CELLULOSE NANOFIBER PREPARATION BY STEAM OR OZONE TREATMENT/Mechanical Fibrillation and its Application for Nanocomposite

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Abstract
Steam and ozone treatments were conducted to disturb wood cell wall supramolecular structure for enhancing the mechanical fibrillation of Pinus koraiensis. Both treatments were effective to generate porous structure in cell wall by partially extracting or degrading hemicellulose and lignin. This morphological characteristic can improve mechanical fibrillation. The fibrillated products by disk milling after both treatments showed nanoscopic fibrous morphology, even though they contain hemicellulose and lignin components after treatment. The paper sheets were prepared and their tensile properties were compared in fibrillated products with and without both treatments. The higher tensile properties were shown in the fibrillated product after both treatments. Depending on the sheet density, maximum tensile strength of 125MPa was obtained and further increase was achieved by the delignification and the removal of hemicellulose. The obtained nanofibers were used as a reinforcement of polyurethane emulsion. Tensile properties were improved with the addition of nanofiber.

1. Introduction
Cell wall structure of lignocellulosic biomass is very recalcitrant against biological and chemical treatments because of its highly sophisticated and multihierarchical characteristics. Recently, the research on how to overcome this strong recalcitrance for the efficient separation of cellulose microfibrils from cell wall has been extensively conducted around the world, and many applications for nanocomposite materials utilizing cellulose microfibrils have been developed. Various preparation methods have been introduced, including chemical treatments such as acid hydrolysis and oxidation and mechanical size reduction using a high-pressure homogenizer and a grinder treatment.¹⁻³

This study introduces the mechanical fibrillation method after steam and ozone treatment of lignocellulosic biomass. Steam treatment is well known for selective extraction of hemicellulose and ozone treatment is effective to degrade mainly lignin. Both treatments can disturb the multihierarchal structure, resulting in the enhancement of followed-by mechanical fibrillation. This combined method has practical and economic benefits for large-scale production as well as a highly efficient pulverization effect generated by a high shearing force.

2 Experimental
2.1 Material
Korean nut pine (Pinus koraiensis) was obtained from Research Forest of Kangwon National University in Korea and cuttermilled into 0.2 mm size. A commercial polyurethane (PU) emulsion (UWS145, Polyester-type PU, anionic liquid) was kindly provided by Sanyo-Chemical Industries, Ltd. (Kyoto, Japan). Sodium chlorite (NaClO₂) and other chemicals used in this study were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan)

2.2 Steam and ozone treatments and disk-milling
Steam treatment was performed at 150°C for 2h using Autoclave (MC-3032S, ALP Ltd, Japan). Hundred grams of wood powder was mixed with 10 times amount of water and kept at room temperature for 2 day before treatment. The steam-treated product was filtrated to remove water-soluble fraction, which amount was 16%, and the filtrated product was provided to disk-milling. Ozone
treatment was conducted in round-type flask at 40°C for 3 h with oxygen flow of 0.5L/min with ozone concentration of 204 g/m³, which is generated from Ozone Generator (D-DG-R5, Ecod Design Ltd, Japan). Sample moisture content was adjusted to be 60%. The obtained product was washed with distilled water several times to remove the remaining ozone and provided for disk-milling. Both treated product was diluted into 2% water suspension and passed through a disk mill (MKCA6-3, Masuko Sangyou Co., Ltd., Japan) 1–10 times with a gap of 20 μm at 1800 rpm.

2.3 Paper sheet preparation and measurements
The fibrillated product was diluted into 0.5 wt% suspension and stirred for 10 min followed by ultrasonication for 0.5min. Paper sheets were prepared by vacuum filtration using membrane filter (PTFE, pore size 0.2μm). Filtration time was measured at this stage. Thus-obtained wet-sheet was hot-pressed between two silicone coated filter paper at 105°C for 30 s with 50Mpa pressure and for 60 s on 150Mpa pressure. Pressed sheets were further vacuum-dried at 40°C for 24 h and kept at room temperature before tensile test (AG-1, 5kN, Shimadzu Ltd, Japan). Cross head speed was 0.5mm/min. Nano-scale morphological characteristics were observed by FE-SEM (S-4800, Hitachi Co. Ltd., Japan) and AFM (JSPM-5200S, JEOL, Japan).

2.4 Composite preparation
The concentration of fibrillated products was adjusted to be 1% of the water suspension. Then, the suspension was mixed with the PU emulsion (35% solid content) and poured in a silicon dish followed by vacuum drying at 40°C. The dried casted films were further heated at 105°C for 2 hours. The thickness of films was found to be 0.4 ± 0.05 mm.

3 Results and discussion
Figure 1 shows the morphology of fibrillated products obtained from original wood, and steam and ozone-treated products. Both treatments were effective to reduce disk-milling time, i.e., a longer time is necessary to fibrillate the original wood into the same morphology scale. Especially, fibrillated product after ozone treatment showed very fine morphology with fiber diameter scale less than 50 nm for very short disk-milling time.

Fig.1. Morphology of fibrillated products from original wood powder (A), and steam (B) and ozone-treated (C) products.

Table 1 shows the dependency of power consumption, pH value, filtration time, and tensile properties of paper sheets on disk milling time in three fibrillated products. Energy efficiency of fibrillation was improved by both treatments. Filtration time and tensile properties were increased in the fibrillated product after both treatments.

The obtained nanofibers were used as a reinforcement of polyurethane emulsion. Tensile properties were improved with the addition of nanofiber.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>DM time (min/g)</th>
<th>Power consumption (kW,h/kg)</th>
<th>pH</th>
<th>Filtration time (min)</th>
<th>Tensile strength (Mpa)</th>
<th>Modulus (Mpa)</th>
<th>Energy efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical/Dev milling</td>
<td>0.38</td>
<td>103.1</td>
<td>4.75</td>
<td>17.0</td>
<td>10.9</td>
<td>2.4</td>
<td>10.09</td>
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<tr>
<td>Ozon - Disc milling</td>
<td>0.55</td>
<td>105.5</td>
<td>4.38</td>
<td>19.7</td>
<td>18.6</td>
<td>3.8</td>
<td>12.6</td>
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<tr>
<td>Dev - Disc milling</td>
<td>0.72</td>
<td>107.4</td>
<td>4.92</td>
<td>21.7</td>
<td>24.8</td>
<td>5.7</td>
<td>18.6</td>
</tr>
<tr>
<td>Steam - Disc milling</td>
<td>0.75</td>
<td>108.3</td>
<td>4.39</td>
<td>20.3</td>
<td>24.8</td>
<td>5.7</td>
<td>18.6</td>
</tr>
<tr>
<td>5% (2hime - Disc milling</td>
<td>0.76</td>
<td>109.5</td>
<td>4.68</td>
<td>21.4</td>
<td>24.8</td>
<td>5.7</td>
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References