (0.07)</td>
</tr>
<tr>
<td>CCC(Pre)</td>
<td>Yes</td>
<td>3</td>
<td>1095 (47.6)</td>
<td>12.57 (1.13)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>1015 (41.9)</td>
<td>10.02 (0.44)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>1062 (65.3)</td>
<td>10.81 (1.31)</td>
</tr>
</tbody>
</table>

¹ Control – untreated wood–HDPE composites, ZB – zinc borate, CCC(Dir) – directly adding CCC during compounding, CCC(Pre) – pretreating wood fiber with CCC before compounding.

b wt% – weight percentage of composites.

c Values in parentheses are standard deviations.

### Table 4

Duncan’s grouping tests on interfacial bonding strength and fungal decay resistance of ZB- and CCC-treated wood–polymer composites at different concentration levels

<table>
<thead>
<tr>
<th>Chemical</th>
<th>0%</th>
<th>0.75%</th>
<th>1.5%</th>
<th>3%</th>
<th>6%</th>
<th>9%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZB</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>CCC(Dir)</td>
<td>A</td>
<td>–</td>
<td>B (α)</td>
<td>B (α)</td>
<td>C (α)</td>
<td></td>
</tr>
<tr>
<td>CCC(Pre)</td>
<td>A</td>
<td>–</td>
<td>A (α)</td>
<td>B (β)</td>
<td>B (β)</td>
<td></td>
</tr>
<tr>
<td>Weight lost by the white rot</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZB</td>
<td>B</td>
<td>A</td>
<td>A</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CCC(Dir)</td>
<td>B</td>
<td>–</td>
<td>B (α)</td>
<td>A (α)</td>
<td>A (α)</td>
<td></td>
</tr>
<tr>
<td>CCC(Pre)</td>
<td>B</td>
<td>–</td>
<td>C (β)</td>
<td>B/A (β)</td>
<td>A (β)</td>
<td></td>
</tr>
<tr>
<td>Weight lost by the brown rot</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZB</td>
<td>A</td>
<td>B</td>
<td>B</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CCC(Dir)</td>
<td>A</td>
<td>–</td>
<td>B (β)</td>
<td>B (β)</td>
<td>B (β)</td>
<td></td>
</tr>
<tr>
<td>CCC(Pre)</td>
<td>A</td>
<td>–</td>
<td>B (β)</td>
<td>B (β)</td>
<td>B (β)</td>
<td></td>
</tr>
</tbody>
</table>

ZB – zinc borate, CCC(Dir) – directly adding CCC during compounding, CCC(Pre) – pretreating wood fiber with CCC before compounding.

The English letters are used for comparison of each property in the same row and the Greek letters are used for comparison of each property in the same column. The same letter indicates no significant difference at the 95% confidence interval.
free ions may further interfere with the mechanical interlocking of HDPE on wood.

Pretreating wood fiber with 3% and 9% CCC before compounding did not significantly differ from directly adding CCC during compounding in tensile strength of the resultant composites, respectively, at the same concentration (Table 4). However, it is not fully understood why at the 6% CCC concentration level pretreatment of wood fiber had a better performance in tensile strength than directly adding CCC during compounding (Table 4).

As shown in Table 5 and 1 5% ZB-, 3% CCC(Dir)- and 3% CCC(Pre)-treated wood–HDPE composites were not significantly different from the control in tensile strength. However, chitosan significantly improved the tensile strength of the resultant composites. Compared with the control, 3% chitosan-treated wood–HDPE composites increased the tensile strength by 22.3% (Table 5). This is possibly attributed to the fact that the amino groups of chitosan formed hydrogen bonding with the hydroxyl groups of cellulose. On the other hand, chitosan possibly acted as dispersion agent to reduce the gaps between wood and HDPE, thus improving the interfacial adhesion in wood–HDPE composites.

3.4. Fungal decay resistance

For the white-rot decay tests, the control and all treated wood–HDPE composites were highly resistant to the decay attack by the white rot fungus Trametes versicolor (Fig. 4a). The weight loss of 0.75% ZB-treated wood–HDPE composites was larger than that of the control, and it gradually increased when ZB concentration increased from 0.75% to 1.5% (Table 4). For CCC(Dir)-treated wood–HDPE composites, the decay resistance at 3% CCC(Dir) was not significantly different from that of the control. However, the decay resistance to the white rot significantly decreased when CCC(Dir) concentration increased from 3% to 6%. It was then almost stabilized in the CCC(Dir) concentration range between 6% and 9%. For CCC(Pre)-treated wood–HDPE composites, the weight loss by the white rot at 3% CCC(Pre) was lower than that of the control, but it gradually increased from 6% to 9% CCC(Pre) (Table 4). At each concentration level, CCC(Pre)-treated composites had a better decay resistance to the white rot than CCC(Dir)-treated composites (Table 4). This may be due to that pretreatment of wood fiber before compounding helped fix more CCC on wood fiber. The weight loss of all CCC-treated wood–HDPE composites by the white rot was less than 3%. The decay resistance of CCC-treated wood–HDPE composites to the white rot decreased when the CCC concentration increased from 3% to 9%. However, the difference in weight loss was less than 1% (Fig. 4a and Table 4). This could be caused by factors such as the difference in vigor of the test fungus and composition of the test samples.

