Effect of pressurized steam treatment on selected properties of wheat straws

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A B S T R A C T

Wheat straw fibers were modified via a pressurized steam treatment. The effect of steam pressure (i.e., 0.2, 0.4, 0.6, 1.0 MPa) and treatment time (i.e., 5 and 10 min) on chemical composition, sorption isotherm, thermal and mechanical properties of the treated fibers was investigated. Differential scanning calorimetry analysis showed that thermal characteristics of the treated straw samples were shifted indicating the improved thermal stability. The ash and extractive content of the treated straw was reduced; and the materials were likely removed when the steam was released. The removal of ash and extractives could improve the wettability of wheat straw when it is used in combination with polymer matrices. Sorption behavior study showed that steam treatment reduced the hydrophilic characteristic of wheat straw. Tensile strength of the treated straw was significantly enhanced. The tensile strength of straw after treatment at a steam pressure of 1.0 MPa for 5 min was more than twice higher than that of the control group. The study demonstrated that pressurized steam treatment is an effective pre-treatment process for wheat straw fibers as possible reinforcement element in polymer matrices.

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1. Introduction

Natural fibers have recently emerged as a viable alternative to glass fiber as reinforced materials in polymer composites. The natural fiber materials offer some advantages over conventional reinforcements due to their low cost, light weight, competitive specific mechanical properties, and “green” attributes. However, low interfacial bonding strength between hydrophilic natural fibers and hydrophobic polyolefin limits the reinforcement imparted to the plastic matrix. As a result, fiber-polymer composites formed show poor dimensional stability of wood products (Giebeler, 1983; Inoue and Norimoto, 1991; Inoue et al., 1993; Rowell et al., 1998, 2000). Some chemical changes were reported during heat and steam treatments (Goring, 1963; Skaar, 1976; Lawther et al., 1996; Rowell et al., 2002). These include: (1) degradation of the hemicellulose to produce simple sugars which may undergo reversion reactions to form highly branched polysaccharides, (2) thermal softening of the cell wall matrix, mainly lignin, (3) crosslinking between carbohydrate polymers and/or between lignin and carbohydrate polymers, and (4) an increase in cellulose crystallinity. The extent of the degradation of the hemicellulose was dependent on moisture content, temperature and time of the treatment. Schmidt et al. (1996) investigated differences in the degradation of the hemicellulose between the steam treated wheat straw and birch wood. It was found that the optimum conditions for degrading hemicellulose of straw fibers by steam treatment were significantly different from those used for wood. When wood is exposed to high temperature, inactivation of

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wood surface occurs. The layers near the surface undergo physical and mechanical changes which result in a modified surface with new characteristics. This reflects a change in the wetting behavior and thus leads to further change in the penetration of liquid into wood (Serenk et al., 2004). It was reported that thermal treatment of spruce wood at 200 °C significantly diminished the hydrophilicity of the wood surface. As a result, the adhesion between the modified wood and polyethylene was improved (Follrich et al., 2006). Wheat straw, over 100 million tons per year available in China alone (Liu, 2004), represents an important industrial crop residue, and wheat straw fibers are increasingly used as raw material for fiber reinforced polymer composite. However, there is very limited work done so far on steam treatment of wheat straw fibers and its effect on fiber properties.

The overall objective of this study was to modify wheat straw fibers via a steam treatment to improve the adhesion between the wheat straw fibers and hydrophobic thermoplastic polymer. Specifically, the objective of the study was to evaluate the effects of pressurized steam treatments on thermal, chemical, and mechanical properties as well as the sorption behavior of wheat straw fibers.

2. Materials and methods

2.1. Raw material selection

Wheat (Triticum aestivum L.) straw materials with air-dry density of 310 kg/m³ were collected from northeastern China. The straw samples were cut into short sections with an average length of 100 mm. The prepared samples were stored in plastic bags prior to testing.

