ALL-CELLULOSE COMPOSITES BASED ON WET-SPUN CELLULOSE FIBERS REINFORCED WITH CELLULOSE NANOCRYSTALS AND HALLOYSITE NANOCLAY

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ABSTRACT

The aim of the study was to develop biobased and lightweight composites with unidirectional cellulose fibers without a matrix polymer, so called all-cellulose composites with excellent mechanical properties. Continuous cellulose fibers are currently gaining interest for composite applications and if these fibers can be welded together without using a polymer resin it would result in an environmentally friendly composite material. The regenerated fibers were prepared using wet spinning of DMAc/LiCl dissolved cellulose where cellulose nanocrystals (CNC) and halloysite nanotubes (HNT) were used as reinforcements. The loading of the nanomaterials into the dissolved cellulose was between 2 to 20 %.

The preliminary results showed that the addition of both CNC and HNT improved the mechanical properties of the regenerated cellulose fibers. It was also seen that low concentration of the nanomaterials was more effective reinforcement than high concentration. Also, the HNT showed slightly better improvement compared to the CNC).

The spun nanocomposite fibers were directly wound to a roll after the wet spinning, compression molded to composite sheet and dried. The all-cellulose composites mechanical properties as well as microstructure including nanomaterials orientation in the spun fibers were studied and composites mechanical properties are compared with theoretical models.

1 INTRODUCTION

All-cellulose composites, where the matrix, as well as the reinforcement are made out of the same material, has gained large interest during the last years. The first concept of all-cellulose was reported by Nishino et al. [1] who embedded ramie fibers in Dimethylacetamide lithium chloride (DMAc/LiCl) dissolved wood pulp producing all-cellulose composites using so called two-step method. The method involved dissolution of the cellulose in a solvent, prior to the regeneration together with a non-dissolved cellulose reinforcement [1]. Also one-step method, in which a solvent is used to dissolve only the surface of the cellulose, is a common way to produce all-cellulose composites [2].

Dimethylacetamide lithium chloride (DMAc/LiCl), N-methyl-morpholine-N-oxide (NMMO), and ionic liquids (IL) have been so far the most used solvents, also in terms of success [2-5]. The promising results of all-cellulose composites combined with the fact that regenerated cellulose (cellulose II) shows much lower mechanical properties than cellulose I lead to the idea of making all-cellulose reinforced continuous single nanocomposite fibers, in order to be used as effective
reinforcement. For further information, the reader is referred to the original review paper published in Composites part A 2017 Oksman et al. [5]. From these solvents, NMMO, used for example in the Lyocell process in order to produce regenerated cellulose fibers, is without doubt nowadays industrially the most successful solvent [6].

Within this project, DMAc/LiCl was used as solvent for cellulose. This solvent is well established in research, because of its efficiency and capacity of dissolving high molecular weight cellulose [5, 6]. The advantage is that the solution is colorless but a drawback is that cellulose has to be activated prior the dissolving. This activation process usually involves a solvent exchange of the cellulose or distillation of the DMAc/LiCl/cellulose [7]. Due to the fact, that the activation process requires extra time and additional solvents, DMAc/LiCl has not made it yet up to an industrial scale. Moreover, the solubility of cellulose increases with bigger LiCl proportions, yet Potthast et al. have reported that the solubility is limited to 8.46 wt% LiCl [7].

2 MATERIALS AND METHODS

Dissolving pulp, obtained from Domsjö Fabriker AB (Örnsköldsvik, Sweden), was used as raw material for dissolving.

Freeze-dried cellulose nanocrystals (2012-FPL-CNC-043), hydrolyzed from cellulose pulp, were kindly provided by USDA Forest Products Laboratory (Madison, USA).

Halloysite nanotubes (HNTs) were purchased from Sigma Aldrich.

Furthermore, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), as well as lithium chloride (LiCl) were acquired from Sigma Aldrich (Sweden). The used nanomaterials structure was studied using Veeco Multimode scanning probe microscope with Nanoscope V software (Santa Barbara, USA). The samples consisted of a drop of diluted aqueous CNC, respectively HNT, suspensions, which were deposited on a fresh mica surface and dried in the oven at 70°C, the materials are seen in the Figure 1 below. Both are needle like materials but the HNT is having a much larger diameter compared to CNC.

![Figure 1. AFM images of cellulose nanocrystals (CNC) (a-d) and halloysite nanotubes (HNT) (e-h).](image)

The preparation of the spinning dope of the dissolving pulp started with the activation, which was made by immersing the pulp in water for 1 h, followed by the removal of the water via vacuum filtration. Then the wet pulp was solvent exchanged to methanol for another 1 h to decrease the water content, after that the material was vacuum filtrated and the last solvent exchange was done using DMAc for 1 h. Once again the cellulose was filtrated and then dried at 70°C. The procedure is shown in Figure 2.
A simple set-up was used, in order to spin the fibers. The set-up consisted of a pump, a 16 mm syringe with a fine nozzle and a long water bath, shown in Figure 3. Before starting the experiment, the spinning dope was degassed in the oven for few hours at 35 °C until no air bubbles were visible. After the degassing, the pump rate was set at 90 ml/hour and the tip of the jet was immersed in the water. As soon as the solution started to flow, the fiber was carried by hand with tweezers along the water bath. This step was repeated for 4-6 fibers. In order to ensure that all the solvent was properly washed out, the fibers remained for 30 min in the coagulation bath. In a next step, the fibers were taken out of the bath and dried. Once again a simple drying technique was used, the fibers were hang up on plastic rolls, as shown in the Figure 3. After 3 min drying, the fibers were still soft and gel-like, then a small weight was added to the fiber-end to apply weak tension which resulted in thinner fibers and is also expected to have some effect on orientation.

