Effects of In Situ Deposited Calcium Carbonate Nanoparticles on Tensile Performance of Single Bamboo Fibers and Their Composites

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Abstract

This article applied an ironic solution reaction to in situ deposit calcium carbonate particles onto bamboo fibers at 5°C, 15°C, 25°C, 45°C and 65°C respectively. The fibers were then vacuum filtered to handsheets and hot compressed into thermoplastic composites with alternatively laminated polypropolene films(1 : 3 by weight). Surface features of individual bamboo fibers and tensile properties of fibers and their composites were investigated.

The results show that nanoparticles and submicron particles grew into the wrinkles and micropores of fibers, the size, morphology and adsorbance of which were distinctively varied at different temperatures. The highest calcium carbonate adsorbance (2.34% of fibers’ weight) was obtained at 25°C. The precipitating treatment is a useful method to densify and hydrophobize bamboo fibers and heal the cell wall defects. The mean values of contact angles increased and the variations within group were reduced as the loading percentage of particles rose, which might be due to reduced hydrophilic groups and lumen space for water after coatings of calcium carbonate particles. Besides, tensile properties of all the treated individual bamboo fibers were enhanced. Comparing to the average tensile strength and modulus of elasticity of the untreated, those of the treated bamboo fibers with the biggest calcium carbonate loading were higher by 30.50% and 32.71% respectively. What’s more, the treatments were approved to enhance the compatibility of bamboo fibers and polypropylene, comparing to tensile strength and modulus of elasticity of the untreated composites, those of the treated bamboo fiber composites with the biggest calcium carbonate loading were higher by 14.6% and 19.6% respectively.

Keywords: In situ precipitated calcium carbonate, Bamboo fiber, Surface modification, Microtensile testing, Wettability, Interfacial compatibility
Introduction

Bamboo, as a durable, sustainable, environment friendly and affordable building material, is one of the traditional construction materials for permanent housing, public structures and temporary shelters all around southern China\textsuperscript{[1]}. It had been estimated that more than 5 million ha. of bamboo were planted all around China and the output of bamboo products was over 82.1 billion yuan in 2010\textsuperscript{[2]}.

In recent years, the composite field shows great passion to exploring natural fibers to manufacture low-weight, environmentally friendly products, for their combination of desirable properties, including renewable resources, low cost, relatively high strength-weight ratio\textsuperscript{[3,4]}. Bamboo fiber, with abundant availability, high strength and length/diameter ratio, is one of the best candidates\textsuperscript{[5,6]}. However, bad interfacial adhesion of hydrophilic cellulosic fibers and hydrophobic polymer matrix, which is responsible for mechanical properties, dimensional stability and life circle of goods under indoor and outdoor situations, has set constraints on the enhanced utilization of bamboo fibers in thermoplastic composites\textsuperscript{[7]}. Therefore, a lot of treatments were employed to improve the compatibility between natural fibers and the matrix in previous studies\textsuperscript{[8]}. Inorganic nanoparticles as cell wall fillers were used for improvements of physical and mechanical properties of paper and fiber reinforced plastic composites, for the reason of its huge specific surface area, to better fiber wetting in the molten polymer matrix and initiate the polymer’s crystalline orientation\textsuperscript{[9-11]}.

The understanding of properties, especially mechanical behavior of single bamboo fibers, as the load-bearing constituent of bamboo, could provide the valuable engineering mechanical data for the optimal design for utilization of bamboo and bamboo fibers-based products, such as pulp and paper, fiberboards, textile and fiber reinforced plastic composites. The study of mechanical behavior of individual plant fibers has gained momentum in recent years, to establish a direct correlation between fiber mechanical properties with plant cell wall microstructure and chemical compositions\textsuperscript{[12-14]}. It is particularly important in biomaterials science to learn from the hierarchically organized structure and from specific molecular mechanistic phenomena at the cell wall level. Fiber defects, like pits and micropores after retting in the cell wall, have been proven to influence mechanical properties and failure mechanisms of natural fibers\textsuperscript{[12,15]}.