2.2. Thermal modification

Steam treatments were conducted at Kyoto University, Japan by using a specially designed apparatus as shown in Fig. 1. Eight batches of oven-dried wheat straws (5 g/batch), measuring 100-mm long by random width were treated in a 1000 ml capacity autoclave at steam pressures of 0.2, 0.4, 0.6 and 1.0 MPa for 5 and 10 min. The samples were put into a thimble filter, which was loosely tied with a metal wire to prevent the straw samples from bursting out of the filter. At the end of each treatment, the steam was gradually reduced to atmospheric pressure before opening the autoclave.

2.3. Differential scanning calorimetry (DSC) analysis

The steam treated straw samples and control samples (without treatment) were ground using a small Wiley grinding mill to pass a 40-mesh screen. Thermal analysis was carried out using a DSC-141 differential scanning calorimeter (DSC, Setaram, Germany). The DSC test was run on a 5-mg sample uniformly packed in an aluminum pan under continuous nitrogen flow at a heating rate of 10 °C/min over a temperature range from 50 to 400 °C.

2.4. Chemical composition analysis

The control and steam-treated straw samples that were treated with 0.4 and 0.6 MPa steam pressure for 5 and 10 min, respectively, and then were selected for chemical analysis. Samples were first ground to pass through a 60-mesh screen, and then dried at 105 °C for 24 h. Chemical composition including holocellulose, Klasson lignin, ash, and phenethyl alcohol extractives contents were determined according to the Chinese national test standards GB 2677.10 (1995), GB 2677.8 (1994), GB 2677.3 (1993), and GB 2677.6 (1994).

2.5. Sorption measurements

Samples for sorption test were prepared from both control and steam-treated straws by cutting samples into 50 mm in length. Five samples from each condition were randomly selected and numbered. They were combined into one group, and a total of eight groups were prepared. Four groups of the samples were randomly selected and dried in an oven at 70 °C for 2 days to reach the air-dry condition for the adsorption test. The remaining four groups were conditioned over distilled water to reach the fiber saturation point for the desorption test. All groups of samples were conditioned at room temperature to reach equilibrium with relative humidity (RH) of 33%, 66%, 81%, and 98% over different saturated salt solutions of calcium chloride, sodium nitrite, ammonium sulfate, and copper sulfate, respectively, in desiccators (Lide, 1996). The initial weight of all specimens was determined. After conditioning, each sample was weighed before and after oven-drying at 105 °C for 24 h. Equilibrium moisture content (EMC) of each sample was calculated based on the oven-dry weight.

2.6. Tensile strength test

The wheat straws without cracks were selected for tensile strength test. They were hand-cut into specimens with a width varying from 3 to 6 mm. Each specimen was notched in the middle section to ensure the failure occurred under relatively uniform stress. Tensile strengths were evaluated after the test specimens were conditioned to reach EMC at 33%, 66%, 81%, and 98% relative humidity. All specimens were tested using an INSTRON test machine at a loading speed of 4 mm/min. Twenty specimens for each treatment and RH condition were tested, and the results were averaged.

3. Results and discussion

3.1. Thermal properties

Fig. 2 illustrates typical DSC diagrams of the treated wheat straw samples under various steam conditions. All treated straw samples recorded heat flow peaks around 335 °C, which are higher than the peak temperature of 325 °C for the untreated straw samples used as...
the control. This indicates that the thermal stability of straws after steam treatment was improved at all steam pressure levels used in this study. It is believed that the crystalline structure of lignocellulosic fibers was changed during the steam treatment (Rowell et al., 2002). Inoue and Norimoto (1991) reported that heating wood under pressure resulted in an increase in cellulose crystallinity. The increased cellulose crystallinity of the treated straws would contribute to the improved thermal stability. Pan et al. (2008) reported that the thermogravimetric (TG) curves showed degradation peaks at 370 and 325 °C for thermomechanically refined wheat straw fibers and wheat straw pellets, respectively. A similar peak occurred at 325 °C (Fig. 2) from our tests. This is in agreement with the peak temperatures from the other studies mentioned above. Straws treated under different steam conditions had the same DSC patterns, indicating very little variations in their thermal properties for the treatment conditions used in this study.