Compared to the control and other treated wood–HDPE composites, 3% chitosan-treated wood–HDPE composites had the best decay resistance against the white rot, while wood had the worst decay resistance (Table 5). The decay resistance of 1.5% ZB-treated wood–HDPE composites was lower than that of the control. However, all 3% CCC-treated wood–HDPE composites had better decay resistance than 1.5% ZB-treated wood–HDPE composites. The decay resistance of 3% CCC(Pre)-treated wood–HDPE composites was better than that of 3% CCC(Dir)-treated wood–HDPE composites, but 3% CCC(Dir)-treated wood–HDPE composites were not significantly different from the control in decay resistance (Table 5). As shown in Fig. 4b, ZB-treated wood–HDPE composites were more effectively against the brown-rot fungus Gloeophyllum trabeum than the control. However, the decay resistance of ZB-treated wood–HDPE composites did not significantly change when ZB concentration was between 0.75% and 1.5% (Table 4). The weight loss of the control was as high as around 10%, but that of ZB-treated wood–HDPE composites was less than 3% (Fig. 4b). For CCC(Dir)-treated wood–HDPE composites, the decay resistance at 3% CCC was significantly improved with respect to the control. The decay resistance at high CCC concentration did not significantly change (Table 4). Nevertheless, the weight loss of all CCC-treated wood–HDPE composites was less than 3% (Fig. 4b). At 3% CCC, CCC(Dir)-treated wood–HDPE composites had a better decay resistance against the brown rot than CCC(Pre)-treated wood–HDPE composites. At high CCC concentration (>3%), however, the latter was better in decay resistance against the brown rot than the former (Table 4). This further indicates that pretreatment of wood fiber before compounding effectively improved the decay resistance of the resultant composites.

Although the control was much better to resist the attack by the brown rot than wood, it was not effective in decay resistance as aforementioned (Fig. 4b and Table 5). Similarly, chitosan-treated wood–HDPE composites also had a poor performance in decay resistance against the brown rot. However, both ZB- and CCC-treated wood–HDPE composites presented an excellent resistance to the brown rot (Table 5). In this study, the decay

Table 5

Duncan’s grouping tests for interfibril bonding strength and fungal decay resistance of different composites

<table>
<thead>
<tr>
<th>Performance</th>
<th>Control 3%</th>
<th>Chitosan 1.5%</th>
<th>ZB 3%</th>
<th>CCC(Dir) 3%</th>
<th>CCC(Pre) 3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Weight loss by</td>
<td>B</td>
<td>D</td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>white rot</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Weight loss by</td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>brown rot</td>
<td></td>
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</tbody>
</table>

Control — the untreated wood–HDPE composites, ZB — zinc borate, CCC(Dir) — directly adding CCC during compounding, CCC(Pre) — pretreating wood fiber with CCC before compounding.

The same letter in the same row indicates no significant difference at the 95% confidence interval.
resistance results of ZB-treated wood–HDPE composites agreed well with those reported by Verhey and Laks (2002) and Verhey et al. (2001). Moreover, CCC-treated wood–HDPE composites performed similarly as ZB-treated wood–HDPE composites in decay resistance against the white and brown rots.

4. Conclusions

Chitosan in CCC had high chelating efficiency with copper. For CCC, the copper content and chelating efficiency were on average 15% and 91%, respectively. Copper, mainly acting as bivalent cations, reacted with the nitrogen atoms of amino groups in chitosan and oxygen atoms in water to form a stable octahedral structure. Two hypothetical chelating structures of CCC were proposed in this study.

CCC-treated wood–HDPE composites were close to the untreated and ZB-treated wood–HDPE composites in thermal behavior and stability. Incorporation of CCC in wood–HDPE composites did not significantly influence panel density of the resultant composites. However, the tensile strength significantly decreased at high CCC concentration. For all CCC-treated wood–HDPE composites, the weight loss by the white and brown rots was less than 3%. Furthermore, the interfacial bonding strength and fungal decay resistance of CCC-treated wood–HDPE composites were well balanced at 3% CCC.

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