The objectives of the current study involve in situ depositing treatments of calcium carbonate (CaCO\textsubscript{3}) particles onto bamboo fibers through the ionic reaction of sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) and calcium chloride (CaCl\textsubscript{2}) aqueous solution, their impacts on surface features, wettability and tensile properties of single bamboo fibers and mechanical properties of laminated thermoplastic composites reinforced by modified fibers.
Materials and Methods

Sample preparation

All fibers were extracted with the blended chemical solutions of hydrogen peroxide and glacial acetic acid from the outer-chipped 3-year bamboo sticks (Neosinoealamus affinis, Changning County, Sichuan Province). The detailed preparation method was described by Leslie H. Groom\cite{16}. Na$_2$CO$_3$ and CaCl$_2$ (Regent grade, Sinopharm Chemical Reagent Beijing Co., Ltd) were digested into 0.1 mol/l aqueous solution with distilled water. Ethylenediamine tetraacetic acid disodium (EDTA-2Na) applied as crystalline control agent, was provided by Sinopharm Chemical Reagent Beijing Co., Ltd, too. Air-dried bamboo fibers and 300ml 0.1 mol/l CaCl$_2$ aqueous solution (1:50 g/ml) were mixed by mechanical stirring at 5°C, 15°C, 25°C, 45°C and 65°C separately for 20 minutes, then the chemical additive was added, following 300ml 0.1 mol/l Na$_2$CO$_3$ aqueous solution at the rate of 25 ml/min. The whole together were blended for another 25 minutes. Excess CaCO$_3$ particles between fibers and other by-products were removed under running water. Afterwards, the retted fibers as control samples and the treated fibers were air-dried and stored in a constant temperature and humidity chamber, at 20°C, with the relative humidity(RH) of 65%.

The retted fibers as control samples and the treated fibers were made into circle handsheets with a diameter of 100 mm, and dried in a circulation oven at 103°C for 20 min, then stored in sealed plastic bags. Afterwards, the mats were laminated by fiber handsheets and polypropylene (PP) films alternatively, with the ratio of 1:3 by weight, and put into platens that preheated to 100°C. It took about 12min to raise the temperature between platens up to 180°C, then a pressure of 2MPa was applied to the mat constantly for 2min, and the platens were not open until cooled to 40°C. Three panels were obtained for each level and the control.

Physical and Mechenceal Properties of Bamboo Fibers

Surface morphology of fibers and element analysis of particles were conducted by field emission scanning electron microscopy(FESEM XL30, FEI Incorporated, Holand). Fibers were coated with 15nm thick carbon film to avoid electron charging effect. The microscopy was operated at 5kv in a high vacuum environment, no higher than 5×10$^{-5}$ Pa.

The fibers’ ash contents were under test according to GB-T 742-2008. The CaCO$_3$ loading percentages were calculated by the difference of ash contents between the treated and the control fibers. Two duplicates were measured for each level, with a maximum error of 0.2%.

Dynamic contact angles of bamboo fibers, were obtained by the optical contact angle measuring device (Kruss DSA100, Germany) at ( 25 ± 2 ) °C, ( 50 ± 5 ) %RH, with distilled water droplets as the test liquid. The testing process and the calculating method were depicted by Chen Hong et al. in detail\cite{17}. 15 specimens were test for each level.

The tensile tests were conducted by the microtester (Instron 5848, USA) at room environment
(23°C, 40%RH) with a loading rate of 0.048mm/min, 30 replicates for each treating level. The cell wall area of every broken fiber was determined with a confocal scanning laser microscope (CSLM Meta510, Zeiss, Germany). The mean values as well as standard deviations of tensile strength and modulus of elasticity were calculated from the stress-strain curves. The testing process were conducted as the same as Yu Yan et al[18].

**Tensile Test of Bamboo Fiber Reinforced PP Composites**

The specimens were cut into dog-bone shape using a laser cutting machine (CMA-1610TF, Yue Ming Laser Science Co., Ltd, Guangdong), half sized referring to GB1040.3-2006-T, 5 replicates for each panel. They were kept in a desiccator for 2 days at least prior to testing. The tensile tests were conducted by Instron 5848 at room environment with a strain rate of 2mm/min. The mean values and standard deviations of tensile strength and modulus of elasticity were calculated from the stress-strain curves.