3.2. Chemical composition

High temperature steam treatment of lignocellulosic materials can result in degradation of hemicellulose and lignin, possible crosslinking of polysaccharide chains, and polymerization of some degraded compounds from carbohydrate and lignin during heating treatment (Rowell et al., 2002). Also, Norimoto (1994) reported that the formation of interlinkages between wood polymers occurred during heating treatment of wood. Fig. 3 and Table 1 show the chemical compositions of the treated wheat straws under different steam conditions. It is apparent that after steam treatment, the hollocellulose content increased whereas lignin content decreased. This means that part of extractives and ash were volatilized and removed by steam when the steam was released. One of major differences between wood fiber and agricultural fiber is their chemical properties. Previous study showed that crop materials commonly contained high percentages of ash and extractives compared with wood (Youngquist et al., 1993; Loxton and Hague, 1996). The ash content of the wheat straw before the treatment was nearly 5% in this study which is much higher than wood (normally less than 1%). It was reported that more than 90% of the ash in the wheat straw was silica (Sauter, 1996). Sawatari et al. (1996) concluded that the silicon atoms in rice and wheat straws were extremely concentrated in the surface layer. The wettability of wheat straw, which is prerequisite for the adhesion between the fiber and polymer matrix, depends on many factors, such as the porosity, hygroscopicity, and chemical composition of the straw. As the presence of extractives and silica in non-wood lignocellulosic materials usually results in a less porous surface of the material, the removal of ash and extractives from wheat straw will contribute to the improvement of its wettability to the matrix, i.e., a better compatibility between straw material and thermoplastic polymers.

3.3. Sorption isotherm

Fig. 4 shows the sorption and desorption properties of treated wheat straws under different RHs. All tested samples followed a typical Brunauer, Emmett, and Teller (BET) type II isotherm when they were exposed to rising RH levels. Their hygroscopic isotherms had S-shaped curves quite similar to wood and many other sorbing substances. Generally, the treated straws had a lower EMC compared with the control for both adsorption and desorption process. This indicates that the treated samples absorbed less water. The chemistry of the material dictates its interaction with water vapour. Reduction of hemicellulose content in the treated straws is most

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**Table 1** Chemical compositions of wheat straw treated under different steam conditions.

<table>
<thead>
<tr>
<th>Steam pressure (MPa)</th>
<th>Treatment time (min)</th>
<th>Hollocellulose (%)</th>
<th>Lignin (%)</th>
<th>Ash (%)</th>
<th>Phenethyl alcohol extractives (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment</td>
<td></td>
<td>66.46</td>
<td>22.75</td>
<td>4.99</td>
<td>5.80</td>
</tr>
<tr>
<td>0.4</td>
<td>5</td>
<td>76.63</td>
<td>15.36</td>
<td>3.39</td>
<td>4.66</td>
</tr>
<tr>
<td>0.6</td>
<td>10</td>
<td>78.68</td>
<td>14.24</td>
<td>3.28</td>
<td>3.81</td>
</tr>
</tbody>
</table>

* The listed hollocellulose contents may include hollocellulose and other reconstituted compounds that cannot be distinguished by the test method used in this study.
likely the cause of the reduction in sorption. Additionally, heat treatment at high humidity is known to increase the crystallinity index of cellulose in wood samples (Debzi et al., 1991). Increase in crystallinity reduces affinity for moisture. The sorption isotherm of the steam-treated straws reflects a change in their wetting behavior. The straws became less hydrophilic after treatment, and thus might be more compatible with hydrophobic thermoplastics. In addition, a sorption hysteresis was observed for all tested materials. The treated straws showed a greater sorption hysteresis than the control. Table 2 shows that steam treatments on straw samples had greater effect on desorption isotherm than on adsorption isotherm.

### 3.4. Tensile strength

The mechanical properties of materials are significantly affected by thermal degradation and heating at elevated temperatures (Park et al., 2004). Thus it is important to evaluate the mechanical strength of wheat straws treated under high temperature steam. The tensile properties of the treated wheat straws at various steam conditions are summarized in Table 3 and plotted in Fig. 5. The tensile strength of the treated straws at all steam pressure levels was significantly enhanced. The tensile strength value of the treated straws at the steam pressure of 1.0 MPa for 5 min was more than twice higher than that of the control. There was little difference in tensile strength values among the straw samples treated under lower steam pressure levels of 0.2–0.6 MPa, but they were still nearly 1.5 times that of the control samples. It was also noticed that at all steam pressure levels, the tensile properties of the straws treated for 10 min were lower than those of the straw treated for 5 min. This indicates that long, severe treatment may damage straw fibers, consequently may lead to a reduction in the mechanical properties.