The fiber spinning process was slightly modified to the continuous spinning process in which the spinning dope was prepared in the similar way as described earlier but the fibers were spun to the water bath and collected to a roll, which is a drawing unit. The speed of the drawing unit was 11 m/min, after that the fibers were held in the water bath to remove the solvent, and to be welded together. Then the fibers were dried and compression molded during and compression molded to composite sheets with unidirectional fibers as shown in the Figure 4.

Nikon ECLIPSE LV100NPOL (Japan) optical microscopy was used to evaluate the roughness of
the fibers and also their flexibility. Furthermore, the optical microscope was used to obtain the average fiber diameter. The diameter was measured at five different locations for each fiber.

JEOL JCM-6000 NeoScope (Japan) scanning electron microscope (SEM) was used to study the morphology of the cross sections. The spun fibers were broken in liquid nitrogen.

A universal tensile testing machine Shimadzu was used to measure the mechanical properties of the nanocomposite fibers and the all-cellulose nanocomposites sheets. The test was run at a constant strain rate 2 mm/min and the gauge length was 20 mm. The measured average temperature and relative humidity during the tests were 20.5 °C and 28 % RH respectively. Prior the testing, the samples were stored in a conditioning chamber at 23 °C and 50 % RH for at least for 48 hours. At least 7 samples were tested for each material combination. The average values as well as the standard deviations are reported.

3. RESULTS

The properties of the spun fibers are shown in Figure 5 and in the Table 1. Figure 5 shows the optical microscopy images of the spun fibers with 2wt% CNC and HNT. Both the fibers are flexible, the fiber with HNT are slightly thinner which is also seen the values presented in the Table 1.

Table 1: Comparison of the mechanical properties

<table>
<thead>
<tr>
<th>Materials</th>
<th>Stiffness (GPa)</th>
<th>Strength (MPa)</th>
<th>Strain (%)</th>
<th>Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>11.8 ± 1.0</td>
<td>265 ± 25</td>
<td>11.1 ± 1.7</td>
<td>79 ± 6</td>
</tr>
<tr>
<td>2 CNC</td>
<td>16.0 ± 0.8</td>
<td>345 ± 11</td>
<td>9.3 ± 2.4</td>
<td>61 ± 3</td>
</tr>
<tr>
<td>5 CNC</td>
<td>14.5 ± 1.0</td>
<td>300 ± 8.1</td>
<td>8.0 ± 1.0</td>
<td>75 ± 6</td>
</tr>
<tr>
<td>10 CNC</td>
<td>9.7 ± 1.4</td>
<td>204 ± 28</td>
<td>8.6 ± 1.6</td>
<td>82 ± 9</td>
</tr>
<tr>
<td>20 CNC</td>
<td>7.5 ± 1.7</td>
<td>161 ± 49</td>
<td>10.3 ± 2.0</td>
<td>93 ± 14</td>
</tr>
<tr>
<td>2 HNT</td>
<td>18.5 ± 2.1</td>
<td>384 ± 32</td>
<td>8.3 ± 1.4</td>
<td>55 ± 3</td>
</tr>
<tr>
<td>5 HNT</td>
<td>18.4 ± 1.5</td>
<td>345 ± 30</td>
<td>7.5 ± 0.8</td>
<td>61 ± 3</td>
</tr>
<tr>
<td>10 HNT</td>
<td>17.8 ± 3.0</td>
<td>364 ± 44</td>
<td>8.2 ± 0.4</td>
<td>66 ± 4</td>
</tr>
<tr>
<td>20 HNT</td>
<td>16.8 ± 1.6</td>
<td>305 ± 33</td>
<td>7.4 ± 0.9</td>
<td>65 ± 4</td>
</tr>
</tbody>
</table>

Figure 6 is showing a schematic illustration of the process developed. The spun fibers, fibers after stretching and winding welded together, and finally compression molding of the welded fibers to composite sheet.
Figure 6: The schematic illustration of the all-cellulose fiber composite processing.

The mechanical properties of the composites are currently under testing and the results will be discussed in the conference.

4. CONCLUSIONS

Continuous regenerated cellulose nanocomposite fibers with different CNC and HNT contents were successfully manufactured using a simple wet spinning process. The results from the mechanical testing demonstrated that the incorporation of the CNC, as well as the HNT led to increased mechanical properties. The best results were achieved for the fibers prepared with low nanomaterials contents. E-modulus and strength were enhanced by 36 % and 30 %, respectively with 2 wt% CNC and the addition of 2 wt% HNT improved the stiffness by 57 % and the strength by 45 %.

Even though, promising results were obtained using the simple wet spinning setup, there is space for improvement of the processing. It is believed that a better fiber drawing process would improve the orientation of the cellulose as well as the nanoreinforcements, resulting in an enhancement of the overall mechanical properties.

Moreover, we have developed an interesting processing method for all-cellulose composites where the swelled fibers were wound directly after the water bath, and welded together forming a unidirectional fiber composite sheet without using any additional chemicals or polymer.

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