**Results and Discussion**

**In situ CaCO$_3$ Growth on the Treated Bamboo Fibers’ Surface**

Surface morphologies of bamboo fibers were shown in Figure 1. Figure 1(A) represented the untreated fiber surfaces, with visible micropores, such as pits, longitudinal wrinkles formed during air-drying and pores emerged where lignin and hemicelluloses were removed. These micropores could benefit the impregnation of ionic solutions along the fibers and provide sites for CaCO$_3$ crystals’ deposition. There were a few nanoparticles in the pores of bamboo fibers at 5°C, and the crystals appeared single, irregularly tetrahedral. As the temperature ascended, Figure 1(C) displayed that the sizes and amounts of CaCO$_3$ particles got larger, and more pits and wrinkles were filled. Since Ca$^{2+}$、CO$_3^{2-}$ ions moved faster and the solubility of CaCO$_3$ went down, more CaCO$_3$ crystals were ready to form[19]. As CaCO$_3$ particles continued to grow, they could not fit the pores anymore, more likely to be removed during washing, as shown in Figure 1(E,F).

![Image](a) The untreated  
(b) 5°C  
(c) 15°C
Effects of CaCO$_3$ Precipitation on Contact Angles of Bamboo Fibers

Table 1 displayed that CaCO$_3$ loadings went up at first, then declined slightly when the temperature rose, as the similar trend with contact angles. Fibers treated at 25°C had the highest adsorbance. Although the differences of CaCO$_3$ loadings among the variables were no more than 1% fibers’ oven dried weight, the particles filled and grew from micropores of fibers, the surface roughness of which may change consequently. The mean contact angle values of bamboo fibers changed within 2°. But it shouldn’t be neglected that the mean values of fibers modified at 15 °C and 25°C did get an increment and the standard deviations of contact angles declined at the same time. The coating of CaCO$_3$ nanoparticles may result in a smoother surface and reduced hydrophilic groups. As the particle sizes grew larger, combined with decreased CaCO$_3$ loading percentages, particles could not be well-distributed on the fibers. Therefore, the surfaces were rough again, and the mean values of contact angles decreased while the standard deviations got increments. These might influence interlacements of fibers and interfacial adhesion between fibers and polymer matrix.

Table 1 CaCO$_3$ Adsorbance and Static Contact Angles of Single Bamboo Fibers

<table>
<thead>
<tr>
<th>The Treated Conditions (°C)</th>
<th>CaCO$_3$ adsorbance (%)</th>
<th>Static Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The untreated</td>
<td>-</td>
<td>65.75</td>
</tr>
<tr>
<td>5</td>
<td>1.01</td>
<td>68.07</td>
</tr>
<tr>
<td>15</td>
<td>1.57</td>
<td>69.63</td>
</tr>
<tr>
<td>25</td>
<td>2.34</td>
<td>70.91</td>
</tr>
<tr>
<td>45</td>
<td>1.49</td>
<td>68.91</td>
</tr>
<tr>
<td>65</td>
<td>1.61</td>
<td>69.56</td>
</tr>
</tbody>
</table>
Tensile Properties of Individual Bamboo Fibers

Table 2 show that tensile properties of all the treated individual bamboo fibers were enhanced, with the peak of a 30.50% increase in tensile strength (from 1035.87MPa to 1383.99MPa) and a 32.71% increase in modulus of elasticity (from 27.36GPa to 36.30GPa) was obtained for the fibers treated at 25°C, and then decreased a bit when the temperature rose, as the same trend of CaCO₃ adsorptions. Analysis of variances present that tensile strength and modulus of elasticity had distinct differences among groups and no significant variance within groups. These might be explained by the fact that CaCO₃ nanoparticles filled fiber defects, like pits, where large microfibril angles were around and plastic deformation occurred first[15]. The improvement in the tensile properties should also be attributed to the impregnation of CaCO₃ particles in fiber cell wall, which increases the density of the fibers[20]. For the modified fiber, during the tensile process, the stress around the pits could be passed to the fillers, thus the rapid deformation and rupture of pits might be effectively prevented.