The mechanical properties of cellulose depend on the proportion of crystalline and amorphous regions and the spiral angle of microfibrils (Hon and Shiraishi, 2001). As a result, the mechanical properties of fibers increase as the portion of crystallinity increases.

#### Table 2

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>EMC (%)</th>
<th>0.2 MPa/5 min</th>
<th>0.4 MPa/5 min</th>
<th>0.6 MPa/5 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>8.84/8.49</td>
<td>8.30/8.03</td>
<td>7.19/7.12</td>
<td>7.45/8.52</td>
</tr>
<tr>
<td>66</td>
<td>11.89/12.20</td>
<td>10.05/11.24</td>
<td>9.35/9.52</td>
<td>8.64/11.88</td>
</tr>
<tr>
<td>81</td>
<td>14.92/15.18</td>
<td>11.88/15.26</td>
<td>11.97/12.80</td>
<td>12.53/14.64</td>
</tr>
<tr>
<td>98</td>
<td>32.44/35.44</td>
<td>31.12/32.12</td>
<td>30.56/33.56</td>
<td>29.26/31.26</td>
</tr>
</tbody>
</table>

EMC = equilibrium moisture content, RH = relative humidity.

#### Table 3

<table>
<thead>
<tr>
<th>Steam pressure (MPa)</th>
<th>Treatment time (min)</th>
<th>Moisture content (%)</th>
<th>Sample dimension</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thickness (mm)</td>
<td>Width (mm)</td>
</tr>
<tr>
<td>No treatment</td>
<td>11.89</td>
<td></td>
<td>0.72 (0.12)</td>
<td>2.13 (0.35)</td>
</tr>
<tr>
<td>0.2</td>
<td>10.05</td>
<td></td>
<td>0.46 (0.06)</td>
<td>1.40 (0.26)</td>
</tr>
<tr>
<td>0.4</td>
<td>9.35</td>
<td></td>
<td>0.37 (0.08)</td>
<td>1.42 (0.25)</td>
</tr>
<tr>
<td>0.6</td>
<td>8.45</td>
<td></td>
<td>0.43 (0.07)</td>
<td>1.42 (0.25)</td>
</tr>
<tr>
<td>1.0</td>
<td>8.23</td>
<td></td>
<td>0.38 (0.09)</td>
<td>1.27 (0.23)</td>
</tr>
<tr>
<td>0.2</td>
<td>9.66</td>
<td></td>
<td>0.41 (0.08)</td>
<td>1.40 (0.28)</td>
</tr>
<tr>
<td>0.4</td>
<td>9.15</td>
<td></td>
<td>0.55 (0.07)</td>
<td>1.55 (0.31)</td>
</tr>
<tr>
<td>0.6</td>
<td>8.48</td>
<td></td>
<td>0.47 (0.10)</td>
<td>1.53 (0.25)</td>
</tr>
<tr>
<td>1.0</td>
<td>8.32</td>
<td></td>
<td>0.30 (0.07)</td>
<td>1.27 (0.35)</td>
</tr>
</tbody>
</table>

* Results are given as average values with standard deviations in parentheses from the mean values of 20 randomly chosen samples.
Thermal characteristics were shifted showing improved thermal stability of the treated materials.

- The lignin content of treated straw decreased.
- The ash and extractives content of treated straws were reduced as a function of increased heat treatment.
- Thermal treatment diminished the hydrophilicity of the wheat straw.
- The tensile strength of the treated straw tested at 66% RH was significantly enhanced under the treatment conditions used in this study.

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**References**


Follrich, J., Muller, U., Ginld, W., 2006. Effects of thermal modification on the adhesion between spruce wood (Picea abies Kärst) and a thermoplastic polymer. Holz als Roh- und Werkstoff 64, 373–376.