Table 2 Tensile properties of single bamboo fibers modified under different temperatures

<table>
<thead>
<tr>
<th>The treated conditions (°C)</th>
<th>Tensile strength (MPa)</th>
<th>Modulus of elasticity (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The untreated</td>
<td>1035.87(280.37)</td>
<td>27.36(6.88)</td>
<td>4.21(1.42)</td>
</tr>
<tr>
<td>5</td>
<td>1136.64(286.82)</td>
<td>29.80(6.90)</td>
<td>4.09(0.95)</td>
</tr>
<tr>
<td>15</td>
<td>1237.71(406.61)</td>
<td>30.70(8.55)</td>
<td>4.33(0.90)</td>
</tr>
<tr>
<td>25</td>
<td>1383.99(413.50) *</td>
<td>36.30(8.92) *</td>
<td>3.89(0.52)</td>
</tr>
<tr>
<td>45</td>
<td>1176.71(261.80)</td>
<td>31.50(6.71)</td>
<td>3.97(0.66)</td>
</tr>
<tr>
<td>65</td>
<td>1167.18(265.89)</td>
<td>29.43(8.00)</td>
<td>4.34(0.91)</td>
</tr>
</tbody>
</table>

In the parentheses are the standard deviations. * was significantly different at α= 0.05 according to results of multiple comparison with Fisher’s Least Square method.

Tensile Properties of Bamboo Fiber Reinforced PP Composites

For all the treatment conditions in Table 3, the bamboo fibers reinforced PP composites showed improvement in both tensile strength and tensile modulus. The composites’ tensile strength and modulus of elasticity increased firstly, then decreased a bit as the temperature rose, and they had distinct differences among groups and no significant variance within groups. Furthermore, multiple comparison demonstrated that tensile properties of the composites were remarkably enhanced when CaCO₃ nanoparticles in situ deposited in micropores of bamboo fibers at 15°C and 25°C as shown in Table 3. The composites reinforced with the fibers treated at 25°C gave the highest tensile strength and modulus, which were 14.6%, 19.6% separately higher than those reinforced with untreated fibers, which might be explained by the fact that CaCO₃ nanoparticles played a role of heterogeneous nucleation in PP crystallization, the degree of PP crystallization increased while the crystal size became smaller, so that the mechanical properties of PP composites got reinforced[20]. On the other hand, the wettability of fibers had a significant improvement at the same level. In summary, CaCO₃ nanoparticles contributed to the progress in compatibility of bamboo fibers and PP.
matrix to a dramatic extent.

Table 3 Tensile strength and modulus of elasticity of bamboo fibers/PP composites

<table>
<thead>
<tr>
<th>The treated conditions (°C)</th>
<th>Tensile strength (MPa)</th>
<th>Modulus of elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The untreated</td>
<td>48.91 (6.32)</td>
<td>1.78 (0.27)</td>
</tr>
<tr>
<td>5</td>
<td>51.27 (7.37)</td>
<td>1.90 (0.27)</td>
</tr>
<tr>
<td>15</td>
<td>54.49 (4.21)</td>
<td>1.96 (0.22)</td>
</tr>
<tr>
<td>25</td>
<td>56.04 (4.79) **</td>
<td>2.13 (0.14) **</td>
</tr>
<tr>
<td>45</td>
<td>50.73 (5.20)</td>
<td>1.86 (0.20)</td>
</tr>
<tr>
<td>65</td>
<td>52.27 (5.95)</td>
<td>1.88 (0.28)</td>
</tr>
</tbody>
</table>

Standard deviations are in the parentheses. * and ** were significantly different at α= 0.05 and 0.01 respectively according to results of multiple comparison with Fisher’s Least Square method.

![Fracture surface of composites reinforced by bamboo fibers modified under different temperatures](image)

Conclusions

CaCO₃ nanoparticles and submicron particles in situ grew into micropores of bamboo fibers. Although the loading percentages of CaCO₃ were small, distinct improvements of surface wettability and mechanical properties of fibers and modified fibers/PP composites appeared.
Optimal temperature for CaCO$_3$ nanoparticles treated bamboo fibers was 25°C, the CaCO$_3$ adsorbance and contact angle of fibers were 2.34%, 70.9; the average tensile strength and modulus of elasticity of modified fibers reached 1.35GPa and 36.3 GPa, 30.50% and 32.71% higher than those of the unteated respectively. The average tensile strength and modulus of elasticity of modified fibers reinforced composites arrived at 56.04 MPa and 2.13 GPa, higher by 14.6%, 19.6% separately, comparing to those of the unteated.

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**References**


